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Application of the Quasi-Long Chain Approximation to Structural Perturbations in Polymethine Dyes*

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ABSTRACT

A topological approach is presented for the treatment of the optical and chemical behaviour of polymethine dyes, and which can be regarded as a theory for structural perturbations of a polymethine chain caused by arbitrary end-groups. The theoretical basis of the method is discussed in terms of Green's functions, and various alternative ways to the formalism developed are reviewed briefly. Special attention is paid to a simple computational technique for estimating certain molecular parameters. A variety of applications of the method are considered, namely in the search for stable infrared polymethine dyes, the design of structural modifications to yield desired spectral effects, and the determination of the electrophilic and nucleophilic reaction centres in heterocycles.

1 INTRODUCTION

Quasi-linear π-conjugated systems constituting a class of polymethine compounds play a significant role in organic chemistry since they can be regarded as an intrinsic part of any conjugated chemical entity. Their molecules consist of a polymethine chain (PC) with two end-groups, EG_1 and EG_2, bound to it:

$$EG_1—(CH)_N—EG_2$$

where $N = 1, 2, 3$. Having a relatively simple structure, they are convenient molecules for theoretical investigations, and studies on them give an insight into the nature of more complex systems.

* Dedicated to the memory of Professor Georgii Dyadyusha who opened the captivating world of conjugated compounds for me.

From a practical standpoint, among compounds of this type, particular attention has been paid to polymethine dyes (PMD, where N is an odd integer and EG_1 and EG_2 are heterocyclic residues, generally). PMD having optical properties such as intense near infrared light absorption have been reported for application in the dye industry, information recording, and in quantum electronics.[1-4] The past two decades have witnessed intense theoretical and experimental efforts aimed at the synthesis of PMD with desired spectral parameters. The requirements necessary for the molecular design of these compounds have advanced understanding of PMD colour relationships, and have resulted in several new methods for predicting the optical behaviour of the compounds concerned.[5-7]

The focus of this report is on an original approach referred to as the 'quasi-long chain approximation' (QLCA), which was developed from the initial work by Dyadyusha and Kachkovskii.[8-10] The method is intended to elucidate the relations between the constitution of EGs in a PMD molecule and the behaviour of its frontier energy levels, which are known to be responsible for a number of substantial spectral and chemical properties.[11]

With regard to its ideology, QLCA is related on the one hand to the methods of solid state physics, and on the other hand to Dewar's perturbation theory. We will consider the diverse sources of the approach in question, and the scope of its interpretations, which suggests the fundamental character of QLCA. The method implies an analytical treatment of structure–property relationships, in contrast to the usual computational techniques pertinent to quantum chemistry studies. It should also be noted that QLCA, based on the simple Hückel topological method, involves only a 'paper and pencil' technique for the estimation of the PMD parameters; computer procedures will be required only during the large-scale search for the desired compounds.

In some respects the method is applicable not only to PMD, but can also be extended to polymethine compounds containing an even number of methine units, as well as to certain other conjugated entities which cannot readily be classified as polymethines.

2 BACKGROUND AND THEORETICAL BASIS OF THE METHOD

The central concept of QLCA (relating it to the methods of solid state physics) is that the PC is rather long, so that near the Fermi level it is the chain which mainly determines the energy spectrum of a PMD molecule, whereas the contributions of EGs are small enough to be regarded as perturbations. The approach is concerned with an analytical treatment

of how perturbations of this type affect the behaviour of the frontier molecular orbitals (MO). Its main advantage is in revealing the relationships between the structural parameters of EGs considered as variable fragments of the dye molecule, and the integral molecular characteristics, e.g. the region of light absorption or redox ability.

