

**SYMMETRIC POLYMETHINE DYES
WITH A CENTRALLY DISPOSED CONJUGATED BRIDGE:
A TOPOLOGICAL ANALYSIS OF FRONTIER ENERGY LEVELS**

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For polymethine dye molecules constituted of two pairs of identical end fragments symmetrically bound to a central bridge of C_{2v} symmetry, general expressions are derived within the long-polymethine-chain approximation which relate the topology of constituent molecular moieties to the frontier energy levels of the integral system. The results are presented in terms of the Green's function formalism and exemplified by squarylium and thiosquarylium compounds containing a variety of end groups normally used in dye chemistry. A simple relation has been obtained for the shift of the first electronic transition wavelength of a bridged molecule relative to its analogue with the opened polymethine chain. It is shown that the sign of the shift depends on effective parameters of end groups and the central bridge, as well as on the polymethine chain length.

Among π -conjugated polymethine molecules, a highly important place is occupied by those containing various cyclic fragments in the middle of the polymethine chain. For instance, photochemically stable and selectively absorbing long-wavelength light squarylium dyes show much promise in electrophotography, light energy conversion [1], optical information storage [2], nonlinear optics [3] etc. The technological needs invite theoretical studies to reveal relationships between chemical constitution and spectral properties of the compounds concerned. Particular attention is deserved by description of frontier molecular orbitals and those lying in close proximity to them, as these energy levels are

responsible for optical behavior of molecules. For instance, a three-level model was reported to be invoked in calculations of third-order nonlinear optical susceptibilities for squaraines [4].

Theoretical analysis of molecular orbitals for conjugated compounds owes, to a large extent, its remarkable progress to graph theoretical approaches which proved to be in no case only the subject of mathematical interest (this line can be exemplified by Refs. [5,6,7,8]; for comprehensive treatment of the subject see monographs [9]). Two decades ago, this area was replenished by an original methodology subsequently called the long-polymethine-chain approximation (LPCA) [10,11,12,13]. It takes advantage from the fact that molecules containing a sufficiently long polymethine chain are characterized by a rather small distance between frontier levels which in addition can be expressed as a rapidly convergent power series in the reverse chain length [12]. As a result, the model of a long chain provides an adequate description even for short-chain species and the shifts of frontier energy levels caused by the attachment of arbitrary end groups to the polymethine chain are expressible analytically. End groups are characterized by a set of easily calculable effective topological parameters which account for their effect on the molecular electron donor ability as well as their contribution to the increased wavelength of the first electronic transition. Among other applications, these parameters reported previously for a variety of end groups proved to be very helpful in the analysis of nonlinear optical properties of polymethine compounds [14,15].

Rationalization of chemical and optical behavior of bridged polymethine dyes is also attributed much to LPCA. Qualitative prerequisites for this avenue in the treatment of a cyclized conjugated chromophore burgeoned even in the early sixties when Dyadyusha pioneered a qualitative symmetry-based consideration of the spectral changes caused by a cyclic bridge centrally incorporated into the main chain of polymethine dyes [16]. Further advance in research on bridged polymethine species was gained in the framework of the well-elaborated LPCA, by the analysis of their energy spectra using the secular polynomial technique [17,18]. The conditions for the existence of local levels as well as absorption maximum shifts in dye vinylogous series were thus studied in the above Refs.

In the present paper, we aim at gaining an insight into bridge effects on the frontier level positions for polymethine dyes. With this object in view, the long-polymethine-chain approximation is generalized to conjugated molecules constituted by four arbitrary fragments bound to a bridge of C_{2v} symmetry. Specifically, our concern here is with the systems constituted by two Γ_1 and two Γ_2 end fragments attached by bonds with the respective resonance integrals β_1 and β_2 to the central fragment, or bridge, Q (see Fig. 1a). Let the four end fragments, though unbound to each other, be regarded as a single molecular subsystem Γ . From here on we switch from dyes as molecular objects characterized by a certain geometry to the corresponding chemical graphs (with weighed vertices and edges) which are determined by their adjacency matrices; spectra of such graphs coincide (accurate to units of measurement) with the Hückel energy spectra of molecules, and this relationship is given much space in the literature (see, e.g., Refs. [5] and [9]). It is also noteworthy that the above-mentioned symmetry referring to molecular geometrical parameters is in fact even lower than that of the corresponding topological objects; thus, we are allowed to use regularities resulting from this symmetry in the treatment of the chemical graphs concerned.

The elements of the inverse of the adjacency matrix of the subsystem Γ called also Green's functions (GF) which account for the indirect coupling and perturbation transmission between the atoms j and j' binding the end subsystem to the central bridge,

$$g_{jj'}^{(\Gamma)}(z) = \left\langle j \left| (z \cdot \mathbf{1} - \mathbf{H}_\Gamma)^{-1} \right| j' \right\rangle \quad (1)$$

are the functions of the energy variable z and have poles at energy levels of the subsystem Γ , i.e., at eigenvalues of the Hamiltonian H_Γ (coinciding with those of the fragments Γ_1 and Γ_2).

