Russian Chemical Reviews **66** (8) 647 – 664 (1997) © 1997 Russian Academy of Sciences and Turpion Ltd

UDC 541.65:667.662

The nature of electronic transitions in linear conjugated systems

A D Kachkovskii

Contents

I.	Introduction	647
II.	Specific features of electronic structure	647
III.	Topology of polymethine chromophore	650
IV.	Changes in the structure of the polymethine chromophore	656
V.	Systems with several polymethine chromophores	659
VI.	Terminal groups as local chromophores	660

Abstract. The current state of investigations of the relationship between electronic transitions and molecular topology of linear conjugated systems, *viz*. polymethine dyes and α,ω-disubstituted **polyenes, is considered. The effect of parity of methine groups in a polymethine chain, of filling of the electronic shell, molecular symmetry, and the topology of terminal groups on the electronic structure of polymethines and polyenes are described. Spectral effects arising upon changes in the structures of chromophores, and the nature of the first and higher transitions in linear conjugated compounds containing several chromophores are discussed. The localisation of transitions in molecular fragments and the conditions for the inversion of the polymethine and local electronic transitions in polyenes and polymethines are considered. The bibliography includes 242 references.**

I. Introduction

According to current theoretical concepts on the electronic structure of conjugated systems, in particular, the triad theory being developed by Daehne,[1–4] the conjugated compounds with a stable closed electronic shell can be classed into three basic types: aromatic compounds, polymethines, and polyenes. Aromatic compounds have a cyclic structure, the CC bond lengths are equalised and the carbon atoms bear no noticeable charge. The linear conjugated systems (LCS) under consideration always have the *trans*-conformation. Polymethines are distinguished by the alternation of significant positive and negative charges on the carbon atoms and by maximum equalised CC bonds. On the contrary, polyenes are characterised by a significant alternation of the CC bond lengths and the lack of charges.

Linear conjugated systems contain, as a rule, terminal groups (TG) conjugated with the polymethine chain (PC). In the general case, LCS with a non-branched PC and one π-system can be represented as follows:

$$[G_1 \cdots (CH)_m \cdots G_2]^z ,$$

1

A D Kachkovskii Institute of Organic Chemistry, Ukrainian National Academy of Sciences, ul. Murmanskaya 5, 252660 Kiev, Ukraine. Fax (038-44) 552 83 08

Received 30 July 1996
Uspekhi Khimii **66** (8) 715 – 734 (1997); translated by M G Ezernitskaya

where G_1 and G_2 are TG, m is the number of the methine groups, z is the charge ($z = 0; \pm1; \pm2$). Individual atoms, simple groups of atoms, and complex carbo- and heterocyclic residues with a branched π-system can serve as TG.

Traditionally, LCS with an odd number of polymethine groups in the PC are termed polymethine dyes (PMD); systems with an even number of π-centres in PC are termed α,ω-hetero-substituted polyenes or heterylpolyenes (HP).[5–13] Symmetric PMD and HP differ substantially in several chemical and spectral properties, therefore, these two types of conjugated compounds are usually studied separately (it is especially true for experimental studies).[6,9,14–16] If LCS have an asymmetric structure, the difference between PMD and HP decreases.

Linear conjugated systems are suitable and favourite objects for the studies of problems of the colour theory. A chromophore in these systems has a relatively simple structure that can be easily varied; their absorption and fluorescence spectra manifest relatively narrow and intense bands, especially in the case of PMD. It permits a reliable identification of electronic transitions and successful application of methods of quantum chemistry to studies of the relationship between structure and colour.

Due to unique spectral characteristics of LCS, they have found widespread practical application connected with the transformation of light energy. For example, LCS are used as optical sensitisers,[13,17–19] active media and passive modulators of the duration of lasers,[20–24] initiators for polymerisation reactions,[25–28] organic photoconductive materials,[29–32] systems with a high polarisability for non-linear optics,[33–37] and fluorescent markers.[33,39]

The creation of novel promising compounds with a given range of absorption and a number of other properties usually presumes preliminary estimation of the most important of their characteristics. This estimation is based on the well-developed colour theory or more precisely, on the theory of electronic transitions. The present review is devoted to the consideration of the current status of investigations of the relationship between molecular topology of LCS and the nature of their electronic transitions.

II. Specific features of electronic structure

1. Boundary molecular orbitals and classification of linear conjugated systems

Boundary molecular orbitals (BMO), *viz*., the highest occupied (HOMO), and the lowest unoccupied (LUMO) orbitals, and the

orbitals close to them in energy are the most interesting for the theory of electronic transitions in LCS.

Symmetrical LCS (see **1**, where $G_1 = G_2 = TG$) can be subdivided into four groups according to the symmetry of BMO and the parity of the number of the methine groups in PC.[40]

1. Polymethines of class A in which m is odd, the HOMO is symmetric, and the LUMO is antisymmetric relative to the central atom;

2. Polymethines of class B in which m is odd, the HOMO is antisymmetric, and the LUMO is symmetric relative to the central atom;

3. Polyenes of class A in which m is even, the HOMO is symmetric, and the LUMO is antisymmetric relative to the midpoint of the central bond;

4. Polyenes of class B in which m is even, and the symmetry of the HOMO and LUMO is opposite to that of LCS of group 3.

Lengthening of the chain of PMD or HP by one vinylene group is accompanied by a change in the class of the compound. The class of LCS depends also on the number of the HOMO: the addition or removal of a pair of π-electrons changes the class to the opposite one.

The linear conjugated systems can exist in several forms depending on the ratio between the number of π-electrons and p-centres. Thus for non-substituted polymethines or PMD with alternant hydrocarbons as the TG, two forms are possible, namely, the electron-excess or $(N + 1)$ form (polymethine cation) and the electron-deficient or $(N - 1)$ form (polymethine anion), where N is the number of π-centres. In the case of non-substituted polyenes or HP with alternant TG, three forms are possible: the electron-excess $(N + 2)$ form, the electron-balanced N-form, and the electron-deficient $(N - 2)$-form.[41]

2. Electron donor ability and topological indices of terminal groups

In the Hückel approximation, occupied and vacant levels in unsubstituted polyenes are symmetric relative to the level of the non-bonded π-electron (the Fermi level of π-electrons), whereas non-substituted polymethines contain a non-bonding level that is occupied in anions and vacant in cations. The distance between the Fermi level and neighbouring levels decreases with a lengthening of PC, however, the relative position of the energy gap between the highest occupied and the lowest vacant levels remains the same. The introduction of a TG results, as a rule, in the change in the relative position of the energy gap in LCS.

A φ_0 parameter was proposed[40] for quantitative characterisation of the relative position of boundary levels

$$\varphi_0 = 90^\circ \frac{\varepsilon_e - \alpha}{\varepsilon_e - \varepsilon_0}, \tag{1}$$

where ε_e is the energy of the LUMO, ε_0 is the energy of the HOMO, and α is the energy of the Fermi level.

Another form of the representation of the φ_0 parameter is

$$\varphi_0 = 90^\circ \frac{x_i}{x_e - x_0},$$

where x_i is the energy of an ith MO expressed in the β units and referred to the Fermi level α, $x_i = (\varepsilon_i - \alpha)/\beta$; ε_i is the energy of any ith MO, and β is the resonance integral of the CC bond in PC.

It is seen from formula (1) that an increase in the φ_0 parameter should correspond to an increase in the polarographic reduction potential and the electron affinity and to a decrease in potentials of oxidation and ionisation. The φ_0 parameter reflects the electron donating properties of LCS and is therefore termed as the electron donor ability.[40]

For molecules with stable, closed electronic shell, the φ_0 value is usually positive and falls within the interval

$$0 \leqslant \varphi_0 \leqslant 90^\circ. \tag{2}$$

A model of LCS with a rather long PC appeared to be useful for a quantitative account of the influence of the topology of TG.[12,42–46] In the context of this model, the energies of the boundary and close molecular orbitals (ε_1) can be represented as a function of parameters of individual molecular fragments.

$$\varepsilon_l = \alpha + \frac{2(\Phi_{01} + \Phi_{02} - \pi l/2)}{m + L_1 + L_2}\beta, \tag{3}$$

where m is the number of methine groups in PC, Φ_{01}, Φ_{02}, L_1, and L_2 are topological indices of both TG, l is the number of the MO.

The topological parameter of the zero order Φ_0 corresponds to a displacement of the nodes of BMOs from the positions that they occupy in non-substituted LCS. This parameter characterises the ability of TG to donate the π-electron density to the atoms of PC.[47] It can be compared with the value of additional stabilisation of double bonds (ASDB)[48] introduced by Brooker and with experimental estimations of the properties of TG as bases, for instance, with the parameter b ('basicity') proposed by Platt[49] or 'electron donor ability' D proposed by Il'chenko.[50]

The topological index L reflects quantitatively the effective lengthening of a chromophore at the expense of the π-system of TG and can be expressed by the equivalent number of methine and vinylene groups.

The parameters Φ_0 and L are calculated *via* junior coefficients of the polynomial for TG ($Q = q_0 + q_1x + ...$) and its minor ($R = r_0 + rx_1 + ...$) with no regard to the atom bound to the PC.[44,46]

$$\operatorname{tg}\Phi_0 = -\frac{q_0}{r_0}, \tag{4}$$

$$L = \frac{2q_1r_0 - 2q_0r_1 + q_0^2}{q_0^2 + r_0^2}. \tag{5}$$

In the framework of the model of long LCS, the additive parameters of TG of higher order were also obtained,[51–53] however, only two topological indices Φ_0 and L are used in practice.

It was shown[40] that the topological parameter of the zero order Φ_0 is directly connected with the electron donor ability φ_0 by the following relations:
for PMD

$$\Phi_0 = \lim_{m\to\infty} \varphi_0, \tag{6}$$

for HP

$$\Phi_0 = \lim_{m\to\infty} \varphi_0 \pm 45^\circ. \tag{7}$$

The sign in formula (7) depends on the form in which the HP exists.

The parameter φ_0 characterises the relative position of the boundary levels, *i.e.* it has a distinct physical meaning and can therefore be measured experimentally. For example, linear relationships between redox potentials, the transition energy, or the ionisation potential, on the one hand and calculated energies of MO, on the other hand, can be used for this purpose.[54]

The parameters φ_0 and Φ_0 appeared to be useful for the analysis of the relative stability of LCS, which is understood as the stability of π-systems with the same values of the energy gap, *i.e.* of those absorbing in the same spectral range.[41] The π-system is supposed to be stable if all the bonding levels are mutually filled and antibonding levels are vacant; in this case condition (2) is fulfilled. Molecules with a medium electron donor ability ($\varphi_0 = 45^\circ$) in which the energy gap is symmetrical relative to the Fermi level, appear to be the most stable.

According to formula (1), a change in the number of the HOMO by a unity, *i.e.* the passage from one group of LCS to another, corresponds to a change in the parameter φ_0 by 90 °.

Hence, with regard to condition (2), only one form should be stable within the limits of the model with equivalent bonds. In fact, symmetric PMD that are characterised by equalising of bond lengths in PC exist, as a rule, in one form. Non-substituted polymethines or PMD with alternant TG having the boundary values of the φ_0 and Φ_0 parameters are the exceptions, when two unstable forms are possible.[5,7–12] It is seen from the ratio (6) that the maximum relative stability of PMD is ensured by TG with medium electron donor ability (with $\Phi_0 = 45\ ^\circ$).

