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A simple treatment of bridge-induced shifts of absorption for symmetric polymethine dyes with a bridged chromophore

M.L. Dekhtyar *, A.I. Tolmachev

Institute of Organic Chemistry, National Academy of Sciences of Ukraine, Murmanskaya 5 Kiev-94, 253660 Ukraine

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Abstract

A simple topological model is developed which accounts for the effects caused on the absorption region of symmetric polymethine dyes by a cyclic fragment of the C_{2v} symmetry incorporated in their main chromophore. In the context of the Green's function formalism, relationships between the structure of a dye molecule (represented by additive topological parameters of end groups, bridge, and the polymethine chain) and bridge-induced shifts of absorption maxima are derived. The trends revealed in signs and magnitudes of the absorption shifts are exemplified by treatment of squaraine and thiosquaraine molecules. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Polymethine dyes; Conjugated bridged chromophore; Squaraines; Thiosquaraines; Green's functions; End-group topological parameters

1. Introduction

A significant advance in the rationalization of the chemical and optical behaviour of polymethine dyes is attributed to the long-polymethine-chain approximation [1–4]. This approach enables an adequate description of the shifts of frontier energy levels which are caused by the attachment of arbitrary end groups to the polymethine chain. 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. These parameters, reported previously for a variety of end groups, proved very helpful in the analysis of nonlinear optical properties of polymethine compounds [5,6].

Among 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 [7], optical information storage [8], nonlinear optics [9] etc. Technological needs thus required theoretical studies to evaluate relationships between chemical constitution and spectral properties of the compounds concerned. An interest in them burgeoned even in the early sixties, when Dyadyusha pioneered a qualitative symmetry-based consideration of the spectral changes caused by a cyclic bridge

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* Corresponding author. Fax: +380-44-573-26-43; *E-mail address*: vrozen@mail.kar.net

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centrally incorporated into the polymethine chromophore [10]. Further advance in research on bridged polymethine species was gained by the analysis of their energy spectra using the secular polynomial technique [11,12]. The conditions for the existence of local levels, as well as absorption maximum shifts in dye vinylogous series, were thus studied in the above references.

In the present paper, the long-polymethine-chain approximation is generalized to conjugated molecules constituted by four arbitrary fragments bound to a bridge of the C_{2v} symmetry. Green's function formalism (for a detailed elaboration of it see Ref. [13]) is illustrated by the comparative analysis of spectral properties for open-chained, squarylium, and thiosquarylium dyes.

2. Results and discussion

2.1. General mathematical model for molecules with a bridge of C_{2v} symmetry in the polymethine chain

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.

The elements of the inverse topological 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,

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

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). The energy spectrum of the whole system is determined by the roots of the following Eq. [3]:

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

which represents the generalized Heilbronner-like relation [14]. (Here $\mathbf{g}^{(Q)}(z)$ is the GF matrix of the bridge Q and $\boldsymbol{\beta}^{T}$ denotes the transposed matrix β of interfragment bonds).

With fragments $\Gamma_2 - Q - \Gamma_2$ treated as a new one, $\tilde{Q}$ (see Fig. 1b), the molecular system depicted in Fig. 1a is "linearized". GF for the complex fragment $\tilde{Q}$ and for its constituents are interrelated by the Dyson-like equation [3]:

$$\mathbf{g}^{(\tilde{Q})}(z) = \mathbf{g}^{(Q)}(z) + \mathbf{g}^{(Q)}(z)\boldsymbol{\beta}\mathbf{g}^{(\Gamma_2)}(z)\boldsymbol{\beta}^{T}\mathbf{g}^{(\tilde{Q})}(z) = 0 \tag{3}$$

having, in our specific case, the following solutions:

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

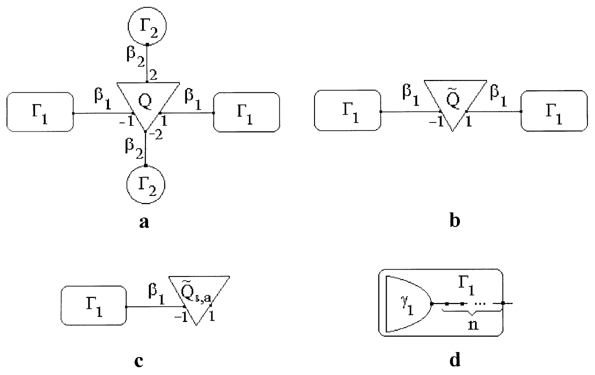


Fig. 1. Topology of the bridged polymethine compounds considered: (a) general form; (b) quasilinear form with $\tilde{Q} = \Gamma_2 - Q - \Gamma_2$; (c) reduced quasilinear form; (d) constitution of the end group Γ_1.