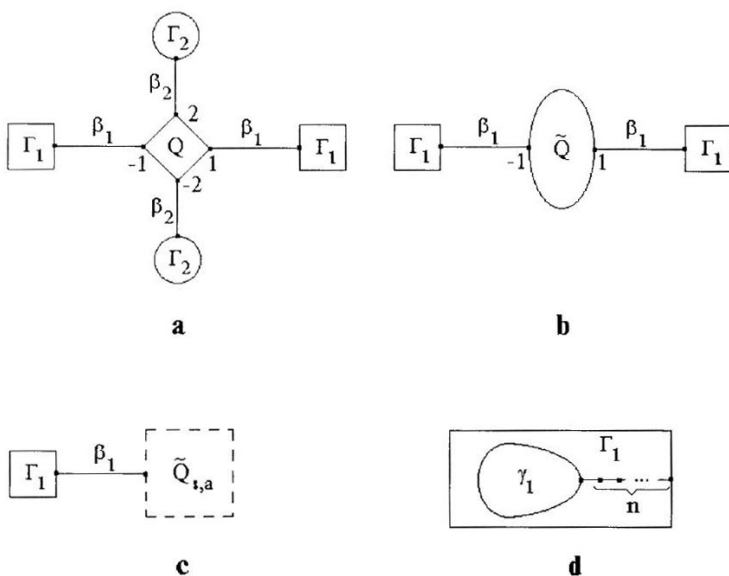


Fig. 1. Topology of the bridged polymethine compounds considered: a - general form; b - quasilinear form with $\tilde{Q} = \Gamma_2 - Q - \Gamma_2$; c - reduced quasilinear form; d - constitution of the end group Γ_1 .

The energy spectrum of the whole system is determined by the roots of the following equation [12]:

$$\det[1 - \mathbf{g}^{(Q)}(z)\beta \mathbf{g}^{(\Gamma)}(z)\beta^T] = 0 \quad (2)$$

that represents the generalized Heilbronner relation [19]. (Here $\mathbf{g}^{(Q)}(z)$ is the GF matrix of the bridge Q and β^T denotes the transposed matrix β of interfragment bonds). From symmetry considerations, this 4th order determinant can be represented as follows:

$$\begin{vmatrix} \mathbf{C}(z) & \mathbf{D}(z) \\ \mathbf{D}(z) & \mathbf{C}(z) \end{vmatrix} = 0, \quad (3)$$

where

$$\mathbf{C}(z) = \begin{pmatrix} 1 - \beta_1^2 g^{(\Gamma_1)}(z) g_{11}^{(Q)}(z) & -\beta_2^2 g^{(\Gamma_2)}(z) g_{12}^{(Q)}(z) \\ -\beta_1^2 g^{(\Gamma_1)}(z) g_{12}^{(Q)}(z) & 1 - \beta_2^2 g^{(\Gamma_2)}(z) g_{22}^{(Q)}(z) \end{pmatrix}, \quad (4)$$

$$\mathbf{D}(z) = \begin{pmatrix} -\beta_1^2 g^{(\Gamma_1)}(z) g_{-1,1}^{(Q)}(z) & -\beta_2^2 g^{(\Gamma_2)}(z) g_{12}^{(Q)}(z) \\ -\beta_1^2 g^{(\Gamma_1)}(z) g_{12}^{(Q)}(z) & -\beta_2^2 g^{(\Gamma_2)}(z) g_{-2,2}^{(Q)}(z) \end{pmatrix}, \quad (5)$$

and $g^{(\Gamma_1)}(z)$ and $g^{(\Gamma_2)}(z)$ denote the diagonal ij elements of the Green's function matrix corresponding to the atoms through which the subsystem Γ is bound to the bridge Q . The Eq. (3) breaks up into two equations describing symmetric and antisymmetric states of the system:

$$\det[\mathbf{C}(z) + \mathbf{D}(z)] = 1 - \beta_1^2 g^{(\Gamma_1)}(z) g_{s1}^{(Q)}(z) - \beta_2^2 g^{(\Gamma_2)}(z) g_{s2}^{(Q)}(z) + \beta_1^2 \beta_2^2 g^{(\Gamma_1)}(z) g^{(\Gamma_2)}(z) \left\{ g_{s1}^{(Q)}(z) g_{s2}^{(Q)}(z) - 4 \left[g_{12}^{(Q)}(z) \right]^2 \right\} = 0 \quad (6)$$

$$\det[\mathbf{C}(z) - \mathbf{D}(z)] = \left[1 - \beta_1^2 g^{(\Gamma_1)}(z) g_{a1}^{(Q)}(z) \right] \left[1 - \beta_2^2 g^{(\Gamma_2)}(z) g_{a2}^{(Q)}(z) \right] = 0, \quad (7)$$

where

$$g_{si,ai}^{(Q)}(z) = g_{ii}^{(Q)}(z) \pm g_{-i,i}^{(Q)}(z), \quad i = 1, 2. \quad (8)$$

The relations derived demonstrate that due to the linkage of fragments Γ_1 and Γ_2 through the bridge Q , their states mix to provide symmetric molecular states transformed by the irreducible representations A_1 and A_2 of the symmetry

group C_{2v} . At the same time, antisymmetric molecular states originating from the fragments Γ_1 and Γ_2 do not mix and are transformed by the irreducible representations B_1 and B_2 ; these are respectively described by the first and the second bracketed expressions, when nullified, in Eq. (7).