In the case of HP, the essential alternation of bond lengths in PC leads to an additional increase in the energy gap, larger displacement being experienced by the boundary level that is located closer to the Fermi level.[41] The relationship between the φ_0 and Φ_0 parameters [see formula (7)] is complicated due to the alternation of bonds, therefore the electron donor ability changes less ($\Delta\varphi < 90\ ^\circ$) on going from one form to another. Thus in the case of polyenes two forms are stable, as a rule (see, for example, a review [6]). Polyenes containing TG with the limiting values of the index Φ_0 equal to 0 or 90 $^\circ$ appear to be the most stable. In this case, even three forms are able to exist: a stable, electron equalised and two less stable, an electron excess and electron deficient ones.[41]

3. Distribution of the electron density on atoms and bonds

a. Atomic charges

Non-substituted polymethines with a closed electronic shell are charged. The values of charges on the carbon atoms are defined as squares of coefficients of non-bonding MO (NBMO). The NBMO has nodes in the even positions. The nodal atoms bear no charges. In the odd positions, the charge value Δz depends on the number of π-centres in the chain (N), and the sign depends on the form of polymethine.

$$\Delta z \simeq \pm \frac{1}{N+1}\,. \tag{8}$$

The introduction of a TG is accompanied by a change in absolute values of charges in the odd positions and by induction of charges in the even positions. Formulae of the perturbation theory [55] can be used for the analysis of changes in the π-electron density $q_{\mu.}$

$$q_\mu = q_\mu^0 + \pi_{1,\mu} h\,, \tag{9}$$

where q_μ^0 is the electron density on the μth atom in non-substituted LCS, $\pi_{1,\mu}$ is atom-atomic polarisability, h is the magnitude of perturbation on the terminal atom of the chain.

For the middle of the chain we have

$$\pi_{1,\mu} \simeq \frac{1}{N+1}\left[\frac{2}{\pi} + (-1)^\mu\right] \text{ at } \mu \to \frac{N}{2} \text{ or } \frac{N+1}{2}\,. \tag{10}$$

It follows from formulae (9) and (10) that the sign of a change in the electron density depends on the sign of the term $(-1)^\mu$, *i.e.* on the parity of the position of TG. Consequently, the effects of TG in neighbouring positions are inverse. If a molecule of PMD contains two TG, their influence is synchronous because the parities of any position relative to both ends of the chain coincide.

According to the rule of 'topological charge stabilisation',[56–58] the significant alternation of the electron density on atoms causes the relatively high stability of odd conjugated systems. *ab initio* Calculations have shown that polymethines are stabilised largely at the expense of a lowering of the potential energy of the π-electrons, while aromatic systems are stabilised due to their low kinetic energy.[57,58]

Hückel, PPP, CNDO/2, and MINDO/3 calculations have shown that the ratio between the absolute values of positive and negative charges on the carbon atoms in neighbouring positions in PMD depends unambiguously on the topological index Φ_0 (Fig. 1).[12,59–61]

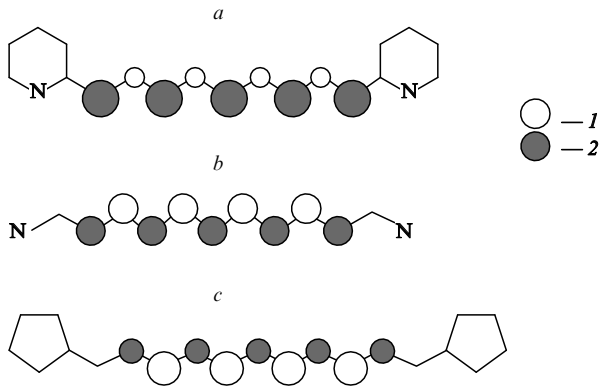


Figure 1. Charges on atoms of PC in the ground state. Charge: (*1*) is positive, (*2*) is negative. Φ_0 /grad: (*a*) 76, (*b*) 45, (*c*) 27.

In contrast to polymethines, the π-electron density in non-substituted polyenes in the stable *N*-form, is uniformly distributed over all the carbon atoms, and the π-charges are lacking. The introduction of one TG induces the alternation of positive and negative charges as in the case for polymethines with one TG. However, in the case of symmetrical HP, the overall influence of two TG differs from that for symmetrical PMD, since for polyenes the parities of any position of carbon atoms in the chain relative to each end are opposite. This results in the annihilation of alternating charges in the middle of the chain in symmetrical HP.[60,61]

The regularities found for the charge distribution in the ground state of PMD and HP are confirmed by experimental observations, in particular, of the changes in chemical shifts in ^{13}C NMR spectra as the molecular topology of LCS varies.[5,62–66,69]

A change in the π-electron density on going to the excited state Δq_ν can be written in the analytical form:[12,60,61]
for PMD

$$\Delta q_\nu = a(-1)^{n+\nu+1} \cos\left(\nu a \frac{\pi}{2}\right) \cos\left[\nu a\left(\frac{\pi}{2} - \Phi_0\right)\right]\,, \tag{11}$$

for HP

$$\Delta q_\nu = a(-1)^{n+\nu} \sin\left(\nu a \frac{\pi}{2}\right) \cos\left[\nu a\left(\frac{\pi}{2} - \Phi_0\right)\right]\,, \tag{12}$$

where $a = 1/(n + L)$, n is the number of vinylene groups in PC, ν is the number of the atom counted from the midpoint of PC.

Changes in populations on neighbouring atoms are opposite in sign due to the first multiplier which is confirmed by calculations using more rigorous approximations.[56–61]

An analysis of formulae (8)–(12) and of the results of quantum-chemical calculations shows that the excitation of the atoms of PC in symmetrical PMD results in recharge, *i.e.* the signs of the charges in the ground and excited states are opposite. In the case of symmetrical polyenes, the signs of the charges remain the same upon the transition of the molecule to the excited state.

b. Bond orders

The π-electron density on atoms of PC in PMD alternates strongly, whereas in HP it is equalised. As far as populations of bonds are concerned, the situation is opposite: populations alternate in polyenes and equalise in polymethines.[1–4]

Calculations of symmetrical PMD predict nevertheless some alternation of the CC bond orders if the topological index Φ_0 (and therefore the electron donor ability φ_0) has an increased or decreased value; the amplitude of alternation is minimum in the midpoint of the chain and increases towards its ends.[61,67] Not

only the $p_{\mu\nu}$ value of bond populations, but also the order of sequence of the bonds with larger or lesser population change with the change in the parameter Φ_0. The absolute value of $p_{\mu\nu}$ depends on the extent to which the parameter Φ_0 differs from the average value of 45 °.

Non-equivalence of the CC bonds in PC of symmetrical PMD is confirmed by X-ray spectroscopy [68, 69] and by direct coupling constants in the NMR spectra.[70–72]

Using analytic expressions for coefficients of MOs and, respectively, for bond orders in unsubstituted LCS,[55, 73–75] the amplitude † of the alternation of bonds can be calculated.

$$\Delta_\mu = p_{\mu,\mu+1} - p_{\mu+1,\mu+2} .$$

It has been shown that at the beginning of the chain of rather long polymethines and polyenes, the Δ_μ value approaches to the same limiting value of $1/\pi$, however, in the middle of the chain, the amplitude of the alternation of bonds differs significantly for different types of LCS:
for PMD

$$\Delta_\mu \simeq \frac{(-1)^{\mu+1}}{(N+1)^2} ; \tag{13}$$

for HP

$$\Delta_\mu \simeq \frac{(-1)^{\mu+1}}{N+1} . \tag{14}$$

Significant alternation of orders and, respectively, of bond lengths in polyenes is predicted by calculations within the more rigorous, *viz*., semiempirical [15, 16] and *ab initio*,[15] approximations. In the majority of cases, the difference between the lengths of neighbouring bonds is close to 0.08 Å. The degree of the alternation changes little upon introduction of donor and acceptor substituents.[76–80]

On going from one form of polyenes to another, the order of sequence of the bonds with larger or lesser population, *i.e*. the sign of the parameter Δ_μ changes to the opposite. In the excited state, the alternation of bond orders decreases though for polyenes and the difference in the orders of neighbouring bonds still remains significantly larger than that for polymethines, the order of sequence of the bonds with increased and decreased population being opposite to that in the ground state.

c. Ideal electronic states

Daehne [1–4] has introduced the concepts of ideal polymethine and ideal polyene states. In the general case, for LCS with an arbitrary TG, the conditions for the realisation of the ideal electronic states can be pointed out using the electron donor ability φ_0 and topological indices of the TG.[40, 61] Thus the ideal polymethine state is achieved in symmetrical PMD with the TG for which $\Phi_0 = 45$ °. In this case, $\varphi_0 = 45$ ° and the boundary levels are located symmetrically relative to the Fermi level, bond orders are equalised in both the ground and excited states, and the charges alternate to the maximum extent. The excitation of ideal polymethines leads to the maximum change in the electron density and to the minimum change in bond orders.

The opposite situation in the distribution of the π-electron density corresponds to the ideal state of polyenes in symmetrical HP. The boundary levels are also located symmetrically and $\varphi_0 = 45$ °, however, it is provided by the terminal residues with $\Phi_0 = 0$. The charges on the atoms in the ground and excited states are absent, but the difference in populations of neighbouring bonds is a maximum; the change in bond orders in the excitation is also a maximum.

† The difference between two values for neighbouring atoms or bonds and for two states, the ground and excited one, is denoted as amplitude.

Hence, both ideal states are achieved at $\varphi_0 = 45$ °, however, ideal polymethines contain a TG with $\Phi_0 = 45$ ° and ideal polyenes contain a TG with $\Phi_0 = 0$ °.

d. Asymmetric LCS

The violation of symmetry in molecules of LCS leads to the shift of nodes of MOs towards one TG. It is convenient to characterise the degree of asymmetry by the difference in the topological indices of the terminal residues

$$\Delta\Phi_{12} = \Phi_{01} - \Phi_{02} ,$$

the numbers of TG are denoted by subscripts 1 and 2.

It follows from calculations of asymmetrical PMD that the charges decrease in the middle of PC as the parameter $\Delta\Phi_{12}$ increases (see Ref. 47). At the ends of the chain of asymmetric PMD, 'the behaviour' of charges is determined by the nature of the neighbouring TG, and the effect of the second TG decreases inversely with the length of PC.

Bond orders in asymmetrical PMD depend on two major factors, namely, the difference in the topological indices of the terminal groups $\Delta\Phi_{12}$ and the electron donor ability, which is connected with the topological indices by the relationship

$$\varphi_0 = \frac{\Phi_{01} + \Phi_{02}}{2} .$$

The latter factor causes an alternation of bonds from the centre of PC to its ends, as in symmetrical polymethines, which is proportional to the absolute value of the difference $|45\ ^\circ - \varphi_0|$. The maximum alternation, uniform along all the chain, is achieved if $\Phi_{01} > 45$ ° and $\Phi_{02} < 45$ °.

In contrast to polymethines, the violation of symmetry in HP leads to an increase in the alternation of charges on neighbouring atoms and to a decrease in the alternation of bond orders in proportion to $\Delta\Phi_{12}$.

It was found that in the excited state the amplitude of the alternation of bond orders in asymmetrical PMD and HP is substantially less than that in the ground state.[47] Note that in solutions the polarity of a medium can also influence the degree of alternation of bonds.[72]

III. Topology of polymethine chromophore

1. Electronic levels and transitions

The colour of LCS is known [1–3] to be determined by intense $\pi \rightarrow \pi^*$ electronic transitions. The intensity of possible $n \rightarrow \pi^*$ transitions is negligibly small, therefore, they will not be considered in the present paper.