$$g^{(\tilde{Q}_a)}(z) \equiv g^{(\tilde{Q})}_{11}(z) - g^{(\tilde{Q})}_{-1,1}(z) = g^{(Q)}_{a1}(z). \tag{5}$$

Here $g^{(\Gamma_2)}(z)$, just as $g^{(\Gamma_1)}(z)$ in what follows, denotes the diagonal *jj* element of the GF matrix corresponding to the atom through which the corresponding end group is bound to the bridge Q. Symmetric (s) and antisymmetric (a) GFs for the bridge defined with respect to end groups Γ_1 and Γ_2 appear as

$$g^{(Q)}_{si,ai}(z) = g^{(Q)}_{ii}(z) \pm g^{(Q)}_{-i,i}(z), \quad i = 1, 2. \tag{6}$$

Due to the quasilinear representation, the spectrum of the integral molecular system concerned is specified by Eqs. (7) and (8).

$$\beta_1^2 g^{(\Gamma_1)}(z) g^{(\tilde{Q}_s)}(z) = 1, \quad \beta_1^2 g^{(\Gamma_1)}(z) g^{(\tilde{Q}_a)}(z) = 1, \tag{7}$$

$$\beta_2^2 g^{(\Gamma_2)}(z) g^{(Q)}_{a2}(z) = 1. \tag{8}$$

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. (For convenience, the group Γ implies a fragment of complex constitution containing an arbitrary conjugated residue γ and the n-methine chain section, as shown in Fig. 1d). 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 [3,4]. In the framework of the long-polymethine-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:

$$z_{s,a1} \approx 2\pi\varepsilon_{s,a}\tilde{F}_{s,a}, \; \varepsilon_{s,a} = [n + 1 + \tilde{\ell}_{s,a}]^{-1} \tag{9}$$

$$\tilde{F}_{s,a} = \{F_{\gamma1} + F_{s,a}\}, \; \tilde{\ell}_{s,a} = \ell_{\gamma_1} + \ell_{s,a} \tag{10}$$

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

$$F_M = \lim_{z \to 0} \frac{1}{\pi} \operatorname{arcctg} \frac{1}{g^{(M)}(z)} \tag{11}$$

$$\ell_M = -\lim_{z \to 0} \frac{2[g^{(M)}(z)]' + [g^{(M)}(z)]^2}{1 + [g^{(M)}(z)]^2} \tag{12}$$

The negative energy levels nearest to the Fermi level are obtainable by the same relations (9) on substituting for $\tilde{F}_{s,a} - 1$ for $\tilde{F}_{s,a}$.

Within the context of the long-polymethine-chain approximation, the parameters $\tilde{F}_{s,a}, \varepsilon_{s,a}$, 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 $\varepsilon_{s,a}$ 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:

$$g^{(\tilde{Q}_s)}(z) = -\frac{\cos[(N-1)\theta/2]}{\cos[(N+1)\theta/2]},$$
$$g^{(\tilde{Q}_a)}(z) = -\frac{\sin[(N-1)\theta/2]}{\sin[(N+1)\theta/2]}, \theta = \arccos(-z/2) \tag{13}$$

and effective parameters assume the form:

$$F_s = \left\{\frac{N+1}{4}\right\}, F_a = \left\{\frac{N-1}{4}\right\}, \ell_s = \ell_a = \frac{N-1}{2}. \tag{14}$$

As evident from Eq. (10), in the case concerned we have: $\tilde{F}_s - \tilde{F}_a = 1/2$ and $\tilde{\ell}_s = \tilde{\ell}_a$ which implies equidistant levels with alternating symmetries (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 an unbridged chain [3,4].