The molecular system depicted in Fig. 1a can be reduced to a quasilinear form if the fragments Γ_2 -Q- Γ_2 are combined into a new one, \tilde{Q} (see Fig. 1b). GF for the complex fragment \tilde{Q} and for its constituents are interrelated by the Dyson-like equation [12]:

$$\mathbf{g}^{(\tilde{Q})}(z) = \mathbf{g}^{(Q)}(z) + \mathbf{g}^{(Q)}(z)\beta\mathbf{g}^{(\Gamma_2)}(z)\beta^T\mathbf{g}^{(\tilde{Q})}(z) = 0 \quad (9)$$

having, in our specific case, the following solutions:

$$\begin{aligned} \mathbf{g}^{(\tilde{Q}_s)}(z) &\equiv \mathbf{g}_{11}^{(\tilde{Q})}(z) + \mathbf{g}_{-1,1}^{(\tilde{Q})}(z) \\ &= \mathbf{g}_{s1}^{(Q)}(z) + 4\beta_2^2\mathbf{g}^{(\Gamma_2)}(z)\left[\mathbf{g}_{12}^{(Q)}(z)\right]^2\left[1 - \beta_2^2\mathbf{g}^{(\Gamma_2)}(z)\mathbf{g}_{s2}^{(Q)}(z)\right]^{-1} \end{aligned} \quad (10)$$

$$\mathbf{g}^{(\tilde{Q}_a)}(z) \equiv \mathbf{g}_{11}^{(\tilde{Q})}(z) - \mathbf{g}_{-1,1}^{(\tilde{Q})}(z) = \mathbf{g}_{a1}^{(Q)}(z). \quad (11)$$

As evidenced by the latter relation, the antisymmetric GFs for the complex fragment \tilde{Q} and for its constituent original bridge Q coincide. Due to the quasilinear representation, the spectrum of the molecular system concerned is expressed in terms of the compact system of equations:

$$\beta_1^2\mathbf{g}^{(\Gamma_1)}(z)\mathbf{g}^{(\tilde{Q}_s)}(z) = 1, \quad \beta_1^2\mathbf{g}^{(\Gamma_1)}(z)\mathbf{g}^{(\tilde{Q}_a)}(z) = 1, \quad (12)$$

$$\beta_2^2\mathbf{g}^{(\Gamma_2)}(z)\mathbf{g}_{a2}^{(Q)}(z) = 1. \quad (13)$$

Indeed, substituting Eq. (10) into the first of Eqs. (12) allows us to return to Eq. (6), whereas the second Eq. (12) (with regard to (11)) and (13) constitute Eq. (7).

The attractive feature of the representation involved is that each of the equations in the above system specifies an energy spectrum of some efficient molecule consisting of two fragments bound by a single bond (see Fig. 1c). Systems of this kind and the corresponding formalism were treated previously, in the analysis of effects caused on the energy spectrum of the polymethine chain by end fragments locally attached to it [12, 13]. In the framework of the long-chain approximation (valid even at $n = 1$ and hence applicable to the system under consideration), the positive energy level which is the nearest to the Fermi level is expressed (in units of $|\beta|$, the magnitude of the resonance integral for a carbon-carbon bond in the polymethine chain) as:

$$z_{s,a1} \approx 2\pi\epsilon_{s,a} \tilde{F}_{s,a} \left[1 - \pi \left(\tilde{\ell}'_{s,a} + \frac{\pi}{6} \tilde{F}_{s,a} \right) \tilde{F}_{s,a} \epsilon_{s,a}^2 \right], \quad (14)$$

$$\epsilon_{s,a} = [n + 1 + \tilde{\ell}_{s,a}]^{-1}$$

$$\tilde{F}_{s,a} = \{F_{\gamma_1} + F_{s,a}\}, \quad \tilde{\ell}_{s,a} = \ell_{\gamma_1} + \ell_{s,a}, \quad \tilde{\ell}'_{s,a} = \ell'_{\gamma_1} + \ell'_{s,a}, \quad (15)$$

where curly bracing of an expression means taking its fractional part and the effective parameters of end fragments, F_M , ℓ_M , and ℓ'_M for $M = \gamma_1, s$, and a are determined by the corresponding GFs $g^{(M)}(z)$ with $M = \gamma_1, \bar{Q}_s$, and \bar{Q}_a :

$$F_M = \lim_{z \rightarrow 0} \frac{1}{\pi} \text{arcctg} \frac{1}{g^{(M)}(z)} \quad (16)$$

$$\ell_M = - \lim_{z \rightarrow 0} \frac{2 \left[g^{(M)}(z) \right]' + \left[g^{(M)}(z) \right]^2}{1 + \left[g^{(M)}(z) \right]^2} \quad (17)$$

$$\begin{aligned}
 \ell'_M = -\lim_{z \rightarrow 0} & \left\{ \frac{2 \left[g^{(M)}(z) \right]''}{1 + \left[g^{(M)}(z) \right]^2} \right. \\
 & \left. + g^{(M)}(z) \frac{8 \left[g^{(M)}(z) \right]' \left(1 - \left[g^{(M)}(z) \right]' \right) + \left[g^{(M)}(z) \right]^2 - 1}{\left[1 + \left[g^{(M)}(z) \right]^2 \right]^2} \right\} \quad (18)
 \end{aligned}$$

(The fragment γ_1 , along with the n-methine chain, constitutes the end fragment Γ_1 , as shown in Fig. 1d). The negative energy levels nearest to the Fermi level are obtainable by the same relations (14) on substituting $\tilde{F}_{s,a} - 1$ for $\tilde{F}_{s,a}$.