In non-substituted conjugated molecules, the π-orbitals are completely delocalised. However, if LCS contain complex TG with a developed π-system, orbitals localised largely on the terminal residues can appear. For the sake of convenience, the orbitals delocalised over all the molecule were suggested to be termed as polymethine MOs and those localised mainly in TG local or more precisely, quasi-local MOs.[81–83]

Thus, in the general case, two major types of $\pi \rightarrow \pi^*$ transitions are possible in LCS, *viz*., transitions between the polymethine MO (levels), the so-called polymethine electronic transitions (PET) and transitions with the participation of local levels, *i.e*. quasi-local and local transitions (LET).

Polymethine and local electronic transitions differ substantially in several characteristics: in the value of dipole moment, in the sensitivity to the length of PC and topology of TG, to the effect of substituents. As a rule, LET is accompanied by a significant intramolecular charge transfer from one fragment to another in which the MOs that take part in the given transition are localised.[39, 82, 83] In this case, the dipole moment of the molecule increases strongly, these transitions are therefore sensitive to the polarity of a solvent.[82–85] The corresponding absorption bands differ also in intensity and contour.[81]

Calculations show that in symmetrical PMD with equalised bonds, electronic levels in the vicinity of the Fermi level are arranged uniformly, and the first excited state is mainly described by the χ_1 configuration (Fig. 2). If the function of the pth excited state Ψ_p^* is represented as the expansion within the basis of χ_i electronic configurations

$$\Psi_p^* = \sum_i T_{ip}\chi_i ,$$

it turns out that $T_{pp} > 0.9$. This allows the use of a one-configurational approximation often to a sufficient accuracy.[5, 7, 12, 47, 61, 67]

Since the boundary MOs of symmetrical LCS have opposite symmetries, the first transition is antisymmetrical, $A_1 \rightarrow B_1$ and the moment μ_1 is directed along the polymethine chain. The next two transitions are symmetrical and are described by a superposition of χ_2 and χ_3 configurations (Fig. 2 *a*); their moments are polarised perpendicular to PC. In the approximation of long LCS, the χ_2 and χ_3 configurations have the same energies E_2^0 equal to double the energy of the χ_1 configuration (Fig. 2 *b*). The interaction of the configurations leads to two excited states with energies

$$E^+ = E_2^0 + h$$

and

$$E^- = E_2^0 - h ,$$

where $h = \langle\chi_2|\hat{\mathbf{H}}|\chi_3\rangle$ is the interaction energy, $|\hat{\mathbf{H}}|$ is the Hamiltonian.

In the case of PMD, the splitting value h is relatively small and the energies of the second and the third electronic transitions exceed significantly the energy of the first PET (see Fig. 2 *b*).

For polyenes, the distance between the boundary levels increases due to the alternation of bond lengths, whereas the next vacant and occupied levels are located closer to the corresponding boundary level (Fig. 3); at a sufficient lengthening of the chain, the levels form zones.[15, 16, 86, 87] As a consequence, the energy of the transition between the boundary levels ($A_1 \rightarrow B_1$) is always larger for polyenes than that for polymethines containing even shorter PC (see Fig. 3), which is confirmed experimentally (for instance, a large body of spectral data are reported[88] for PMD and HP).

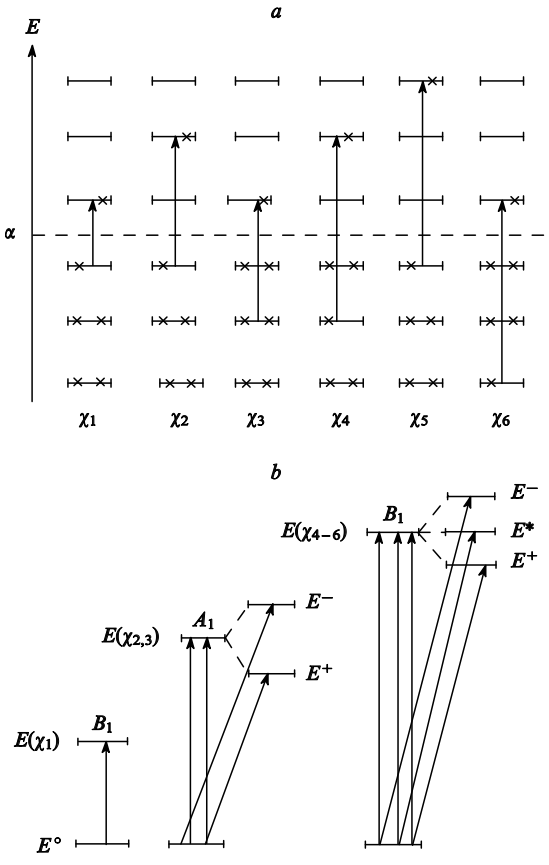


Figure 2. Electronic levels, single-excited configurations χ_i (*a*), and electronic states and transitions (*b*) in polymethines.

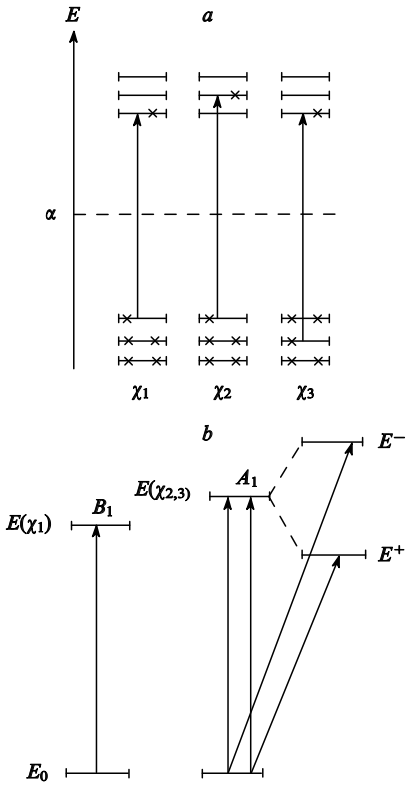


Figure 3. Electronic levels, single-excited configurations χ_i (*a*), and electronic states and transitions (*b*) in polyenes.

In polyenes, the energies of χ_2 and χ_3 configurations differ from that of χ_1 configuration significantly less than in polymethines (see Fig. 3 *a*). If the distance within the zones is relatively small and the interaction of the configurations is significant, the energy of one of the split states of the A_1 symmetry can appear to be even lower than that of the antisymmetrical B_1 state (see Fig. 3 *b*).[15, 16, 89–100] The symmetry forbidden A_1 state was really found experimentally (by two-photon spectroscopy) in non-substituted polyenes as the state with the lowest energy.[15, 93, 101] Note that the excitation of polyenes is accompanied by equalising of the bonds; it can lead to the inversion of excited states of different symmetries. Thus in α,ω-diphenylbutadiene, photoemission occurs from the B_u state whereas absorption corresponds to the transition to the A_g state.[102] In longer polyenes, the A_g state is emitting.

The introduction of a TG and the transition of one form to another lead, as a rule, to an increase in the distance between the levels within the zones and, therefore, to an increase in the difference between the energies of the χ_1 and the higher χ_2 and χ_3 configurations. That is why in these polyenes, the lowest excited state is still described by the χ_1 antisymmetrical configuration; it is the $A_1 \rightarrow B_1$ transition having a larger moment that is responsible for the colour of HP.

2. The length of polymethine chain

Koenig[103] has discovered experimentally that the lengthening of PC in symmetrical PMD shifts regularly the maximum of the absorption band to the long wavelength range. The value of this

shift upon the introduction of one vinylene group was termed as the vinylene shift

$$V = \lambda_{n+1} - \lambda_n ,$$

the V value appeared to remain approximately constant in vinylogous series of PMD and is equal to ~ 100 nm.[5, 48, 49, 88, 104] Therefore, the vinylene shift can be considered as an additive contribution of one vinylene group (topological unit of PC) to this integral characteristic of the molecule as the absorption wavelength λ_n.

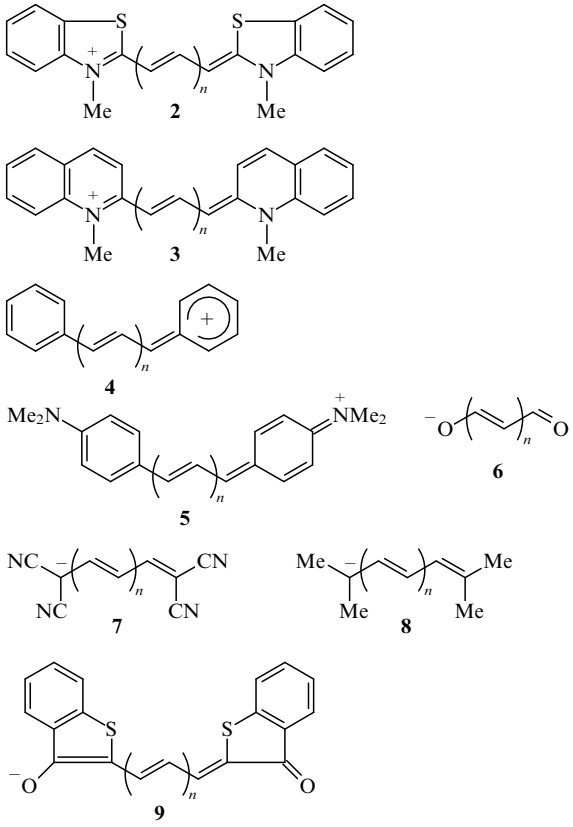
In vinylogous series of HP and asymmetrical PMD, the vinylene shift decreases regularly; Brooker called these series convergent unlike non-convergent series in the case of symmetrical PMD with a constant vinylene shift.[48]

Naturally, similar shifts of the bands with the lengthening of PC is also observed in fluorescence spectra. It was shown that the V values in the fluorescence and absorption spectra of symmetrical PMD are nearly the same.[12, 23, 24, 105–107]

PPP and CNDO/C calculations of the vinylene shift for vinylogous series of LCS show that the value of the parameter V depends, first, on the degree of equalisation of bonds in PC; alternation of bonds leads to an increase in the energy of PET in proportion to the number of bonds thus resulting in a decrease in vinylene shifts.[5, 12, 104] It was shown above that bond orders in PC are 'sensitive' to the electron donor ability φ_0, the type and shape of LCS, symmetry, and topological indices of TG. These factors should also influence the additive contribution of PC into the wavelength of PET.

a. Vinylogous series of polymethine dyes

Since PMD are characterised by equalising of bonds, significant vinylene shifts are observed in their spectra that change little with the lengthening of PC. Figure 4 shows the spectral data for the following vinylogous series of the most known polymethines:



The vinylene shift changes somewhat with the change in the polarity of a solvent.[85, 108, 109]

In some species of PMD, the first vinylene shift deviates from an average value of 100 nm due to the interaction between TG in

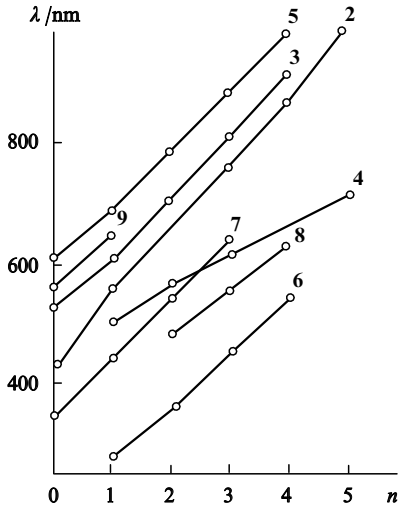


Figure 4. The dependence of wavelengths of the maxima of absorption bands λ_{max} of PMD **2**–**9** on the chain length.

monomethine dyes ($n = 0$), which disappears as the PC lengthens. Thus for quino-2-monomethinecyanines **3**, ($n = 0$), steric hindrances are accompanied by a bathochromic effect and V is equal to 82 nm, whereas the second and the third vinylene shifts are equal to 98 and 100 nm.[104] In the case of dyes **2** and **9**, the V value is influenced by the resonance interaction of valent nonbonded sulfur atoms, and the spectral effect depends on the class of compound: if the monomethine dye belongs to class A (**2**), the first vinylene shift is increased ($V = 182$ nm); if the first member of the series belongs to class B (**9**, $n = 0$), the V parameter decreases and is equal to 65 nm.[110]

The vinylene shift is 'sensitive' to the topology of TG.[104, 111–113] If the Φ_0 index differs significantly from the average value of 45 °, as, for example, in PMD **4** ($\Phi_0 = 0$ °), the alternation of bonds from the centre to the ends appears in PC and the value of the V parameter decreases to 60 nm.[104]

b. Vinylogous series of heterylpolyenes

For polyenes, the dependence of the energy of PET on the PC length and the Φ_0 topological index is even more complicated due to both significant bond alternation and the possibility for the existence of several stable forms. It should be also noticed that the absorption bands for HP are relatively broad, their maxima are poorly resolved (see, for example, Refs 114–117).