The early approach to QLCA, developed by Dyadyusha and Kachkovskii,[8] was an originally constructed unusual kind of perturbation theory. Based on the recurrence relations between characteristic polynomials of molecular fragments,[12] in terms of the Hückel model, trigonometric transformations were performed so that the secular equation for a PMD molecule could be correctly expanded in a power series of small parameter $\varepsilon = (N + 1)^{-1}$, the reciprocal of the chain length. After dropping the terms from the quadratic in ε etc., the approximate equation roots corresponding to the frontier MO energies were found to depend on the relatively simple and physically meaningful functions of the characteristic EG polynomial coefficients. To calculate them, the Sachs–Coulson graph theoretical theorem[13] was used.[14,15]

Additionally, Dyadyusha and Ushomirskii, starting from the trigonometric form of the PMD secular equation, extended the relevant perturbation theory up to an arbitrary order in ε, and thus made it possible to approach the exact eigenvalues and eigenvectors of the Hückel Hamiltonian as close as was needed.[16,17] It is noteworthy that, near the Fermi level, the additivity of the EG contributions holds true not only for the first order of the perturbation theory in question, but also for all the subsequent ones.

Another approach to QLCA originated from the concept of asymptotic non-bonding MOs.[18–22] This approach, borrowing many features from Dewar's perturbation theory,[23–24] is considered in detail in the next section.

Finally, QLCA has recently been rationalised in terms of accepted methods of solid state theory,[25,26] and we follow here this presentation of the subject on the basis of it being the most general and illustrative one.

Thus, let us seek PMD level energies based on the well-known expressions for an unsubstituted PC (see, e.g. Ref. 27):

$$x_q = -2 \cos \theta_q;\ \theta_q = \pi(q + F)/(N + 1);\ (q = 1, \ldots, N). \qquad (1)$$

Here the energy is reckoned from the midpoint of the PC quasi-band, or the Fermi level, and is expressed in units of $|\beta|$, the magnitude of the C—C bond constant. The contribution of EGs to the energy spectrum is defined by the value F, depending both on EG parameters and the sought-for MO energies:

$$F = F(x_q). \qquad (2)$$

(The explicit form of $F(x)$ will be presented later).

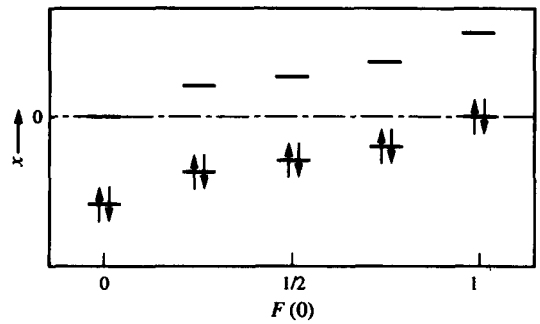

Fig. 1. Electron donor ability as a characteristic of frontier level positions for a PMD molecule.

Thus eqns (1) and (2) constitute an equation system which is exactly equivalent to the corresponding Hückel equation.* The parameter F is a 'correction to level number' naturally varying from 0 to 1, i.e. it describes a shift of the qth PC energy level perturbed by the attachment of EGs relative to its initial position. If treated in this way, the quantity $F(x_q)$ can be considered as a result of the regular perturbation of the quasi-continuous spectrum by locally attached fragments,[26] in the framework of the commonly accepted Lifshits' theory[28] which has given rise to the current concept of local and resonance crystal states.

In this context, provided the electron shell of a PMD molecule is closed,[29] $F(0)$ characterizes the positions of the frontier MOs relative to the Fermi level $x = 0$ (see Fig. 1). Hence the value of $F(0)$ enables a clear chemical interpretation to be made concerning the ability of the PMD to accept or donate electrons. The molecule acts as an electron-acceptor at $0 < F(0) < 1/2$, and as a donor at $1/2 < F(0) < 1$ whereas $F(0) = 1/2$ corresponds to relative redox stability. On this basis the current name of the parameter $F(0)$, i.e. the electron donor ability of EG, is derived.

The nearest levels lying on both sides of the level $x = 0$ participate in the first and most intense electronic transition. Their positions can be found after expanding the trigonometric form of the Hückel equation system (eqns (1) and (2)) in powers of the small parameter ε or, as was finally found, of the even smaller parameter $\tilde{\varepsilon}$:

$$x = 2 \sin \pi\varepsilon F(x) = 2\pi\tilde{\varepsilon}F(0)\left[1 - \pi\left(L'(0) + \frac{\pi}{6}F(0)\right)F(0)\tilde{\varepsilon}^2 + 0(\tilde{\varepsilon}^3)\right] \quad (3)$$

$$\tilde{\varepsilon} = [N + 1 + L(0)]^{-1}; \; L(x) = -2\pi \sin \theta F'(x) \quad (4)$$

where $F(0)$ ranges from 0 to 1 for the positive energy level, and is substi-

* Equation (1) can have more than N roots, due to the breaking of the 'alternation rule' for perturbed and unperturbed levels in some parts of the spectrum; however, QLCA suggests that this is not the case in the vicinity of the concerned Fermi level.