For many applications, the long-chain approximation linear in $\epsilon_{s,a}$ which is hereinafter designated by LCA-0 (as distinct from the approximation (14) accurate to $\epsilon_{s,a}^3$ and designated by LCA-1) proves quite sufficient. Within the LCA-0 context, the parameters $\tilde{F}_{s,a}$, $\epsilon_{s,a}$, and $\tilde{\ell}_{s,a}$ have a straightforward physical meaning. The value $\tilde{F}_{s,a}$ characterizes the positions of levels of the same symmetry relative to the Fermi level, and the value $\epsilon_{s,a}$ describes the energy gap between them that depends on the end-group effective length, $\tilde{\ell}_{s,a}$. If the central bridge is represented by a N-methine chain, then we are led to:

$$\begin{aligned}
 g^{(\bar{Q}_s)}(z) &= -\frac{\cos[(N-1)\theta/2]}{\cos[(N+1)\theta/2]}, & g^{(\bar{Q}_a)}(z) &= -\frac{\sin[(N-1)\theta/2]}{\sin[(N+1)\theta/2]}, \\
 \theta &= \arccos(-z/2)
 \end{aligned} \quad (19)$$

and effective parameters assume the form:

$$F_s = \left\{ \frac{N+1}{4} \right\}, F_a = \left\{ \frac{N-1}{4} \right\}, \ell_s = \ell_a = \frac{N-1}{2}, \ell'_s = \ell'_a = 0 \quad (20)$$

As evident from Eq. (15), in the case concerned we have: $\tilde{F}_s - \tilde{F}_a = 1/2$ and $\tilde{\ell}_s = \tilde{\ell}_a$, which implies equidistant alternating symmetric and antisymmetric levels (see Fig. 2a). The interlevel gap amounts to $2\pi/(N+1+2n+2\ell_{\gamma_1})$, in accordance with the result obtained for polymethine compounds with the unbridged chain [12,13].

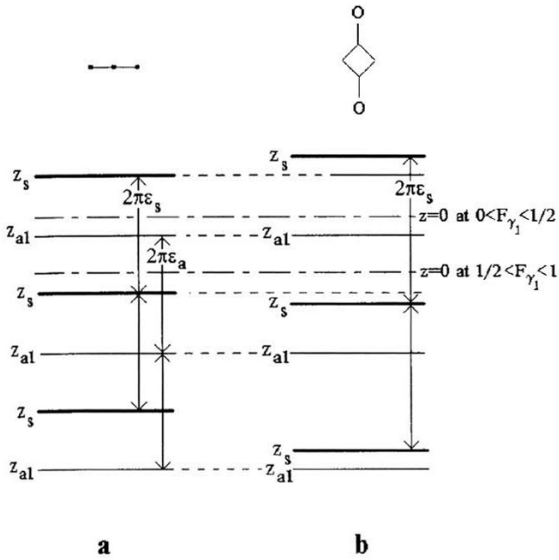


Fig. 2. Energy spectrum in the vicinity of the Fermi level ($z = 0$) for open-chain polymethine compounds (a) and their squarylium analogues (b).

The relations (14)-(18) can be exemplified by squaraine-like dyes, i.e., by polymethine molecules with a four-membered conjugated cycle regarded as the bridge Q and two identical heteroatoms, with the Coulomb integrals α_2 representing fragments Γ_2 . With this parametrization, symmetric and antisymmetric GFs as well as the GF $g_{12}^{(Q)}(z)$ for a square bridge Q appear as follows:

$$\begin{aligned} g_{s1}^{(Q)}(z) = g_{s2}^{(Q)}(z) &= \frac{z}{z^2 - 4}, & g_{a1}^{(Q)}(z) = g_{a2}^{(Q)}(z) &= \frac{1}{z}, \\ g_{12}^{(Q)}(z) &= -\frac{1}{z^2 - 4} \end{aligned} \quad (21)$$

Then, taking account of the explicit form of the GF for the fragment Γ_2 : $g^{(\Gamma_2)}(z) = (z - \alpha_2)^{-1}$ and invoking Eq. (10), the symmetric GF for the fragment \tilde{Q} is easy to derive:

$$g^{(\tilde{Q}_s)} = \frac{z^2 - \alpha_2 z - \beta_2^2}{z^3 - \alpha_2 z^2 - (4 + \beta_2^2)z + 4\alpha_2} \quad (22)$$