The fact that the difference in the lengths of neighbouring bonds is a maximum in non-substituted polyenes causes very small vinylene shifts and their gradual damping as the PC length increases.[15, 88, 104] An increase in Φ_0 with the introduction of TG is accompanied by some increase in the parameter V. Thus for non-substituted polyenes $V = 33–18$ nm at $n = 1–6$, for conjugated α,ω-diketones ($\Phi_0 = 63$ °) $V = 50$; 50; 33; 29; 26 nm at $n = 1–6$.[118]

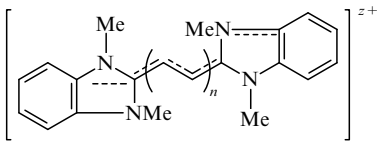
The amplitude of alternation of bond lengths depends also on the shape of a polyene which should also influence the magnitude of the vinylene shift. Thus, for the electron-equalised N-form of α,ω-diphenylpolyenes, $V = 28–17$ nm at $n = 1–6$; for the electron-excess ($N + 2$) form, $V = 50$ and 57 nm at $n = 4$; 5; 6.[88, 104]

It appeared that in the cases when two forms of HP are possible, the more stable form as a system with a larger amplitude of bond alternation has a more shortwave colouration and smaller vinylene shifts; stronger absorption and somewhat larger values of the parameter V are characteristic of the less stable form. Table 1 lists the band maxima of vinylogous series of polyenes **10**–**12** with TG of various electron donor ability for which two forms are known.

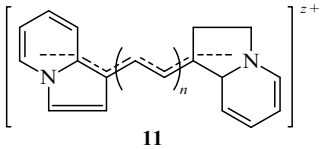
Table 1. The maxima of the absorption bands for different forms of polyenes **10**–**12** (nm).[73,75]

PC	Φ_0 /deg.	n	$(N+2)$-form, $z=0$		N-form, $z=2+$		$\Delta\lambda$ [a]
			λ_{max}	V	λ_{max}	V	
10	76	1	405	–	329	–	76
	76	2	428	23	351	22	77
11	40	1	413	–	459	–	−46
	40	2	430	17	497	39	−67
	40	3	444	14	526	29	−82
	40	4	465	21	554	28	−89
12	27	0	310	–	448	–	−138
	27	1	337	27	486	38	−149
	27	2	359	22	522	36	−163
	27	3	385	26	536	13	−150
	27	4	410	25	575	40	−165
	27	5	423	13	613	38	−190

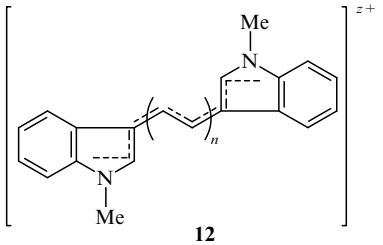
[a] $\Delta\lambda = \lambda_{max}[(N+2)\text{-form}] - \lambda_{max}[N\text{-form}]$.



10



11



12

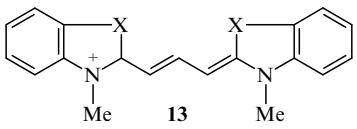
As seen from Table 1, it is stable dications of polyenes **10** with strongly electron donating benzimidazole residuesthat are more highly coloured and for polyenes **12** with low electron donating β-indole nuclei, it is neutral molecules that are more highly coloured. The difference between the maxima of the absorption bands of different forms increases as PC lengthens and the number of alternating bonds increases.

3. Lengthening of chromophore at the expense of terminal groups

The energy of PET is known to be significantly affected by, both the length of PC and the topology of TG.[5,12,48,49,88,104,112,113] Thus, carbocyanines **1** absorb in the range of 500–600 nm,[88] and dyes **14** with the same length of PC absorb in the range of 600–800 nm (Scheme 1).[119]

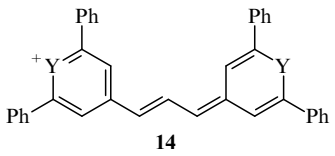
In the framework of the colour theory, it is convenient to consider this effect of TG as an effective lengthening of the polymethine chromophore.[10] Various empirical increments were proposed for its quantitative estimation.[49,120–125] They appeared

Scheme 1



13

X	λ_{max} /nm
CH=CH	607
CMe_2	545
NMe	496
O	485
S	557



14

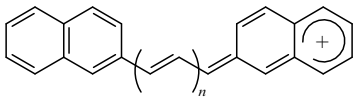
Y	λ_{max} /nm
NMe	638
O	676
S	755
Se	795

to remain approximately constant for the entire vinylogous series. However, they can be used only for the analysis of novel members of vinylogous series of LCS; empirical increments are hardly suitable for prediction of energies of transitions in compounds that have not been synthesised yet. The topological index of the first order L coined in the approximation of long polymethines[42–47] appeared to be more convenient for the theoretical determination of the effect of TG on spectral characteristics of LCS. In this case, the wavelength of PET can be written as

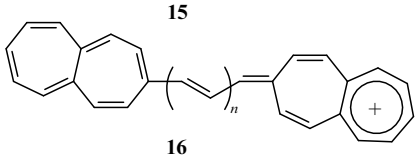
$$\lambda_n = V(n + L)\,. \tag{15}$$

This formula allows the understanding of the physical meaning of the parameter L: this is an effective length of TG expressed as an equivalent number of vinylene groups.

In the case of TG with the linear non-branched π-electron system, the effective length L is proportional to the actual dimensions of the molecule. For complex cyclic systems, it can be less that the real range of delocalisation of electron as it is, for example, in dyes **15** (L = 2.7) or exceed it significantly as in dyes **16** (L = 12).



15



16

The effective length L shows how many vinylene groups the model LCS with equalised bonds should contain for its first absorption band to fall in the same spectral range as the band of a dye with the given TG. Since the index L is calculated from formula (5), it reflects mathematically correctly such topological factors of TG as linearity or branching of the π-system; the presence, the number, position and size of the rings; the position of attachment of PC, the location and characteristics of heteroatoms and heterobonds.[12,42–46]

The concept of effective length of TG appeared to be useful for both the interpretation of the regularities observed in the spectra of LCS and for the search for novel compounds with the required spectral properties, in particular, dyes absorbing in the near IR range. A deep colour can be ensured mainly by two routes: by lengthening of the polymethine chromophore due to the introduction of additional vinylene groups into PC and by the introduction of TG with a large effective length.

The second route is more promising since dyes with a long open chain are not stable as the possibility of rotation about CC bonds increases, which leads to a sharp decrease in the efficiency of sensitisation and quantum yield of fluorescence. The combination of both approaches, *viz*., the use of a long PC fixed rigidly by polymethylene bridges, and the use of pyrylium residues and its

heteroanalogues or benzo[*c*,*d*]indolium with a relatively large effective length, allows the absorption range of 1300–1500 nm to be achieved.[5, 23, 24, 113, 126–133]

Systematic theoretical studies of the effect of the topology of TG on transition energies in LCS, in particular, the effect of cyclization of a part of PC,[12, 45, 134] annelation of TG [135–138] can be performed using the parameter L. In many cases, expressions for the indices Φ_0 and L can be written in the convenient analytical form.

4. Asymmetrical systems

The violation of the symmetry of LCS influences significantly the electronic transitions, spectral effects depending markedly on the type of compound.

Asymmetrical LCS are usually considered as derivatives of the corresponding symmetrical compounds, which are usually referred to the as parent compounds (see, for example,[5, 9, 48–50, 139]). In the construction of asymmetrical systems, a half of the molecule is taken from one symmetrical parent compound, the other half is taken from another parent compound. If the initial systems, PMD and HP, belong to the same class, an asymmetrical system of the same class is obtained, *viz*., polymethine or polyene, respectively; if the classes do not coincide, this gives a system of the opposite type. However, in the case of asymmetrical HP, the ambiguity arises because at least two forms of polyenes differing by a pair of π-electrons have a stable electronic shell.

In order to estimate quantitatively the degree of asymmetry, deviations D are traditionally used, which can be calculated in the following way:[9, 48]

$$D = \frac{\lambda_1 + \lambda_2}{2} - \lambda_a \,, \qquad (16)$$

where λ_1 and λ_2 are absorption maxima of the corresponding symmetrical parent systems, λ_a is the absorption maximum of the asymmetrical molecule.

Kiprianov and Pilyugin [140] and independently Brooker [48] have observed that for polymethine dyes $D > 0$, *i.e*. the position of the maximum for an asymmetrical dye λ_a is shifted towards short wavelengths as compared to the arithmetic mean value from the maxima of the mother dyes λ_1 and λ_2. Thus can be rationalised by the fact that if TG are non-equivalent, the alternation of longer and shorter bonds arises in PC.

Energies of transitions and deviations in asymmetrical LCS can be determined from both absorption and fluorescence spectra; the difference consists in the structure of the initial state.

a. Absorption spectra

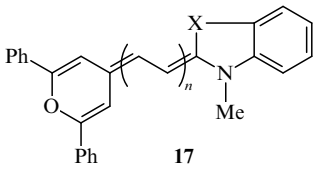
Specific features of absorption spectra of asymmetrical LCS are determined by the specific features of populations of bonds in a polymethine chromophore in the ground state.