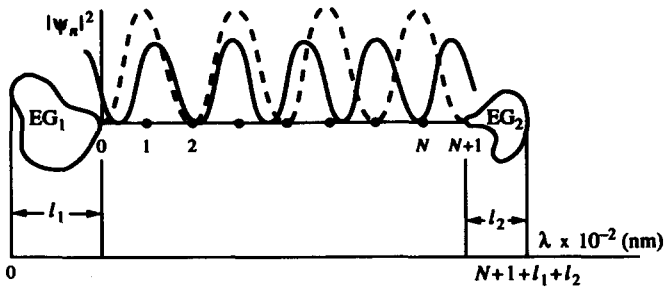

Fig. 2. Effective length for a PMD molecule, $L(0) = l_1(0) + l_2(0)$, and the wavelength of the first electronic transition of the dye. Solid and dashed curves correspond to the electronic densities on PC with and without EGs attached, respectively.

tuted by $F(0) - 1$ for the negative energy level (index q is omitted for brevity). The energy of the first electronic transition is then derived as in eqn (5)

$$\Delta x = 2\pi\tilde{\varepsilon}\{1 - \pi[L'(0)(2F(0) - 1) + \frac{\pi}{6}(3F^2(0) - 3F(0) + 1)]\tilde{\varepsilon}^2 + 0(\tilde{\varepsilon}^3)\}. \quad (5)$$

It differs from the analogous energy gap for an unsubstituted N-methine chain (equal to $2\pi\varepsilon$), since in the case of PMD the quantity $N + 1$ is enhanced by some contribution $L(0)$ arising from the presence of EGs. Figure 2 is a pictorial representation of the relation between the parameter $L(0)$ and the topological 'length' of the PMD molecule. The separation between EGs amounts just to $N + 1$ C—C bonds, and $L(0)$ appears to be an inherent topological, or effective, length of the EGs. Interestingly, the wavelength of the first electronic transition, λ, proved proportional to the total effective length of the molecule concerned, $N + 1 + L(0)$:

$$\lambda = \lambda_0(N + 1 + L(0)) \quad (6)$$

where $\lambda_0 = \hbar c/|\beta| \sim 50$ nm, which is in good accord with the reported spectroscopic data.[7,8,30] The constant $2\lambda_0$, conventionally called a vinylene shift, characterizes an increase in the first-transition wavelength resulting from lengthening of the PC by a vinylene group, —CH=CH—.

It is useful, at this stage, to define the function $F(x)$ in terms of the important EG characteristic, namely the Green function (GF) at the EG atoms. GF is specified in the standard way shown in eqn (7)

$$g_{\nu\nu'}(x) = [x \cdot \mathbf{1} - \mathbf{H}^{-1}]_{\nu\nu'} = \sum_q \frac{\psi_{q\nu}\psi^*_{q\nu'}}{x - z_q} \quad (7)$$

where $\mathbf{H} = \|H_{\nu\nu'}\|$ is a topological matrix (Hückel Hamiltonian), z_q and $\psi_{q\nu}$ are its eigenvalues and eigenfunctions, and $\mathbf{1} = \|\delta_{\nu\nu'}\|$ is the unity matrix. GF $g_{\nu\nu'}(x)$ describes the response of the νth atom to the perturba-

tion occurring on the ν'th atom of the system. As far as the EG is concerned, perturbation results from the local attachment of PC to the 0th (or $(N + 1)$th) EG atom (see Fig. 2).