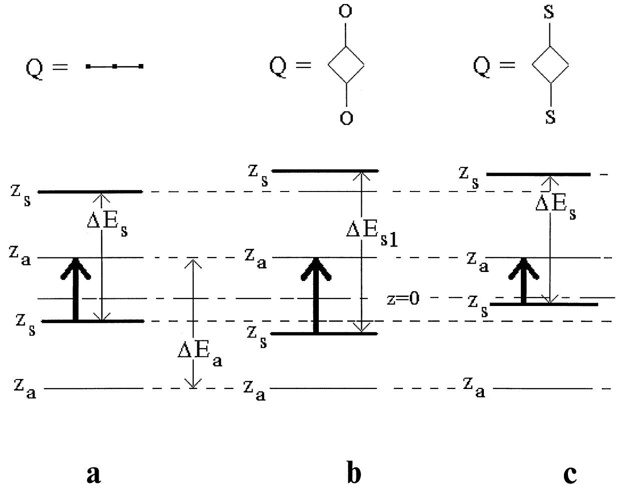


Fig. 2. Energy spectrum in the vicinity of the Fermi level ($z = 0$) for (a) open-chained polymethine compounds, and (b) their squarylium and (c) thiosquarylium analogues.

2.2. Application to squaraines and thiosquaraines

The relations (9)–(12) 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. Symmetric and antisymmetric GFs, as well as the GF $g_{12}^{(Q)}(z)$ for a square bridge Q, appear as follows:

$$g_{s1}^{(Q)}(z) = g_{s2}^{(Q)}(z) = \frac{z}{z^2-4}, g_{a1}^{(Q)}(z) = g_{a2}^{(Q)}(z) = \frac{1}{z},$$
$$g_{12}^{(Q)}(z) = -\frac{1}{z^2-4} \tag{15}$$

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. (4), the symmetric GF for the fragment $\tilde{Q}$ is easy to derive:

$$g^{(\tilde{Q}_s)} = \frac{z^2 - \alpha_2 z - \beta_2^2}{z^3 - \alpha_2 z^2 - (4+\beta_2^2)z + 4\alpha_2} \tag{16}$$

Substituting this function, along with $g^{(\tilde{Q}_a)}(z)$, into Eqs. (11) and (12) leads to:

$$F_s = \frac{1}{\pi}\operatorname{arcctg}\left(-\frac{4\alpha_2}{\beta_2^2}\right) \underset{\alpha_2<\beta_2<0}{\approx} \frac{\beta^2}{4\pi|\alpha_2|},$$
$$\ell_s = \frac{8(\alpha_2^2+\beta_2^2)+\beta_2^4}{16\alpha_2^2+\beta_2^4} \tag{17}$$

$$F_a = \frac{1}{2}, \ell_a = 1, \tag{18}$$

As may be seen from Eq. (17), $\ell_s > 1/2$ and, with $\alpha_2 < \beta_2 < 0$, $\ell_s < 1$. It is noteworthy that the values of the effective parameters indicated in Eq. (18) for a square bridge coincide with those for a three-methine chain (see Eq. (14) at $N=3$). For this reason, antisymmetric states 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. (8) for the energy levels of antisymmetric states can be written as the quadratic equation:

$$z_{a2}(z_{a2} - \alpha_2) = \beta_2^2 \tag{19}$$

For squarylium and thiosquarylium dyes which contain two oxygen or two sulfur atoms as fragments $\Gamma_2(\alpha_2 = -2, \beta_2 = -1$ and $\alpha_2 = -0.7,$

$\beta_2 = -0.7$) bound to the four-membered cycle, we respectively arrive at:

$$z_{a2} = 0.4142, F_s = 0.0396, \ell_s = 0.6308. \tag{20}$$

$$z_{a2} = 0.4326, F_s = 0.0551, \ell_s = 1.0000 \tag{21}$$

The values indicated in Eqs. (18), (20) and (21) 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 the long-polymethine-chain approximation by formulae (9) and (10) with $n = 1$, as well as by the Hückel method, are also presented. The parameter $F_{\gamma 1}$, 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 as class A, in distinction to class B, characterized by $0 < F_{\gamma 1} < 1/2$ and inverse symmetries of the frontier levels in the resulting polymethine compound [10].

The results listed in Table 1 demonstrate the high accuracy of the results calculated by the long-polymethine-chain approximation with reference to the Hückel method. The wavelength of the first electronic transition polarized along the axis $\Gamma_1 - \mathrm{Q} - \Gamma_1$ is specified as:

$$\lambda = \frac{2\pi}{z_{a1} - z_s}\lambda_0, \frac{\bar{h}c}{|\beta|} \approx 50\,\mathrm{nm} \tag{22}$$

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 comparison with the available spectroscopic data [1], 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 the long-polymethine-chain approximation to bridged polymethine compounds allows prediction of their properties, just as for their unbridged counterparts [1,3,4,6].