As was shown above, the bonds with a larger or smaller order alternate in PC of asymmetrical PMD; the amplitude of the alternation of π-populations of neighbouring bonds (bond orders) is proportional to the difference in basicities of TG or the difference $\Delta\Phi_{12}$. Accordingly, deviations of absorption bands also increase.[9, 48–50] In asymmetrical chromophore, however, the alternation of populations of bonds from the centre to the ends can additionally arise if the electron donor ability φ_0 differs from the average value of 45 °. That is why deviations are sensitive not only to the difference in the topological indices $\Delta\Phi_{12}$, but also to the parameter φ_0, which relates to indices of TG in the case of asymmetrical PMD in the following way:

$$\varphi_0 = \frac{\Phi_{01} + \Phi_{02}}{2} \,.$$

Deviations appear to be a maximum if $\Phi_{01} > 45$ ° and $\Phi_{02} < 45$ °. In this case the alternation of bonds in the vicinity of nuclei is synchronous with that along the chain, and its amplitude is maximum at a given $\Delta\Phi_{12}$ difference. If both TGs have either increased ($\Phi_{01} > 45$ °, $\Phi_{02} > 45$ °) or decreased ($\Phi_{01} < 45$ °, $\Phi_{02} < 45$ °) basicity, the alternation is weakened, and the deviations in these PMD are practically lacking (or insignificant), though they still grow somewhat as the $\Delta\Phi_{12}$ difference grows.[9, 48, 141, 142]

The violation of symmetry in polyenes leads to the opposite change in bond orders as compared to that in PMD: bonds in asymmetrical HP are more equalised than in the corresponding parent compounds. For this reason, the deviations calculated from formula (16) should be negative, which was proved by experimental studies of vinylogous series of asymmetrical polyenes (**17**) with one constant nucleus and variable residues.[143, 144] The spectral characteristics are listed in Table 2.



17

As is seen from the presented data, the deviations are really negative, *i.e*. the absorption maximum of an asymmetrical polyene is shifted to the long wavelength range as compared to the arithmetic mean from the maxima of the corresponding symmetrical parent HP. The absolute value D increases regularly with an increase in the topological index Φ_0 of the variable residue in the series indolenine–benzothiazol–2-quinoline.

Table 2. Spectral characteristics of asymmetrical polyenes **17**.[144]

X [a]	Φ_{02} /deg	n	λ_{max} /nm	V /nm	D
CMe_2	45	0	442	–	−18
		1	472	30	−8.5
		2	495	23	−7.5
S	56	0	454	–	−24.5
		1	483.5	29	−10
		2	506	29.5	−13
CH=CH	55	0	456.5	–	−80.5
		1	495	38.5	−36.5
		2	515.5	20.5	−32.5

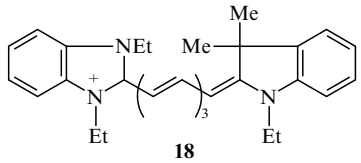
[a] The value Φ_{01} for all considered polyenes is 44.

b. Emission spectra.

Specific features of the structure of the excited state should influence the energies of transitions determined from fluorescence spectra. As was mentioned above, in the case of asymmetrical LCS, bond orders equalise substantially on excitation. For this reason, emisson spectra are remarkably less sensitive to the violation of symmetry, and the additive formula should be true for them

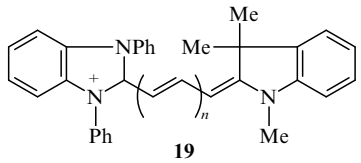
$$\lambda_n^{fl} = V^{fl}\left(n + \frac{L_1 + L_2}{2}\right) . \qquad (17)$$

An analysis of the spectra has shown that deviations of the maxima of fluorescence are 1–2 orders of magnitude less than those of absorption maxima.[23, 24, 106, 107] Thus, for dye **18** with a rather long PC, the deviation calculated from the absorption spectra is 176 nm whereas that of the fluorescence maximum is only 3 nm.[106]

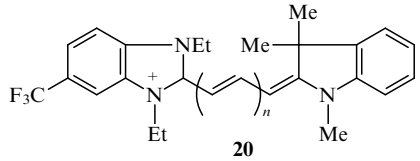


18

The studies of vinylogous series of asymmetric of dyes **19** and **20**



19



20

have shown that the contribution of PC also appears to be additive.[24, 106, 107, 145–147] As is seen from the data of Table 3, the V^{fl} parameter is virtually equal to 100 nm and changes little with the lengthening of PC while V is significantly smaller and decreases on going to higher vinylogues.

The alternation of bonds in polyenes and asymmetrical polymethines leads to the formation of photoisomers in the excited state, which can appear in fluorescence spectra, especially when measured by flash spectrometry.[148–151] Calculations show that the height of the conformational barrier depends on the nature of TG.[148, 149, 152–154]

Table 3. Spectral data for asymmetrical PMD **19** and **20** (nm).

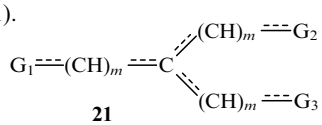
Dye	n	EtOH				CH_2Cl_2			
		λ_{max}	V	λ^{fl}_{max}	V^{fl}	λ_{max}	V	λ^{fl}_{max}	V^{fl}
The data of Ref. 107									
19	1	506	–	553	–	512	–	554	–
	2	580	74	657	104	600	88	659	105
	3	615	35	763	106	662	62	762	103
The data of Ref. 108									
20	1	450	–	517	–	450	–	517	–
	2	497	47	620	103	528	68	622	105
	3	515	18	721	101	560	32	718	96

Note. The following notations are accepted: λ_{max} and λ^{fl}_{max} are wavelengths of the absorption and fluorescence maxima, respectively; V and V^{fl} are vinylene shifts of the absorption and fluorescence bands, respectively.

Substantial difference in the energies of transitions observed in the absorption and emission spectra is used in practice for the creation of dyes with large Stokes shifts. These dyes are applied in quantum electronics (see, for example, review[24]).

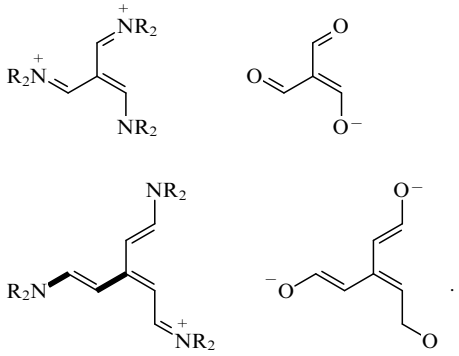
5. Branching of a chromophore

Symmetrical branching of a chromophore observed in the so-called tri-nuclear dyes (TPMD) is of special interest. The effect of this change in molecular topology manifests itself most clearly (**21**).



21

Simultaneous lengthening of each branch of PC yields homologous series of TPMD. A stable closed electronic shell is characteristic of TPMD in the form of monocations (monoanions) or dications (dianions), as for example,



If all three TGs have identical structures, the ion of TPMD in the ground state has the C_3 symmetry, which is confirmed by the ^{13}C NMR spectra.[155, 156] In the crystalline state, the C_3 symmetry is maintained only for single-charged dyes having one counterion; in the case of TPMD with two counterions, this symmetry is violated.[156] The C_3 symmetry of the chromophore leads to the degeneracy of the antisymmetrical MO. For TPMD with an even number of methine groups m, the LUMO is degenerate in each branch, for those with an odd m, the HOMO is degenerate.

Note that branching of a chromophore is also possible if a central cycle, three-[158, 159] or four-membered[160] one, is introduced.

a. Trimethine shifts

The degeneracy of one of the boundary orbitals leads to the degeneracy of PET; therefore, two transitions are responsible for the observed longwave band.[161, 162] The violation of the equivalence of bonds in branched PC causes broadening of absorption bands (to 1300–1500 cm^{-1})[162] as compared to PMD with two TGs ($\sim$ 900 cm^{-1}).[163]

The contribution of PC into the wavelength of PET in the case of TPMD is evaluated as the so-called trimethine shift T

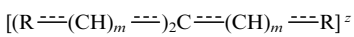
$$T = \lambda_m - \lambda_{m-1}\,. \tag{18}$$

It has been shown[164] that the parameter T depends on the parity of the number of the methine groups the topological index m and Φ_0

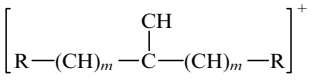
$$T = V + (-1)^m \Delta\left(\frac{\pi}{2} - 2\Phi_0\right), \tag{19}$$

where $\Delta = V/3\pi \simeq 10$ nm.

Due to the $(-1)^m$ multiple the trimethine shift alternately exceeds or is less than as the vinylene shift V, which is in accordance with the experimental data for TPMD **22** with indolenine residues (Table 4).



22



23

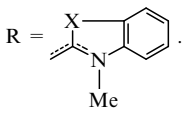
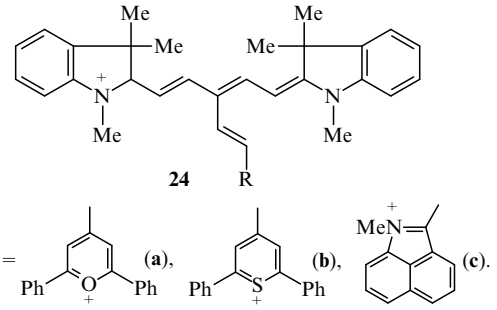


Table 4. Spectral characteristics of trinuclear (TPMD) **22** and binuclear (BPMD) **23** dyes (nm).[157]

X	*m*	TPMD (**22**)			DPMD (**23**)	
		z	λ_{max}	*T*	λ_{max}	*V*
CMe_2	1	+1	522	–	544	–
	2	+2	635	83	636	90
	3	+1	755	120	745	109
S	1	+1	534	–	556	–
	2	+2	635	101	650	94
CH=CH	1	+1	678	–	708	–
	2	+2	788	110	813	92

b. Asymmetrical trinuclear polymethine dyes

The violation of the C_3 symmetry lowers the degeneracy of MO and, hence, the degeneracy of electronic transitions; the splitting of the levels is proportional to the difference between the effective lengths of TG. When the topological indices differ sufficiently, two transitions in asymmetrical TPMD can manifest themselves in the spectra as separate maxima, which was observed for asymmetrical [2.2.2]heptamethinecyanines **24** containing two identical TGs and one differing in structure.[161, 162]



If effective lengths of the nuclei differ insignificantly (for 2-quinoline, benzothiazole, benzimidazole, $L = 3.0-3.5$), the absorption band has one maximum. The introduction of residues with a relatively high L value such as pyrylium (6.06), thiopyrylium (7.26), benzo[*c*,*d*]indole (6.50), causes splitting of the absorption band (Fig. 5).

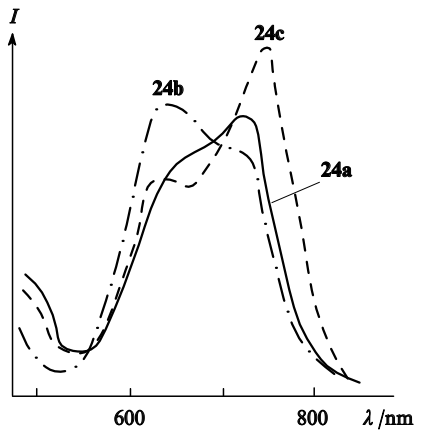
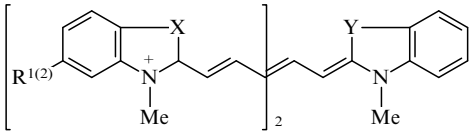


Figure 5. Absorption spectra of asymmetrical trinuclear dyes **24a**–**c**.

c. Excited states

Population of the degenerate excited state of symmetrical TPMD should be accompanied, according to the Jahn–Teller rule, by a significant change in the molecular geometry. If lifetime of the excited state is sufficiently long, one of the branches of TPMD deviates from the plane, and the symmetry of the chromophore lowers. It was pointed in a number of publications[156, 157, 165–167] that in the excited state one of the branches is located perpendicular to the plane of the rest of the molecule. Similar situation seems to occur in asymmetrical TPMD with symmetrical branching of PC at a small splitting of the energies of the states.