Let the resonance integrals expressed in the units of $|\beta|$, $\beta_{01}/|\beta| \equiv \eta_1$ and $\beta_{N,N+1}/|\beta| \equiv \eta_2$ characterize the bonds between EGs and PC; GFs $g_{00}(x) \equiv g_1(x)$ and $g_{N+1,N+1}(x) \equiv g_2(x)$ refer to the EG atoms bound to PC; the function $F(x)$ can then be presented in its explicit form as shown below:[26]

$$F(x) = f_1(x) + f_2(x)$$

$$f_j(x) = \frac{1}{\pi} \operatorname{arcctg} \frac{1 + \eta_j^2 g_j(x) \cos \theta}{\eta_j^2 g_j(x) \sin \theta}; j = 1,2. \tag{8}$$

The additivity of the quantity in question permits notable simplification of the treatment, so that at $x \to 0$, individual contributions of both EGs can be derived:

$$F = \{f_1 + f_2\}; f_j = \pi^{-1} \operatorname{arcctg} [\eta_j^2 g_j(0)]^{-1}$$

$$L = l_1 + l_2; l_j = -\frac{\eta_j^2 [2g_j'(0) + \eta_j^2 g_j^2(0)]}{1 + \eta_j^4 g_j^2(0)}. \tag{9}$$

From here on, the argument $x = 0$ is omitted for functions F and L; based on the definition of F, only its fractional part, $\{F\}$, is considered. A simple technique for calculating these parameters is discussed in the next section.

From another point of view, taking into account the additivity of F and L, the physical meaning of these parameters can be inferred from the expression for the wave function on PC atoms:[26]

$$\Psi_n = \left(\frac{2}{N + 1 + L(x)}\right)^{1/2} \sin [\pi f_1(x) - n\theta]$$

$$\underset{x \to 0}{\longrightarrow} (2\tilde{\varepsilon})^{1/2} \sin \left[\left(\frac{\pi}{2} + \pi\tilde{\varepsilon}F\right)n - \pi\tilde{\varepsilon}f_1(N + 1)\right]. \tag{10}$$

Whereas the first function in eqn (10) is an exact one, being equivalent to the Hückel MO, the latter describes asymptotic MO behaviour in the proximity of zero. As shown, at $L = F = f = 0$ this approximate wave function for PMD reduces to that for an unsubstituted PC, and corresponds to the energy level $x = 0$. The non-zero L, added to $(N + 1)$, provides a decrease in the wave amplitude which originates from the effective lengthening of PC, and hence greater delocalization of electrons. Correspondingly, F and f_j describe the wave phase shifts which lead to transfer of the electron density into the EGs (see Fig. 2).[9,17] The significance of such an asymptotic orbital in the determination of EG parameters is discussed below.

3 CONCEPT OF ASYMPTOTIC NON-BONDING MOLECULAR ORBITALS

Odd alternant hydrocarbons are the only class of organic conjugated compounds which possess non-bonding MO (NBMO),[23,24,31,32] the form of which can be found as a non-trivial solution of the corresponding Hückel homogeneous system of equations:

$$\sum_{\nu'} H_{\nu\nu'}\Psi_{\nu'} = 0. \tag{11}$$

For most other conjugated entities, no non-trivial solution exists. However, long-chain PMDs are an unusual case. As the PC length tends to infinity ($N \to \infty$), the frontier MOs indefinitely approximate to the Fermi level, giving rise to two degenerate levels which can be considered as approximating to $x = 0$. The concept of an asymptotic non-bonding MO (ANBMO) can now be considered.

On the basis that the PC is sufficiently long, in solving the system of eqns (11) for ANBMO, any incompatibility or discrepancy in the ANBMO form can be transferred to the 'infinitely' distant PC atom. As a consequence, any equation involving ANBMO coefficients on PC atoms can be extracted from the system of eqns (11), making it underdetermined, and hence having at least one non-trivial solution. We are concerned with the part of this solution referring to the ANBMO form within the EG (see, for instance, the left EG in Fig. 2), and we thus focus on the corresponding equations (the EG atoms are numbered 0, 1', ..., $M - 1$; α_ν are Coulomb integrals):

$$\alpha_\nu\Psi_\nu + \sum_{\nu'(\neq\nu)=0}^{M-1} \beta_{\nu\nu'}\Psi_{\nu'} + \beta_{\nu 1}\Psi_1 = 0 \tag{12}$$

where $\nu = 0, 1', \ldots, M - 1$. When solved for the ANBMO coefficients Ψ_ν, these equations give a better insight into GF as a response function:

$$\Psi_\nu = \eta_1 g_{\nu 0}(0)\Psi_1. \tag{13}$$

Indeed, with the bond resonance integral η_1 treated as the perturbation of the 0th EG atom by the attachment of the first PC atom, $g_{\nu 0}$ governs a transmission of the perturbation effect to the νth EG atom.