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 $\Gamma_2 - \mathrm{Q} - \Gamma_2$, but it may be difficult to observe due to its low intensity.

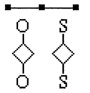
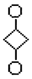
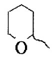
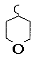
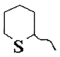
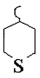
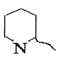
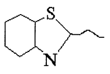
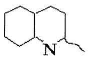
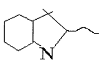
In Ref. [15], the shift of the first absorption maximum, $\Delta\lambda$, was measured for squarylium dyes with end groups 6–8 relative to their open-chained analogues. The shifts amounted to 12, 18, and −9 nm, respectively. The possibility for negative shifts $\Delta\lambda$ to occur for this type of dyes containing end-groups 1–4 was subsequently pointed out, and presumedly associated with the low basicity of the end groups involved [16]. 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, increases.

This issue can be studied in detail using analytical potentialities of the long-polymethine-chain approximation. 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 $z_{a1} < 0$и$z_s > 0$. The difference in the absorption wavelength (Eq. (22)) between bridged and corresponding open-chained polymethine molecules, if derived with parameters specified by Eqs. (10), (17), (18), and (14) at $N = 3$, appears as follows, accurate to $\varepsilon_{s,a}$:

$$\Delta\lambda \approx -4\lambda_0[(n + 2 + \ell_{\gamma 1})F_s + (1 - \ell_s)F_{\gamma 1}] < 0, \quad n = 1, 3, ... \tag{23}$$

The negative shift $\Delta\lambda$ originates from the fact that the minimum positive level z_s increases in passing from unbridged dyes to their squarylium analogues, whereas the minimum negative level z_{a1} retains its position (see Fig. 2b). The next negative level z_s lies higher 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-chained counterpart. This feature is of

Table 1
End groups γ_1, their effective parameters, $F_{\gamma 1}$ and $\ell_{\gamma 1}$, and the frontier energy levels of the corresponding open-chained, squarylium, and thiosquarylium dyes in the Hueckel (HMO) and in the long-polymethine-chain (LPC) approximations

No.	γ_1	$F_{\gamma 1}$	$\ell_{\gamma 1}$	 z_{a1} (HMO) z_{a1} (LCA)	 z_s (HMO) z_s (LCA)	 $z_{a2} = 0.4142$ z_s (HMO) z_s (LCA)	 $z_{as} = 0.4326$ z_s (HMO) z_s (LCA)
1.		0.7889	3.001	0.2707 0.3025	−0.2290 −0.2210	−0.1976 −0.1914	−0.1638 −0.1633
2.		0.7889	3.001	0.2663 0.3025	−0.2396 −0.2210	−0.2057 −0.1914	−0.1686 −0.1633
3.		0.7358	4.602	0.1790 0.1949	−0.2346 −0.2184	−0.2086 −0.1951	−0.1788 −0.1728
4.		0.7358	4.602	0.1778 0.1949	−0.2441 −0.2184	−0.2164 −0.1951	−0.1839 −0.1728
5.		0.9220	1.706	0.5232 0.5634	−0.1042 −0.1041	−0.0556 −0.0557	−0.0304 −0.0305
6.		0.8172	2.284	0.3847 0.3772	−0.2098 −0.2174	−0.1771 −0.1831	−0.1449 −0.1518
7.		0.8669	2.227	0.3602 0.4410	−0.1648 −0.1600	−0.1238 −0.1210	−0.0941 −0.0937
8.		0.7500	2.250	0.3055 0.2992	−0.2825 −0.2992	−0.2558 −0.2709	−0.2154 −0.2332

The Coulomb, α_x, and the resonance, β_{xx}, integrals for atoms and bonds are defined respectively as $\alpha_C + h_x\beta_{CC}$ and $\eta_{xx^1}\beta_{CC}$ with commonly used h_x and η_{xx^1} values: $h_C = 0$, $h_N = 1$, $h_O = 2$, $h_S = 0.7$; $\eta_{CC} = \eta_{CN} = 1, \eta_{CO} = 0.8$, $\eta_{CS} = 0.4$; for exocyclic oxygen and sulfur atoms of bridge fragments, $\eta_{CO} = 1, \eta_{CS} = 0.7$.