If TPMD contains one nucleus differing from the others, two conformers are possible: one corresponds to symmetrical binuclear dye with a substituent in the meso position, the other corresponds to the meso-substituted asymmetrical dye. A substantial change in geometry upon excitation leads also to significant Stokes shifts $\Delta\nu_C$. Table 5 lists the luminescence spectral data for asymmetrical TPMD **25**. The Stokes shifts are infact greater than those for binuclear dyes for which $\Delta\nu_C$ is 400–500 cm^{-1}. In the case of TPMD **25c** and **25h** bearing TG with significantly different basicities (indolenine, benzimidazole), two conformers with different fluorescence maxima were observed.[162, 168]



25

Table 5. Spectral characteristics of TPMD **25**.[162, 168]

Type of dye **25**	X	Y	R^1	R^2	λ_{max} /nm	λ_{max}^{fl} /nm	$\Delta\nu_C$ /cm^{-1}
a	S	S	H	H	632	639	1517
b	CH=CH	S	H	H	666	735	1390
c	S	CH=CH	H	H	636	709	1610
d	CH=CH	CH=CH	H	H	690	759	1318
e	CMe_2	CMe_2	H	H	628	698	1616
f	NPh	NPh	CN	CN	605	652	1176
g	CMe_2	NPh	H	CN	630	654 694	1464
h	NPh	CMe_2	CN	H	556	626 663	2901

IV. Changes in the structure of the polymethine chromophore

In addition to the basic topological factors that were comprehensively considered above, the energy of PET is appreciably influenced by such changes in the structure of polymethine chromophore as substitution of the methine groups by heteroatoms, introduction of substituents and the acetylene-cumulene bond, steric hindrances, cyclization of a part of PC, *etc*. These effects can be interpreted relatively reasonably within the framework of perturbation theory.[169–174] The final expressions resemble the well-known Hammett relationship

$$\Delta\lambda_{max} = \rho\sigma\,, \qquad (20)$$

where $\Delta\lambda_{max}$ is the spectral effect of perturbation, ρ is the change in the electronic structure of the chromophore upon excitation, and σ is the magnitude of perturbation.

Let us consider the most important types of perturbations of the structure of chromophore.

1. Replacement of methine groups by heteroatoms.

Within the framework of perturbation theory, this change in the structure can be simulated by varying the electronegativity of the μth atom or more precisely, the h_μ Coulomb integral. A change in

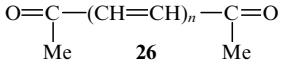
the wavelength of PET appear to be proportional to a change in the electron density (Δ_μ) upon excitation.[170–172]

$$\Delta\lambda = a\Delta_\mu h_\mu , \qquad (21)$$

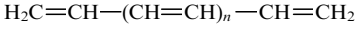
where

$$a = \frac{V(n+L)^2}{\pi} .$$

It was shown above that PMD are characterised by a remarkable changes in atomic populations during electronic transitions, whereas in HP chromophore Δ_μ values are substantially smaller. As a result, the heterosubstitution in polyenes affects the spectra much less. Thus the spectral effect of the replacement of the methine group by the nitrogen atom in PMD can exceed 100–120 nm, especially for the middle of the chain; on approaching the nuclei, the maximum is less shifted.[5, 9, 10, 170–172, 175] The changes in the spectra of polyenes are much less. Moreover, it should be taken into account that for HP the influence of the change in the degree of conjugation of the heterobond relative to the CC bond can overlap the effect of changes in electronegativity of the atom . It is the case, for example, for α,ω-diketones **26** in comparison to polyenes **27**.



26

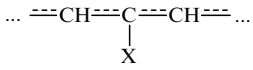


27

n	λ_{max} /nm		$\Delta\lambda$ /nm
	26 [118]	**27** [104]	
1	228	256	−28
2	278	289	−11
3	328	317	+11
4	351	343	+8
5	380	366	+14
6	406	384	+22

2. Conjugated substituents

Heteroatom X with a lone electron pair can be an example of the simplest conjugated substituent.



X = F, Cl, Br, OR, SR, NR_2 ... .

If the distance between the levels of a substituent and the boundary levels of the polymethine chromophore is significantly less than the energy gap, the formula for the displacement of the $\Delta\lambda$ maximum resembles formula (21). In the general case, with $\lambda = V(n + L)$, the formula can be written for the middle of the chain

$$\Delta\lambda = (-1)^{n+\mu+1}\left(\frac{\lambda^0_{max}}{\pi}\right)\delta_X ;$$

$$\delta_X = \frac{C^2_{vj}}{\varepsilon_j}\beta_{CX} , \qquad (22)$$

where atoms are numbered from the midpoint of PC, so that $\mu = 0$ for the meso position. The parameter δ_X characterises numerically the effect of the substituent: β_{CX} is the resonance integral between substituent X and the chromophore, C_{vj} is a coefficient of the jth MO of the substituent at the vth atom bound to the μth atom of the chromophore, and ε_j is the energy of the level of substituent.

Formula (22) reflexes qualitatively the known Förster–Dewar–Nott rule [172–174] concerning the direction of the shift of the longwave absorption band depending on the nature and the place of perturbation: the introduction of donor substutients ($\delta_X > 0$) or replacement of the methine groups by more electronegative atoms ($h_\mu > 0$) in the meso- and vinylogous positions (*i.e.* in the positions with the same parity, μ is even) in dyes A lead to bathochromic effects; on the contrary, the introduction of acceptor substituents ($\delta_X < 0$) or heterosubstitution by less electronegative atoms ($h_\mu < 0$) is accompanied under the same conditions by a shift of the maximum of the absorption band towards the shortwave region. For neighbouring positions and upon changing the class (*i.e.* the change in the number of vinylyne groups n in PC), the sign of the effect changes to the opposite, which is confirmed by a large body of experimental observations.[88, 170, 176, 177]

Note that for a more rigorous quantitative estimate, the inductive effect of substituents should be also taken into account. Thus the following correlational equation connecting the absorption frequency for thiacarbocyanines with the constants of resonance δ_{res} and inductive δ_{ind} interactions was found:[176, 178]

$$\Delta\nu = 67 - 1170(\delta_{ind} + 5.28\delta_{res}) . \qquad (23)$$

3. Rules of sensitivity

Spectral effects are rather sensitive to electron donor ability of LCS for the effect of conjugated substituents depends clearly on the distance between the interacting levels. A study of the influence of polar groups in thiazole and benzthiazole dyes [179] has shown that the spectral effect of electron donor groups decreases with an increase in the basicity of the dyes, and vice versa, the effect of electron-withdrawing substituents decreases under identical conditions.

Indeed, in PMD with high electron donor ability for which Φ_0, $\varphi_0 > 45$ °, the boundary levels are up-shifted and located nearer to the vacant level of the electron-accepting substituent (for instance, cyano or nitro group). And on the contrary, the boundary levels appear to be distant from the occupied level of the donor substituent. Since the interaction between the levels is inversely proportional to the distance between them, these dyes, other conditions being identical, are more sensitive to acceptor substituents; on the contrary, donor substituents cause smaller shifts of the absorption band.

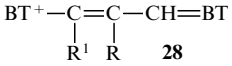
In dyes with a decreased electron donor ability (Φ_0, $\varphi_0 < 45$ °), the boundary levels are located nearer to the level of the donor substituent. For this reason, these dyes are more sensitive to similar substituents. Acceptor substituents should cause lesser effect, for their levels are more remote from the boundary levels responsible for the electronic transition. PMD, derivatives of benzo[*c*,*d*]indole with a decreased electron donor ability can provide the experimental evidence;[180] the introduction of donor groups leads to a larger shift of the maximum of the absorption band than the introduction of the electron-withdrawing nitro group.

Another rule concerns the magnitude of hypsochromic and bathochromic effects. An analysis of energies of transitions and mutual location of a chromophore and a substituent shows that the bathochromic shifts of the band of PET result from the interaction between the level of the substituent (both donor and acceptor) and the boundary level that is located closer to it, and hypsochromic shifts result from the interaction with the substituent having the more distant level. Bearing in mind that the levels usually repel and the shift of levels is inversely related to the distance between them, the following rule can be formulated: the introduction of conjugated substituents should cause larger, other conditions being identical, bathochromic shifts of absorption bands in the spectra, the difference between the values of the bathochromic and hypsochromic shifts being the larger, the greater is the energy gap.

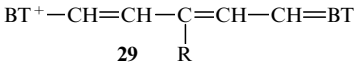
Table 6. Spectral data for chromophore-substituted PMD **28**–**31**.

Dye	R	R^1	λ_{max} /nm	$\Delta\lambda$ /nm
The data of Ref. 176				
28	H	H	556	–
	CN	H	610	+54
	H	CN	529	−33
29	H	–	636	–
	CN	–	613	−23
The data of Ref. 181				
30	H	–	758	–
	CN	–	810	+52
31	H	–	766	–
	CN	–	884	+118

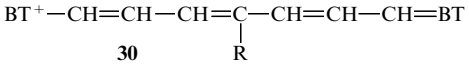
This can be illustrated by the spectral data for cyano-substituted thiacyanines (BT is the benzothiazole residue) presented in Table 6.



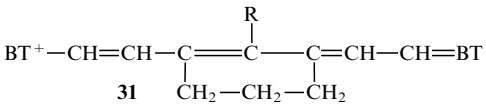
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29



30

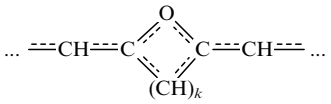


31

In the case of heterosubstitution, the absolute values of the hypsochromic shifts appear to be bigger than those of the bathochromic shifts due to the alternation of bonds arising in the chromophore.[171, 175]

4. Cyclisation of a part of the chain

Let us consider a fragment of the chromophore in which the bridge Q can be an ordinary bond, an atom (O, S), or a group of atoms (NR, $(CH_2)_m$, CH=CH, *o*-C_6H_4, *etc*.).



Spectral effects of symmetrical cyclization can be predicted.[182] The influence of cyclization with involvement of a single bond can be simulated within the framework of perturbation theory by increasing the resonance integral from zero to some finite value. Spectral effects may be rather significant (of the order of 100–200 nm).[10, 182]

The formation of cycles *via* bridges resembles the introduction of conjugated substituents with the only difference that two bonds are used instead of one. However, it is an increase in the number of bonds formed between the reacting systems (the chromophore and the bridge) that determines the principal difference on cyclization.

The change in the energy of MO upon cyclization is described by the general formula:

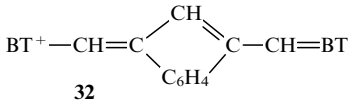
$$\varepsilon_i = \sum_j \frac{1}{\varepsilon_i - \varepsilon_j} \left(\sum_\mu \sum_\nu C_{i\mu} C_{j\nu} \beta_{\mu\nu} \right)^2 , \qquad (24)$$

where ε_i and $C_{i\mu}$ are energy and coefficients of MO of the chromophore, respectively, ε_j is energy, and $C_{j\nu}$ are coefficients of the MO of the bridge Q; $\beta_{\mu\nu}$ are resonance integrals of the bonds formed upon cyclization.

Analysis of the formula (24) shows that the effect of cyclization differs from the sum of effects of two conjugated substituents by a factor that includes the composition of the coefficients of four atoms μ, μ' and ν, ν' involved in the formation of two bonds between the chromophore and the bridge: $2C_{i\mu}C_{i\mu'}C_{j\nu}C_{j\nu'}$. Hence, not only the signs of populations of orbitals on atoms determined by squares of coefficients are clearly taken into account, as in the case of substituents, but also the signs of the coefficients of MO. With regard to whether the signs of the coefficients coincide or not, the effect of cyclization can either exceed the overall effect of substituents or be practically absent as is proved experimentally using the cyclization *via* *o*-phenylene,[183–186] vinylene, [187, 188] and polymethylene [64, 126, 181, 187, 188] bridges as examples.