Thus, the ANBMO is expressed through the GF matrix at $x = 0$, which is the same as the inverse topological matrix, accurate to the sign (see eqn (7)). If there is no need to normalize ANBMO, then the value Ψ_1 can be chosen arbitrarily, and it is convenient to make it equal to η_1^{-1}, so that with PC bound to the μth atom of EG, the vector Ψ of the ANBMO coefficients will be identical to the μth column of the GF matrix $\mathbf{g}(0) = \|g_{\nu\mu}(0)\|$ for the EG. It is apparent, therefore, that the matrix $\mathbf{g}(0)$

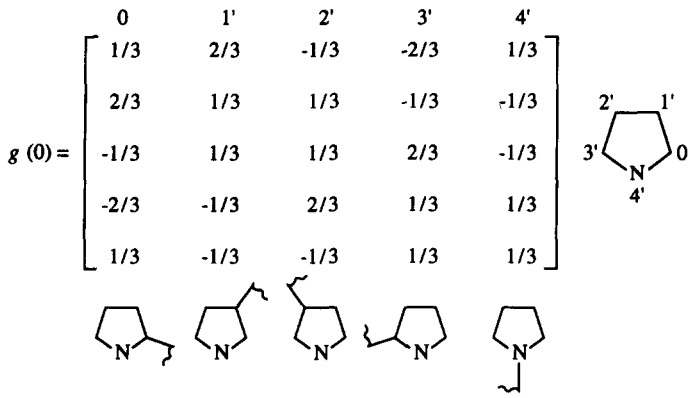

Fig. 3. Green function matrix for a pyrrole molecule; its columns are identical to the corresponding ANBMO vectors.

is constituted by the ANBMOs characteristic of all possible EGs derived from a given molecule by varying the atom bound to the PC (see Fig. 3). We now consider how the numerical values of GF presented in Fig. 3 were obtained.

A convenient 'paper-and-pencil' technique originating from the well-known Longuet-Higgins' rule[32] for solving equation systems such as the system of eqns (12) is suitable for calculating ANBMO coefficients[19] and, equally, Green functions. The graphic solving of such equations for 2-pyrrolyl EG is given in Fig. 4. It can be seen that, for a GF to be found, it is not necessary to use the GF definition, eqn (7), which implies the calculation of the whole corresponding energy spectrum and all the wave functions.

It should be noted that the simple technique shown is of general

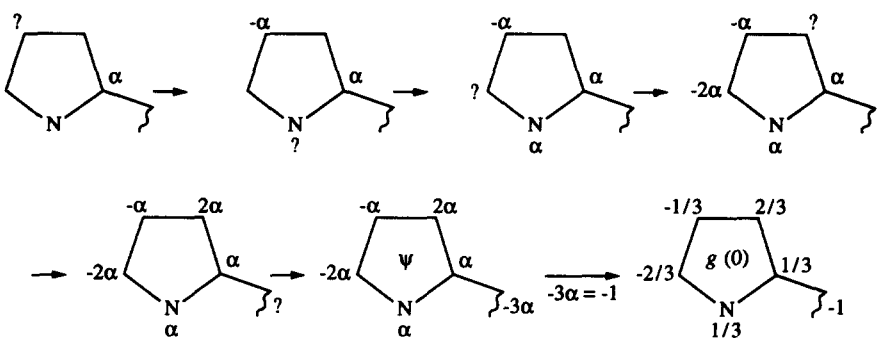

Fig. 4. Step-by-step procedure for determining **g**(0) from eqns (12). ($\beta_{\nu\nu'} = -1$ for all bonds, $\alpha_\nu = 0$ for carbon atoms and -1 for a nitrogen atom; α is an arbitrary parameter to be determined after the last step is performed).

nature, as it can easily be extended to GFs of an arbitrary argument x (by adding the value x to the Coulomb integrals of all EG atoms). Hence it may be regarded as a graphic version of conventional methods used for solving the linear equation systems or for finding inverse matrices. Also, based on the identity $\mathbf{g}^{(n)}(z) = (-1)^n n!\mathbf{g}^{n+1}(z)$, it is possible to use the same procedure to obtain an arbitrary-order GF derivative with respect to x.