Substituting this function, along with $g^{(\tilde{Q}_a)}(z)$, into Eqs. (16)-(18) leads to:

$$\begin{aligned} F_s &= \frac{1}{\pi} \operatorname{arccctg} \left(-\frac{4\alpha_2}{\beta_2^2} \right)_{\alpha_2 < \beta_2 < 0} \approx \frac{\beta_2^2}{4\pi|\alpha_2|}, \\ \ell_s &= \frac{8(\alpha_2^2 + \beta_2^2) + \beta_2^4}{16\alpha_2^2 + \beta_2^4}, & \ell'_s &= 2\alpha_2\beta_2^2 \frac{\beta_2^4 + 16\beta_2^2 + 8\alpha_2^2 + 128}{(16\alpha_2^2 + \beta_2^4)^2}, \end{aligned} \quad (23)$$

$$F_a = \frac{1}{2}, \quad \ell_a = 1, \quad \ell'_a = 0 \quad (24)$$

As may be seen from Eq. (23), $\ell_s > 1/2$ and, with $\alpha_2 < \beta_2 < 0$, $\ell_s < 1$. It is noteworthy that the values of the effective parameters indicated in Eq. (24) for a square bridge coincide with those for a three-methine chain (see Eq. (20) at $N=3$). For this reason, antisymmetric states transformed by the irreducible representation B_1 are invariant under the substitution of the three-methine chain by the complex fragment \tilde{Q} . As the effective lengths ℓ_s and ℓ_a are not the same and the difference $F_s - F_a$ is not equal to $1/2$, alternating symmetric and antisymmetric levels are no longer equidistant (see Fig. 2b).

Eq. (13) for the energy levels of antisymmetric states transformed by the irreducible representation B_2 can be written as the quadratic equation:

$$z_{a2}(z_{a2} - \alpha_2) = \beta_2^2 \quad (25)$$













For squarylium and thiosquarylium dyes which contain two oxygen or two sulfur atoms as fragments Γ_2 ($\alpha_2 = -2$, $\beta_2 = -1$ and $\alpha_2 = -0.7$, $\beta_2 = -0.7$) bound to the four-membered cycle, we respectively arrive at:

$$z_{a2} = 0.4142, \quad F_s = 0.0396, \quad \ell_s = 0.6308, \quad \ell'_s = -0.1676. \quad (26)$$

$$z_{a2} = 0.4326, \quad F_s = 0.0551, \quad \ell_s = 1.0000, \quad \ell'_s = -1.4710. \quad (27)$$

The values indicated in Eqs. (24) and (26), (27) remain constant, no matter what end fragments γ_1 are attached to the central bridge. In Table 1, various groups γ_1 are listed, with the corresponding effective parameters indicated. The values z_s and z_{a1} calculated in LCA-0 and LCA-1 by formulae (14) and (15) with $n=1$ as well as by the Hückel method are also presented. The parameter F_{γ_1} normally referred to as the end-group electron donor ability falls into the range from 0.5 to 1 for the groups listed and thus provides the situation when the z_s and z_{a1} levels nearest to the Fermi level lie respectively below and above it (see Fig.2b). Groups of this kind are classified with the class A, in distinction to the class B characterized by $0 < F_{\gamma_1} < 1/2$ and inverse symmetries of the frontier levels in the resulting polymethine compound [16].

Table 1. End groups γ_1 , their effective parameters, F_{γ_1} , ℓ_{γ_1} , and ℓ'_{γ_1} , and the frontier energy levels of the corresponding open-chain, squarilium, and thioquarilium dyes in the HMO, LCA 0, and LCA-1 approximations (energies are expressed in units of β), the magnitude of the resonance integral for a carbon carbon bond in the polymethine chain). The Coulomb, α_0 , and the resonance, β_{CC} , integrals are defined respectively as $\alpha_0 = \text{HpxOe}$ and HpxPc ; with commonly used $\beta = 1$ eV values: $\ell_{\text{O}} = 0.18$, $\ell_{\text{N}} = 1.10$, $\ell_{\text{S}} = 2.18$, $\ell_{\text{C}} = 0.7$, $\ell_{\text{C}=\text{C}} = 1.10$, $\ell_{\text{C}=\text{C}} = 0.4$, for exocyclic oxygen and sulfur atoms of bridge fragments, $\ell_{\text{C}=\text{C}} = 1.10$, $\ell_{\text{C}=\text{C}} = 0.7$.