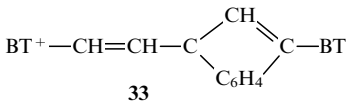
Polyphenylenes and polyphenylenevinylene can be considered as polyenes with the vinylene bridges.[189] This change in the topology of PC leads to an increase in the energy gap. Analogous cyclization *via* the sulfur atoms is followed by a shift of zones of the levels.[190, 191] This case, local levels of substituents appear between the zones, and the electronic transition is accompanied by the electron transfer through the conjugation chain. This phenomenon finds wide application in molecular electronics.[191–193]

The above-formulated rule about a bigger absolute value of the bathochromic shifts of the absorption band is true for spectral effects of cyclization. To illustrate this, below are given formulae of thiacyanines [184] **32**, **33** and malocyanines [183] **34**, **35** with the *o*-phenylene bridge in PC that obey this rule.



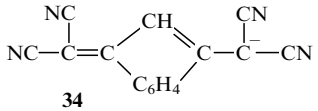
32

λ_{max} = 755, $\Delta\lambda$ = +100 nm



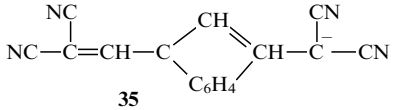
33

λ_{max} = 615, $\Delta\lambda$ = −40 nm



34

λ_{max} = 630, $\Delta\lambda$ = +290 nm



35

λ_{max} = 534, $\Delta\lambda$ = −30 nm

5. Change in the resonance interaction

A change in the conjugation takes place in the case of steric hindrances, with the introduction of acetylene/cumulene bonds and heterobonds, for example, −N=N−, −P=P−, *etc*. These perturbations can be conveniently simulated by varying the resonance integral $\delta\beta_{\mu\nu}$. Then the change in the energies of MO ($\delta\varepsilon_i$) and the wavelength of PET ($\delta\lambda$) will be written in the form [10, 12, 170, 171]

$$\delta\varepsilon_i = 2\sum_{\mu\nu} C_{i\mu} C_{i\nu} \delta\beta_{\mu\nu} , \qquad (25)$$

$$\Delta\lambda = -b\sum_{\mu\nu}\Delta_{\mu\nu}\delta\beta_{\mu\nu}\,, \tag{26}$$

where $b = 2(V/\pi)(n + L)^2$, and $\Delta_{\mu\nu} = \rho^*_{\mu\nu} - \rho^0_{\mu\nu}$ is the change in the order of the bond being varied in the excitation.

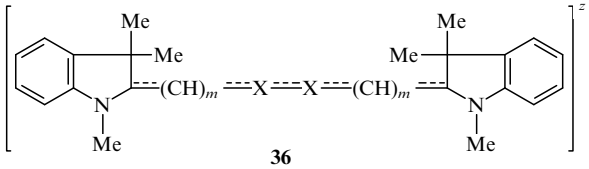
Since in polymethines the nodes of the boundary orbitals are located in the vicinity of atoms and in polyenes they are located near the middle of the bonds, the influence of the change in the resonance interaction between neighbouring atoms ($\nu = \mu \pm 1$) should be substantially less for PMD than for HP.

Spectral effects arising in PMD with steric hindrances and upon the introduction of an acetylene bond have been comprehensively studied.[5, 9, 171, 194–198] The shift of the absorption maximum was found to depend on the basicity of TG (especially strongly in the perturbations at the ends of PC). However, for polymethines with a medium electron donor ability, the sign of the effect in the middle of the chain depends only on the nature of perturbation.[171, 194]

Changes in the spectra of HP differ in principle. The analysis of formulae (25) and (26) and the signs of the boundary MO allow one to formulate the following rule: an increase in the resonance interaction along the formally double bond of PC in HP is accompanied by a hypsochromic shift, and that along the formally ordinary bond causes a bathochromic shift of the absorption band; a decrease in the resonance interaction along the formally double bond leads to bathochromic shifts, that along the ordinary bond results in a hypsochromic shift of the maximum.

Spectral data for acetylenes and cumulenes serve as the best experimental evidence. The introduction of additional π-bonds perpendicular to the major π-system in these compounds leads to a change in the CC bond lengths; in this case electronegativity of the atoms changes: for acetylenes the hypsochromic shifts, and for cumulenes the bathochromic shifts are observed.[88]

If in PC of symmetrical polyenes only the central bond is substituted, the sign of the effect depends on the class of the compound. It can be illustrated by the data of Table 7 for indopolyenes **36** the longwave band of which is reliably assigned to the polymethine band.



36

As is seen from the data presented, the sign of the effect changes every time in accordance with the above-formulated rule, when the class of HP is somehow changed: either by change in the chain length or by change in the number of the HOMO.

Table 7. Spectral data for HP **36** (nm) [115–117]

m	X	(*N* + 2)-form, *z* = 0			*N*-form, *z* = 2+		
		class	λ_{max}	$\Delta\lambda$	class	λ_{max}	$\Delta\lambda$
1	CH	A	410	–	C	450	–
1	N	A	464	+54	C	382	−68
2	CH	B	435	–	A	454	–
2	N	B	387	−48	A	492	+38

V. Systems with several polymethine chromophores

In some cases, LCS can contain several π-systems. In addition in order to give more spectacular interpretation it is more convenient sometimes to split the common chromophore into constituents that are responsible for individual bands. However, the spectra of molecules with several chromophores or aggregates of molecules with one chromophore differ from those of the initial systems due to the so-called interaction of chromophores.[199, 200] The theoretical interpretation of this phenomenon is given[201] in terms of the dipole-dipole approximation. It was shown that the interaction of chromophores leads to an extension of the absorption maxima against the position of the corresponding maxima in parent chromophores. The nature of this extension can be explained using a model proposed for the analysis of the excited states of molecular crystals.[202]

If the system contains two chromophores having the transition energies E_a and E_b ($E_a < E_b$) and the energy of the interaction H_{ab} is small, the energies of two new transitions E_- and E_+ are determined as follows:

$$E_- \simeq E_a - \frac{H_{ab}}{E_a - E_b}\,,$$

$$E_+ \simeq E_b + \frac{H_{ab}}{E_a - E_b}\,. \tag{27}$$

It is seen from these formulae that the interaction should result in the movement apart of the absorption maxima, the effect being the larger the closer the maxima are located. If the energies of the parent chromophores coincide, the formulae change somewhat

$$E_\pm = \frac{1}{2}\left(E_0 \pm \sqrt{E_0^2 + 4H_{ab}^2}\right). \tag{28}$$

It is impossible to say which of the bands belongs to the excitation of one chromophore and which belongs to the other. Both bands are associated with the excitation of both chromophores, but during one transition the chromophores are excited in phase, and during the other they are excited in antiphase.

In the dipole approximation, the energy of the interaction H_{ab} is calculated using the moments of transitions of the parent chromophores M_a and M_b

$$H_{ab} = \frac{e^2}{R^3}[(M_aM_b)\mathbf{R}_{ab}^2 - 2(M_a\mathbf{R}_{ab})(M_b\mathbf{R}_{ab})]\,, \tag{29}$$

where R is the length of the $\mathbf{R}_{ab}$ vector directed from the chromophore a to the chromophore b.

If two chromophores are arranged linearly, the longwave transition appears to be more intense, if they are located in a parallel way, the shortwave transition is more intense. If the dipoles are oriented arbitrarily with a ϑ angle between them, the ratio of intensities of the longwave I_- and shortwave I_+ transitions is

$$\frac{I_-}{I_+} = \mathrm{tg}^2\frac{\vartheta}{2}\,. \tag{30}$$

This approximation gives good results if the distance between chromophores exceeds their own dimensions.[200, 201, 203]

1. Bisdyes

Widely studied bisdyes are the simplest and most convenient systems in which two PET manifest themselves in the visible and near-IR ranges of the spectrum.

$$G_1-(CH=CH)_k-CH=G_2-M-G_3-(CH=CH)_l-CH=G_4$$

37

Here M is the bonding bridge that can be both conjugated and non-conjugated. In the spectra of bisdyes of symmetric structure ($G_1 = G_4$, $G_2 = G_3$, $k = l$), the absorption band corresponding to the parent PMD splits into two bands. The distance between the split bands and the ratio of their intensities depend on the degree

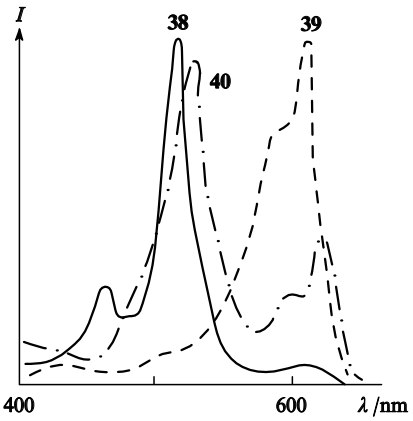
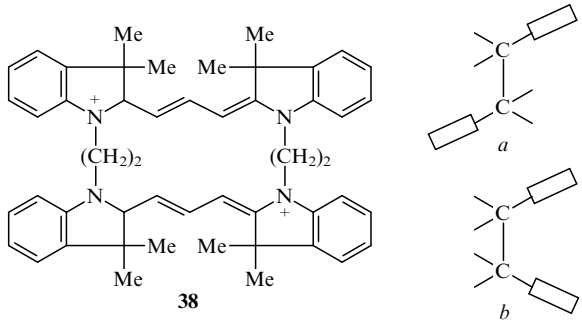


Figure 6. Absorption spectra of bisdyes **38**–**40**.

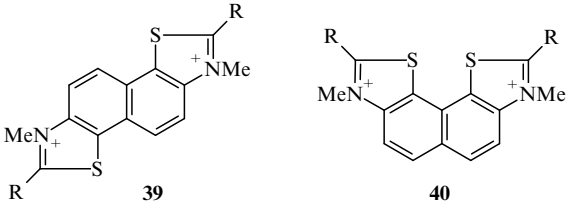
of conjugation, the distance and the angle between chromophores.[200, 203–206]

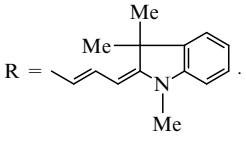
An experimental study of cyanine dyes bound by a non-conjugated polymethylene bridge, $-(CH_2)_m-$, has shown that the distance between the first and the second maxima decreases with an increase in the number of the methylene groups.[207] If the non-conjugated chromophores are arranged in the strictly parallel manner as in bisdyes **38**, the longwave transition is symmetry forbidden ($I_- = 0$) and all the intensity is concentrated in the shortwave band (Fig. 6).[208]



Note that the spectrum of the bisdye **38** was assigned to the erroneously observed conformation *a* of the dye in which any overlap of the π-orbitals and, hence, their interaction are lacking.[208] In fact the spectrum is in accordance with the conformation *b* with a dihedral angle between the π-systems of the chromophores of ~ 40 ° and a minimum distance of ~ 2.5 Å between the π-centres of both chromophores, which is sufficient for the effective interaction of the π-systems.

The interaction of the chromophores is more substantial in bis-dyes with conjugated bridges,[209–212] for example, in compounds **39** and **40**.