Returning to the calculation of EG parameters from eqn (9), it can be seen that the attachment of PC to the arbitrary μth EG atom gives rise to the f_μ, l_μ pair determined solely by the diagonal elements $g_{\mu\mu}(0)$ and $g'_{\mu\mu}(0)$. The non-diagonal elements $g_{\nu\mu}$ are involved in considerations necessary for estimating the effects of structural changes in EGs on the stability and light-absorption region of the corresponding PMD:

$$\frac{\partial f_\mu}{\partial H_{\nu\nu'}} = \frac{1}{\pi}(2 - \delta_{\nu\nu'}) \frac{\eta_\mu^2 g_{\nu\mu}(0) g_{\nu'\mu}(0)}{1 + \eta_\mu^4 g_{\mu\mu}^2(0)} \tag{14}$$

$$\frac{\partial l_\mu}{\partial H_{\nu\nu'}} = 2(\delta_{\nu\nu'} - 2) \frac{\eta_\mu^2 [g'_{\nu\mu}(0) g_{\nu'\mu}(0) + g_{\nu\mu}(0) g'_{\nu'\mu}(0)}{1 + \eta_\mu^4 g_{\mu\mu}^2(0)}$$

$$- 2\pi\eta_\mu^2 g_{\mu\mu}(0)(l_\mu + 1) \frac{\partial f_\mu}{\partial H_{\nu\nu'}}. \tag{15}$$

In this way the concept of the asymptotic NBMO can be applied in the general case to describe realistic PMDs having no exact NBMOs. This bears some resemblance to the theory put forward by Dewar, who made use of NBMOs of conjugated compounds when considering their NBMO-free derivatives.[23,24] In terms of his approach, perturbation brought into a NBMO-containing system is regarded as the energy of a slight structural transformation causing disappearance of the NBMO. Therefore, a PMD should be treated as an odd-N-methine chain, possessing NBMO, which is perturbed by the attachment of EGs. However, in contrast to Dewar's approach, the ANBMO concept does not imply that perturbations should necessarily be small. A limitation of a quite different nature arises here, namely sufficient length of the PC.

4 PRACTICAL APPLICATION OF THE QUASI-LONG CHAIN APPROXIMATION

With respect to which systems the approach in question is applicable, a surprising property of QLCA is that it is valid beginning from chains

having even $N = 3$ and $N = 1$, which are the most typical chains for real polymethine dyes.[7,8] This application of the approximation follows from estimates of corrections of the order $\tilde{\varepsilon}^2$ in eqn (3); for small fragments, the coefficient of $\tilde{\varepsilon}^2$ is found to be numerically small, while for large fragments of M atoms this correction corresponds in order of magnitude to $\eta_j^2 g_j(0) M[(1 + \eta_j^2 g_j(0))(N + M)^2]^{-1} \ll 1$, even at small values of N (this result is actually due to the change from the parameter ε to the even smaller $\tilde{\varepsilon}$). On the other hand, the range over which this approximation is valid (as is true of any approach ignoring the interelectron repulsion) is limited to values of N which are not too large, so that the energy gap which arises in the spectrum of infinite one-dimensional systems may be ignored. As shown previously,[33] as the limit $N \to \infty$ is approached, a state with a gap becomes preferable to the gapless state only for $N \gtrsim 10$. Moreover, the construction of GFs from the appropriate wave functions[33] makes it possible to extend the method developed to chains of arbitrarily great length.