No	γ_1	F_{γ_1}	ℓ_{γ_1}	ℓ'_{γ_1}				
1.		0.7889	3.001	2.943	z_1 (HMO) 0.2707 z_1 (LCA-1) 0.2789 z_1 (LCA-0) 0.3025 z_2 (HMO) -0.2290 z_2 (LCA-1) -0.2326 z_2 (LCA-0) -0.2210	z_1 (HMO) 0.2663 z_1 (LCA-1) 0.2641 z_1 (LCA-0) 0.3025 z_2 (HMO) -0.2396 z_2 (LCA-1) -0.2405 z_2 (LCA-0) -0.2210	z_1 (HMO) 0.4142 z_1 (LCA-1) -0.1976 z_1 (LCA-0) -0.2001 z_2 (HMO) -0.2057 z_2 (LCA-1) -0.2064 z_2 (LCA-0) -0.1914	z_1 (HMO) 0.4326 z_1 (LCA-1) -0.1638 z_1 (LCA-0) -0.1664 z_2 (HMO) -0.1686 z_2 (LCA-1) -0.1707 z_2 (LCA-0) -0.1633
2.		0.7889	3.001	4.884	z_1 (HMO) 0.1790 z_1 (LCA-1) 0.1795 z_1 (LCA-0) 0.1949 z_2 (HMO) -0.2346 z_2 (LCA-1) -0.2369 z_2 (LCA-0) -0.2184	z_1 (HMO) 0.2663 z_1 (LCA-1) 0.2641 z_1 (LCA-0) 0.3025 z_2 (HMO) -0.2396 z_2 (LCA-1) -0.2405 z_2 (LCA-0) -0.2210	z_1 (HMO) 0.4142 z_1 (LCA-1) -0.1976 z_1 (LCA-0) -0.2001 z_2 (HMO) -0.2057 z_2 (LCA-1) -0.2064 z_2 (LCA-0) -0.1914	z_1 (HMO) 0.4326 z_1 (LCA-1) -0.1638 z_1 (LCA-0) -0.1664 z_2 (HMO) -0.1686 z_2 (LCA-1) -0.1707 z_2 (LCA-0) -0.1633
3.		0.7358	4.602	6.051	z_1 (HMO) 0.1778 z_1 (LCA-1) 0.1745 z_1 (LCA-0) 0.1949 z_2 (HMO) -0.2441 z_2 (LCA-1) -0.2432 z_2 (LCA-0) -0.2184	z_1 (HMO) 0.2663 z_1 (LCA-1) 0.2641 z_1 (LCA-0) 0.3025 z_2 (HMO) -0.2396 z_2 (LCA-1) -0.2405 z_2 (LCA-0) -0.2210	z_1 (HMO) 0.4142 z_1 (LCA-1) -0.1976 z_1 (LCA-0) -0.2001 z_2 (HMO) -0.2057 z_2 (LCA-1) -0.2064 z_2 (LCA-0) -0.1914	z_1 (HMO) 0.4326 z_1 (LCA-1) -0.1638 z_1 (LCA-0) -0.1664 z_2 (HMO) -0.1686 z_2 (LCA-1) -0.1707 z_2 (LCA-0) -0.1633
4.		0.7358	4.602	8.043	z_1 (HMO) 0.5232 z_1 (LCA-1) 0.5483 z_1 (LCA-0) 0.5634 z_2 (HMO) -0.1042 z_2 (LCA-1) -0.1044 z_2 (LCA-0) -0.1041	z_1 (HMO) 0.2663 z_1 (LCA-1) 0.2641 z_1 (LCA-0) 0.3025 z_2 (HMO) -0.2396 z_2 (LCA-1) -0.2405 z_2 (LCA-0) -0.2210	z_1 (HMO) 0.4142 z_1 (LCA-1) -0.1976 z_1 (LCA-0) -0.2001 z_2 (HMO) -0.2057 z_2 (LCA-1) -0.2064 z_2 (LCA-0) -0.1914	z_1 (HMO) 0.4326 z_1 (LCA-1) -0.1638 z_1 (LCA-0) -0.1664 z_2 (HMO) -0.1686 z_2 (LCA-1) -0.1707 z_2 (LCA-0) -0.1633
5.		0.9220	1.706	0.2280	z_1 (HMO) 0.3847 z_1 (LCA-1) 0.3919 z_1 (LCA-0) 0.3772 z_2 (HMO) -0.2098 z_2 (LCA-1) -0.2113 z_2 (LCA-0) -0.2174	z_1 (HMO) 0.2663 z_1 (LCA-1) 0.2641 z_1 (LCA-0) 0.3025 z_2 (HMO) -0.2396 z_2 (LCA-1) -0.2405 z_2 (LCA-0) -0.2210	z_1 (HMO) 0.4142 z_1 (LCA-1) -0.1976 z_1 (LCA-0) -0.2001 z_2 (HMO) -0.2057 z_2 (LCA-1) -0.2064 z_2 (LCA-0) -0.1914	z_1 (HMO) 0.4326 z_1 (LCA-1) -0.1638 z_1 (LCA-0) -0.1664 z_2 (HMO) -0.1686 z_2 (LCA-1) -0.1707 z_2 (LCA-0) -0.1633
6.		0.8172	2.284	-1.262	z_1 (HMO) 0.3602 z_1 (LCA-1) 0.3898 z_1 (LCA-0) 0.4410 z_2 (HMO) -0.1648 z_2 (LCA-1) -0.1661 z_2 (LCA-0) -0.1600	z_1 (HMO) 0.2663 z_1 (LCA-1) 0.2641 z_1 (LCA-0) 0.3025 z_2 (HMO) -0.2396 z_2 (LCA-1) -0.2405 z_2 (LCA-0) -0.2210	z_1 (HMO) 0.4142 z_1 (LCA-1) -0.1976 z_1 (LCA-0) -0.2001 z_2 (HMO) -0.2057 z_2 (LCA-1) -0.2064 z_2 (LCA-0) -0.1914	z_1 (HMO) 0.4326 z_1 (LCA-1) -0.1638 z_1 (LCA-0) -0.1664 z_2 (HMO) -0.1686 z_2 (LCA-1) -0.1707 z_2 (LCA-0) -0.1633
7.		0.8669	2.227	2.559	z_1 (HMO) 0.3055 z_1 (LCA-1) 0.3093 z_1 (LCA-0) 0.2992 z_2 (HMO) -0.2825 z_2 (LCA-1) -0.2869 z_2 (LCA-0) -0.2992	z_1 (HMO) 0.2663 z_1 (LCA-1) 0.2641 z_1 (LCA-0) 0.3025 z_2 (HMO) -0.2396 z_2 (LCA-1) -0.2405 z_2 (LCA-0) -0.2210	z_1 (HMO) 0.4142 z_1 (LCA-1) -0.1976 z_1 (LCA-0) -0.2001 z_2 (HMO) -0.2057 z_2 (LCA-1) -0.2064 z_2 (LCA-0) -0.1914	z_1 (HMO) 0.4326 z_1 (LCA-1) -0.1638 z_1 (LCA-0) -0.1664 z_2 (HMO) -0.1686 z_2 (LCA-1) -0.1707 z_2 (LCA-0) -0.1633
8.		0.7500	2.250	-1.313	z_1 (HMO) 0.0941 z_1 (LCA-1) -0.0946 z_1 (LCA-0) -0.0937 z_2 (HMO) -0.2154 z_2 (LCA-1) -0.2589 z_2 (LCA-0) -0.2709	z_1 (HMO) 0.2663 z_1 (LCA-1) 0.2641 z_1 (LCA-0) 0.3025 z_2 (HMO) -0.2396 z_2 (LCA-1) -0.2405 z_2 (LCA-0) -0.2210	z_1 (HMO) 0.4142 z_1 (LCA-1) -0.1976 z_1 (LCA-0) -0.2001 z_2 (HMO) -0.2057 z_2 (LCA-1) -0.2064 z_2 (LCA-0) -0.1914	z_1 (HMO) 0.4326 z_1 (LCA-1) -0.1638 z_1 (LCA-0) -0.1664 z_2 (HMO) -0.1686 z_2 (LCA-1) -0.1707 z_2 (LCA-0) -0.1633