If in PMD **39** the chromophores are arranged linearly, practically all the intensity is concentrated in the longwave band (see Fig. 6). In the case of the dye **40** with a fixed acute angle between the chromophores, two bands are observed, however, according to formula (30), the band in the shortwave region is more intense.[211, 212]

2. Aggregation of polymethine dyes

There are many publications concerning the structure and application of molecular aggregates of PMD.[213–217]

The phenomenon of aggregation in dyes has been discovered by Scheibe[218] and Jelly.[219] PMD were found to form molecular aggregates both in solution and on the surface of certain crystals. It was shown that in aggregates the molecules of a dye are bound owing to the non-valent resonance interaction. Depending on the conditions and the molecular structure, dyes can form two main types of aggregates (*J* and *H*) that differ distinctly in the spectral properties. The maxima of the absorption bands of *J*-aggregates (*J*-bands) show a bathochromic shift whereas the maxima of the absorption bands of *H*-aggregates (*H*-bands) show a hypsochromic shift relative to the band maxima of isolated molecules (*M*-bands).

It was found that *J*- and *H*-aggregates differ in the value of the angle between the long axis of the chromophore and the axis of the molecular aggregate.[218, 220, 221] In accordance with the theory of interaction of chromophores, different orientation of molecules in the corresponding aggregates leads to the appearance of very intense and very narrow longwave bands in the spectra of *J*-aggregates, unlike the spectra of *H*-aggregates.

It should be noted that the nature of a solvent, the type of the surface of the ionic crystal and some other factors can affect appreciably the aggregation of dyes.[17, 213–215]

VI. Terminal groups as local chromophores

If LCS contain complex conjugated TG with their own strong absorption in addition to the band corresponding to the polymethine chromophore, the bands resulted from the transitions from the orbitals localised predominantly in the terminal nuclei appear in the spectra; therefore, TG can be conventionally considered as local chromophores.

Within the orbital approximation, the simplest type of local transitions is described by the local level and one of polymethine levels delocalised over the whole molecule of LCS (Fig. 7 *a*–*d*). As a result, LET and PET should interact strongly. The assignment of the band to polymethine chromophores depends on which transition, PET or LET, has the lowest energy.

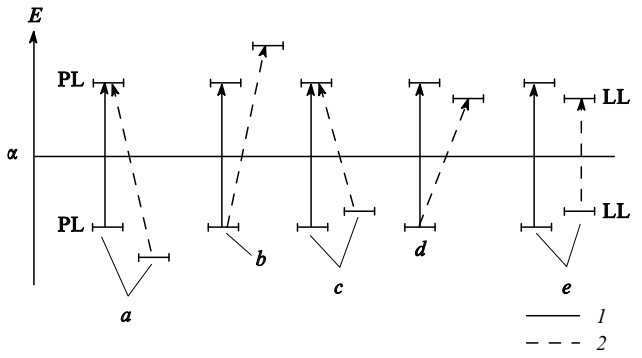
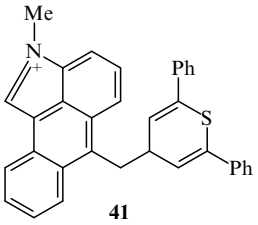


Figure 7. The position of polymethine (PL) and local (LL) levels in LCS with local chromophores (*a*–*d*) and in bis-dyes (*e*); (*1*) PET, (*2*) LET.

1. Local transitions in PMD

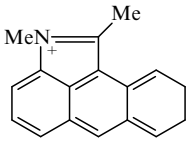
In the case of typical PMD, delocalised polymethine levels are usually arranged nearer to the Fermi level than the local level (see Fig. 7 *a*,*b*). The first transition has the polymethine character, the

second is mainly localised in TG. Asymmetrical cyanines, derivatives of thiazolopyridinium,[222–224] thiazolopyrimidinium,[225–227] 2,6-diphenylpyrylium and its heteroanalogues[228, 229] are compounds with this arrangement of the levels. If both residues have relatively intense absorption of their own as, for instance, in dye **41**, both nuclei can be regarded as local chromophores.[230]

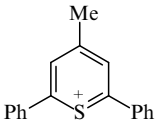


41

λ_{max} = 784; 500; 384 nm



λ_{max} = 543 nm



λ_{max} = 410 nm

Calculations have shown that the first transition is delocalised over the whole molecule, the atoms of the pyrroloanthracene moiety participate predominantly in the second, and atoms of the thiapyrylium nucleus take part in the third.

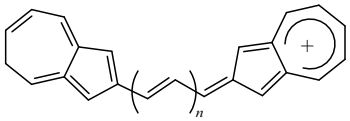
Lengthening of PC little affects the localised levels, however, the polymethine level regularly approaches the Fermi level. For this reason, the band responsible for LET undergoes a bathochromic shift as well as the band corresponding to PET, but the magnitude of this shift is less than that of the vinylene shift of the polymethine band.[81, 222–227, 231]

Symmetrical PMD contain two identical local chromophores. If they do not interact as, for example, in α,ω-di(1-azulenyl)polymethines, the second band observed experimentally is responsible for two practically degenerate LETs.[81] If local chromophores do interact, the bands split, as was observed for symmetrical cyanine dyes, derivatives of thiazolopyridinium.[231]

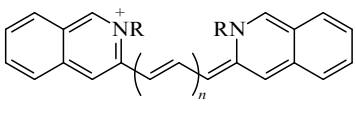
2. Inversion of local and polymethine electronic transitions

If local levels appear nearer to the Fermi level than in polymethines (Fig. 7 *c*,*d*), the local transition has the lowest energy, *i.e.* the inversion of the transitions takes place. The following conditions are necessary for the inversion of PET and LET: TG should have a level located near the Fermi level (it is usually the case when the initial heterocycle is deeply coloured); a relatively big distance between the polymethine levels; a shift of polymethine levels towards the local level (it occurs if PMD contains either strongly basic or weakly basic nuclei, *i.e.* when the Φ_0 index takes the values close to the limiting, 0 or 90 °).

These conditions are realised, for example, in α,ω-di(2-azulenyl)polymethines **42** (Φ_0 = 0 °) or **43** with residues of isoquinoline (Φ_0 = 80 °).

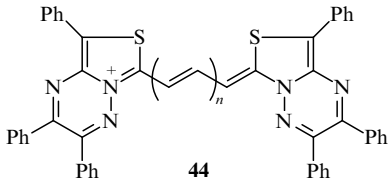


42



43

It has been shown that two first transitions are mainly localised on the atoms of the terminal group (though the atoms in the odd positions also participate in them), which can be conventionally considered as conjugated substituent of the local chromophore. These transitions are characterised by smaller vinylene shifts as compared to the third transition localised in the polymethine chromophore.[81] The polymethine levels come closer together regularly with an increase in the number of vinylene groups, while the position of the local level changes little. Consequently, lengthening of the chain can be accompanied by a change in the nature of transitions.[81]



44

The inversion of PET and LET was observed experimentally in triazolotriazine dyes **44**.[224] As is seen from Fig. 8, the contour of the shortwave band is close to those of the longwave bands corresponding to PET in typical PMD. Obviously, the long wavelength band in the case of dyes **44** can be assigned to the local transition in the residues of thiazolotriazinium.

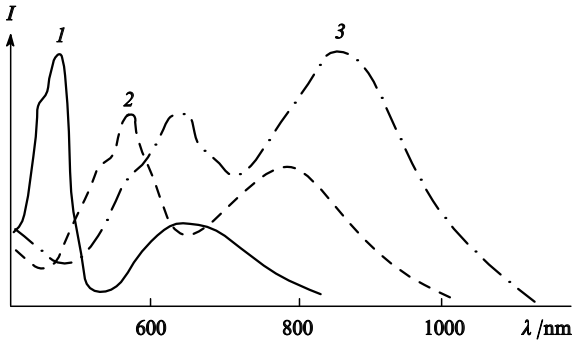


Figure 8. The absorption specta of PMD **44**.
n: (*1*) 0, (*2*) 1, (*3*) 2.

3. Local transitions in heterylpolyenes

A change in the type of LCS, the passage from PMD to HP, influences little the position of local levels, but affects significantly the position of polymethine levels. First, they are shifted by approximately half of the gap due to an additional π-level, upshifted in the case of the reduced form and down-shifted in the case of the oxidised form, in accordance with formula (7). Second, the distance between the highest occupied and the lowest unoccupied polymethine levels and, therefore, the energy of PET increases additionally due to the strong alternation of bonds in PC. As a result, the inversion of electronic transitions is more probable in HP than in PMD with the same TG, especially for a small number of vinylene groups in the chain. As the length of the polymethine chromophore is increased, its levels approach the Fermi level but significantly more slowly than the polymethine levels do in PMD. Since for polyenes $\varphi_0 = \Phi_0 \pm 45$ °, the maximum shift of the polymethine levels is achieved when TG has a medium electron donor ability (Φ_0 = 45 °), in contrast to PMD. α,ω-Di(1-azulenyl)polyenes and their isomers having PC in another position can serve as examples. In the spectra of these compounds in the visible and near-IR regions, two typical absorption bands were observed: a broad longwave and a more narrow, shortwave band.[232, 233] Calculations show that the two first transitions result from excitations in local azylene chromophores, and the third is

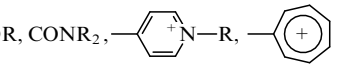
delocalised along the whole molecule of the polyene.[81] Lengthening of the chain by one vinylene group practically does not change the energies of the first and the second transitions, further introduction of vinylene groups can result even in the negative vinylene shift (−8 nm). It is probably associated with the weakening of the interaction between local chromophores. The vinylene shift of the third (polymethine) transition is 30–35 nm, which falls within the interval of values typical of PET in polyenes.

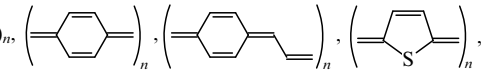
4. Local transitions in asymmetric donor-acceptor polyenes

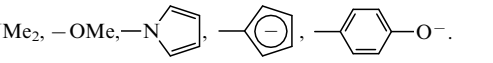
Of especial interest is the case when both boundary levels appear to be local (Fig. 7 *e*) and are localised in different TG as, for example, in donor-acceptor polyenes of the general formula

A—M—D

45

A = C≡N, CHO, COOR, $CONR_2$, ;

M = $(CH=CH)_n$, ,

where D = $-NMe_2$, $-OMe$, .

In these systems, the photoexcitation is accompanied by a significant intramolecular charge transfer, the so-called photoinduced charge transfer.[234–237] In the first approximation, the energy of the electronic transition between the localised HOMO and LUMO is determined by the difference between the ionisation potential of the donor group P_D and the electron affinity of acceptor E_A.[39, 238–240]

$$E = P_D - E_A + C\,, \tag{31}$$

where C is correction for the Coulomb and resonance interactions of electrons.

Localisation of both boundary MO results, as a rule, in a lower intensity of charge transfer transitions. At the same time, the dipole moment of the molecule in the excited state increases significantly, and therefore, asymmetrical donor-acceptor systems **45** exhibit high polarisability. This property determines their wide application in non-linear optics.[33–37, 189–193]

Due to considerable changes in the dipole moment, these local transitions are very sensitive to the polarity of the solvent.[236–238, 241, 242] A decrease in the energy of charge transfer transitions can originate from the rotation of fragments of the molecule in the excited state with the violation of conjugation, for example, of dimethylamino group. In this case, in very polar solvents, fluorescence with an anomalously high Stokes shift and low quantum yield is observed.[39, 236–238]

Hence, local transitions can influence substantially the spectra of LCS changing even the nature of the longwave band, which usually determines the colour of the compound.

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