Thus, it can be realistically expected that the method developed can reliably estimate the spectral properties and redox stability of dyes. Due to its simplicity, it is particularly attractive for use in large-scale searches for PMDs displaying the desired optical behaviour. For instance, computer calculation of f_μ, l_μ pairs for more than 3000 heterocyclic nuclei showed *c.* 1% of them to be promising as EGs of stable dyes absorbing light in the near infrared region ($F = 1/2$, $L > 16$).[34]

Additionally, in the process of the molecular design of PMDs, it is reasonable to take advantage of the derivatives $\partial f_\mu / \partial H_{\nu\nu'}$ and $\partial l_\mu / \partial H_{\nu\nu'}$, in order to determine what chemical modification (introduction of a substituent or heteroatom, annelation, etc.) and in what position of a given EG would be the most efficient for obtaining the required spectral effect.[35,36] Also of value in the treatment of complex EGs are the relations between the QLCA parameters of a whole EG and its fragments,[37,38] the application of the Sachs–Coulson graph theorem,[39] and the ANBMO concept.[22,35,40]

The dipole moment of the first electronic transition proved to be proportional to the effective length of the dye molecule. Thus the parameter L not only characterizes the position of the long-wavelength band but also its intensity and the shifts and splittings arising from dye aggregation.[41]

The established subdivision of polymethine compounds into two classes which distinctly differ in their electronic nature and optical properties, i.e. polymethines and polyenes,[42] can be rationalized in the context of QLCA. The features of the electronic density distribution for both classes are accounted for in terms of EG electron donor abilities and the parity

of PC.[38,43–49] At odd N, a polymethine compound resembles polymethines if the difference in electron donor abilities for both groups is $\Delta f_{1,2} < 1/2$, and resembles polyenes if $1/2 < \Delta f_{1,2} \leq 1$. Ideal polymethines ($\Delta f_{1,2} = 0$) have alternating atomic charges and equalized bond orders, and they undergo atomic charge reversal on excitation, whereas ideal polyenes ($\Delta f_{1,2} = 1$) are characterized by equalized atomic charges and alternating bond orders, the latter reversing on excitation. At even N, the 'polymethinic' and 'polyenic' F-ranges interchange. Thus, use of the parameter F allows a convenient classification of dye type to be made and also the gradual transition from one class to the other, as well as the molecular design of the desired class of dyes to be effected.[38]

The next order of QLCA, and thus the correction discussed above, are of significance if, for example, it is necessary to ascertain the position of the PMD first absorption maximum more accurately,[16,20,26] to estimate the transfer of electronic density between EG and PC on excitation,[17,20] or to estimate the so-called 'topological deviation', i.e. the deviation of the first transition wavelength for an unsymmetric PMD from the arithmetical mean of those for its parent symmetric dyes.[50]

Further, for the sake of accuracy, it is possible to make allowance for electronic interaction. Although its basic framework is 'topological' in nature, QLCA does enable an estimation to be made of the energy of interelectronic repulsion in a PMD molecule, since the MO coefficients needed for this estimation are expressed through the EG parameters F and L.[51] As a result, both singlet and triplet electronic transitions can be treated using this method, with appropriate corrections to the EG effective length, and the vinylene shift then proves to be dependent on EG electron donor abilities, and not to be a constant value.[51,52]

Analytical treatment in terms of QLCA was also fruitfully extended to polymethine compounds of more intricate constitution, e.g. the conjugated entities $E_1—(CH)_m—M—(CH)_n—E_2$ (Ref. 53) or $E_1—M_n—E_2$ (Ref. 54) containing an arbitrary fragment M or even a periodical chain constituted by it. Structures of these types, as well as typical PMDs, are characterized by additive parameters which are contributed by all parts of the conjugated system. On this basis, appropriate molecular fragments giving rise to the desired optical behaviour can be selected.

It can also be noted that the electron donor ability of EG in a PMD molecule, if appropriately determined,[16] describes the electrophilic/nucleophilic nature of the corresponding position in the heterocycle concerned and hence can serve as a reactivity index.[55] This applicability of F enhances the efficiency of F, L criteria in the search for optically and chemically interesting systems.

Finally, QLCA parameters are of use in graph-theoretical treatment

of chemical compounds.[22] In particular, electron donor ability opens the way to constructing graphs having zero values in their spectra, i.e. to compounds having exact non-bonding MOs.

The QLCA applications discussed here clearly indicate its potential, and this is likely to be extended as the method is further developed.

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