The results listed in Table 1 demonstrate the high accuracy of the results calculated by LCA-1, with reference to the Hückel method, and also point to the applicability of the LCA-0 approximation for obtaining quantitative estimates. The wavelength of the first electronic transition polarized along the axis Γ_1 -Q- Γ_1 is specified as:

$$\lambda = \frac{2\pi}{z_{a1} - z_s} \lambda_0, \quad \lambda_0 = \frac{\hbar c}{|\beta|} \approx 50 \text{ nm} \quad (28)$$

where \hbar is the Planck constant, c is the velocity of light in vacuum, and $|\beta|$ denotes the magnitude of the C-C bond resonance integral. As evidenced by the comparison with the available spectroscopic data [10], the approximations involved afford qualitative trends in absorption wavelengths, though with systematically underestimated theoretical values. This shortcoming is attributable to the neglect of electron-electron interactions in the Hückel approach. Nonetheless, the generalization of long-polymethine-chain approximation to bridged polymethine compounds allows predicting their properties, just as for their unbridged counterparts [10, 11, 12, 13, 15].

It is worth noting that in the case of $z_{a2} < z_{a1}$, the first electronic transition, if treated strictly, occurs between the levels z_s and z_{a2} and hence is polarized along the axis Γ_2 -Q- Γ_2 , but it may be difficult to observe due to its low intensity.

In Ref. [20], the shift of the first absorption maximum, $\Delta\lambda$, was measured for squarylium dyes with end groups 6-8 relative to their open-chain analogues. The shifts respectively amounted to 12, 18, and -9 nm. The possibility for negative shifts $\Delta\lambda$ to occur for this type dyes containing end-groups 1-4 was subsequently pointed out and presumedly associated with the low basicity of the end groups involved [21]. With the parametrization used in Table 1, only positive shifts are obtainable for all the compounds concerned, since the position of the upper level z_{a1} remains unchanged on the substitution of a bridge for the 3-methine chain fragment, whereas the lower one, z_s , rises.

This issue can be studied in detail using LCA-0 analytical potentialities. For simplicity sake, it is convenient to begin the consideration with the instance of B-class end groups, i.e., those having $0 < F_{\gamma_1} < 1/2$. It may be strictly proved for them that provided $\alpha_2 < \beta_2 < 0$ and odd values n , the Fermi level is embraced by the levels $z_{a1} < 0$ and $z_s > 0$. The difference in the absorption wavelength (28) between bridged and corresponding open-chain polymethine molecules, if derived with parameters (15), (23), (24), and (20) at $N = 3$, appears as follows, accurate to $\varepsilon_{s,a}$:

$$\Delta\lambda \approx -4\lambda_0 \left[(n+2+\ell_{\gamma_1})F_s + (1-\ell_s)F_{\gamma_1} \right] < 0, \quad n = 1, 3, \dots \quad (29)$$

The negative shift $\Delta\lambda$ originates from the fact that the minimum positive level z_s rises in passing from unbridged dyes to their squarylium analogues, whereas the minimum negative level z_{a1} retains its position (see Fig. 2 b). The next negative level z_s lies deeper than the frontier one of the same symmetry by the energy distance of $2\pi\varepsilon_s$ and since $\varepsilon_s > \varepsilon_a$, it may be found not only above but also below the corresponding level of its open-chain counterpart. This feature is of fundamental significance in the analysis of bridge-induced spectral shifts for the dyes with A-class end groups characterized by $1/2 < F_{\gamma_1} < 1$.