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. (23), we now arrive at:

$$\Delta\lambda \approx 4\lambda_0[(n + 2 + \ell_{\gamma 1})F_s - (1 - \ell_s)(1 - F_{\gamma 1})], \quad n = 1, 3, ... \tag{24}$$

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 $\ell_{\gamma 1}$, and the electron donor ability $F_{\gamma 1}$. To exemplify, the positive shift is typical for the case of a rather long polymethine chain ($n >> 1$) or a sufficiently great end-group effective length ($\ell_{\gamma 1} >> 1$). At the same time, if the inequality

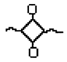
$$\frac{1 - F_{\gamma 1}}{n + 2 + \ell_{\gamma 1}} > \frac{F_s}{1 - \ell_s} \tag{25}$$

holds, the negative shift should be observed. Thus, it can be realized at $n = 1$ and $\ell_{\gamma 1} \gtrsim 1$, or for sufficiently low-electron-donor end groups (in conformity with the assumption of Ref. [16]), i.e. with the value $F_{\gamma 1}$ slightly exceeding 1/2, and also for bridges characterized by rather small values F_s and ℓ_s. Based on Eq. (17), the latter condition is met with the proviso that $\alpha_2 << \beta_2 < 0$; then we arrive at $F_s << 1$ and $\ell_s \to 1/2$.

Interestingly, when passing from n to $n+2$, Eqs. (23) and (24) 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 [11]. 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, $F_{\gamma 1} \to \{F_{\gamma 1} + 1/2\}$, $\ell_{\gamma 1} \to \ell_{\gamma 1} + 1$, and the end group concerned changes its class.

As far as the "pure" bridge effect on dye absorption region is concerned, the values F_s and L_s of the corresponding bridge fragments prove helpful (see Table 2); to exemplify, consider dyes with A-class end groups, i.e. with symmetric negative and antisymmetric positive frontier levels. As compared to the 3-methine section of the polymethine chain in a parent unbridged dye, the O-containing four-membered bridge in a squaraine molecule is characterized by a slightly increased value F_s and a slightly decreased value L_s, which respectively suggests that the system of symmetric levels is somewhat shifted up with reference to antisymmetric levels, and has larger interlevel separations. The molecular energy gap is narrowed by the former effect and widened by the latter, and competition between them results in a slightly red-shifted or blue-shifted absorption. For thiosquaraines, the values F_s and L_s are much larger than for squaraines [cf. these parameters in equalities (20) and (21) and in Table 2] and, accordingly, they are more prone to manifest red-shifted absorption (with reference to their open-chained counterparts). In any case, an increase in $\Delta\lambda$ should be expected for the thiosquaraines, all other factors being equal. This inference is in line with the experimental fact that thiosquarylium dyes containing end groups 1–4 absorb light at longer wavelength than the corresponding squaraines by 20, 40, 23, and 32 nm, respectively [17].

Table 2
Topological parameters of unbridged chain and bridge fragments

Bridge	F_s	F_a	ℓ_s	ℓ_a
 (no bridge)	0	1/2	1	1
	0.0396	1/2	0.6308	1
	0.0551	1/2	1	1

3. Conclusions

Bridge-induced changes in the energy spectrum of polymethine dyes, and hence spectroscopic effects manifested by them, are explicable in terms of the electron donor ability (F) and the effective length (ℓ) of end-groups and the bridge contained in their molecules. Trends in directions and magnitudes of the absorption maximum shift can be traced using simple relationships (23)–(25) between these parameters and $\Delta\lambda$, with regard to the symmetry class of the compounds under study. An effect of a fundamental nature, i.e. the occurrence of blue-shifted absorption for bridged polymethines, can be elucidated from this standpoint. Quantitative description of the experimental situation for specific molecules with standard atomic and bond parameter values is hardly possible in the framework of the Hückel model, 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 (25), which accounts for the more realistic negative $\Delta\lambda$ values. However, the main emphasis should be placed on the fact that the topological Hückel method, and its analytical long-polymethine-chain approximation, provides an insight into the origin and prediction of trends in spectral behaviour of compounds with a bridged polymethine chromophore.

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