Indeed, switching from B to A class implies the exchange of symmetries for dye frontier levels, so that they become: $z_s < 0$ and $z_{a1} > 0$. By analogy with Eq. (29), we now arrive at:

$$\Delta\lambda \approx 4\lambda_0 \left[(n+2+\ell_{\gamma_1})F_s - (1-\ell_s)(1-F_{\gamma_1}) \right], \quad n = 1, 3, \dots \quad (30)$$

As evident, the absorption shift $\Delta\lambda$ can in principle take on both positive and negative values, depending on the polymethine chain length n , the end-group effective length ℓ_{γ_1} , and the electron donor ability F_{γ_1} . To exemplify, the positive shift is typical for the case of a rather long polymethine chain ($n \gg 1$) or a

sufficiently great end-group effective length ($\ell_{\gamma_1} \gg 1$). At the same time, if the inequality

$$\frac{1 - F_{\gamma_1}}{n + 2 + \ell_{\gamma_1}} > \frac{F_s}{1 - \ell_s} \quad (31)$$

holds, the negative shift should be observed. Thus, it can be realized at $n=1$ and $\ell_{\gamma_1} > 1$, or for sufficiently low-electron-donor end groups, i.e. with the value F_{γ_1} slightly exceeding $1/2$, and also for bridges characterized by rather small values F_s and ℓ_s . Based on formulae (23), the latter condition is met with the proviso that $\alpha_2 \ll \beta_2 < 0$; then we arrive at $F_s \ll 1$ and $\ell_s \rightarrow 1/2$.

Interestingly, when passing from n to $n+2$, relations (29) and (30) yield a negative and a positive change in $\Delta\lambda$ (by the value $2\lambda_0 F_s$) for B-class and A-class end groups, respectively, which is consistent with the previously obtained results [17]. Noteworthy is that the case with even values n is reducible to that with odd n , provided one methine group is included into the end group γ_1 . As a result, $F_{\gamma_1} \rightarrow \{F_{\gamma_1} + 1/2\}$, $\ell_{\gamma_1} \rightarrow \ell_{\gamma_1} + 1$, $\ell'_{\gamma_1} \rightarrow \ell'_{\gamma_1}$ and the end group concerned changes its class.

Fig. 3 presents the dependence (30) of the absorption shift, $\Delta\lambda$, on the parameter β_2 of the exocyclic heteroatoms (with $\alpha_2 = -2$) at the bridge for the squarylium-like dyes containing end groups 6-8. As may be seen from the plot, the shifts are the largest for end group 7 and the smallest for end group 8, in qualitative agreement with experimental evidence [20]. The quantitative correlation could be reached with the values β_2 ranging from -0.8 to -0.6 . To obtain negative shifts $\Delta\lambda$ for squarylium dyes with end groups 1-4, still smaller magnitudes $|\beta_2|$ would need to be involved. Regarding their thiosquarylium analogues, $\Delta\lambda > 0$ should be expected for them, as they are characterized by much larger values F_s (cf. this parameter in (26) and (27)).

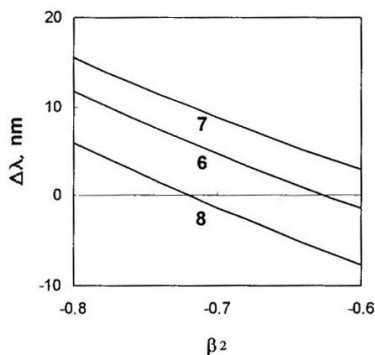


Fig. 3. Bridge-induced spectral shifts $\Delta\lambda$ for squarylium-like dyes with the end groups 6, 7, and 8 (from Table 1) versus resonance integral β_2 of exocyclic heteroatoms (with $\alpha_2 = -2$) at the four-membered cyclic bridge.

That the experimental situation for specific molecules is better described with non-standard parameter values is not new for the Hückel method which provides no explicit consideration of electron-electron interaction. With this effect included, the bridge electron donor ability, F_s , may somewhat decrease thus making inequality (31) more realistic. However, the main emphasis should be placed on the advantages provided by the analytical character of the long-polymethine-chain approximation which, in contrast to the common Hückel method, on the one hand, and to up-to-date computational strategies, on the other hand, enables structure-property relationships to be revealed explicitly (irrespective of the accuracy aspect). This serves as a basis for elucidation of the origin and prediction of trends for bridge-induced spectral effects manifested by compounds with the bridged polymethine chromophore.

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