Theor Chim Acta (1986) 69:247-258

Theoretica Chimica Acta

Studies of the energy spectrum of ω,ω'-substituted polymethine chains

III. Many-atom substituents*

N. Tyutyulkov[1], O. E. Polansky[2], F. Dietz[3], J. Fabian[4] and A. Mehlhorn[4]

[1] Institute of Organic Chemistry, Academy of Sciences, 1113 Sofia, Bulgaria
[2] Max-Planck-Institut für Strahlenchemie, D-4330 Mülheim/Ruhr, Federal Republic of Germany
[3] Sektion Chemie, Universität Leipzig, 7010 Leipzig, German Demokratic Republic
[4] Sektion Chemie, Technische Universität, 8027 Dresden, German Demokratic Republic

(Received May 10, revised October 25/Accepted November 6, 1985)

It is shown that upon substitution of polymethines $R—(CH)_N—R$ with complex many-atom substitution R—, in the energy gap of polymethine chains ($N \to \infty$) may arise states which are responsible for longest-wavelength transition. For certain substituents the energy of the electron transitions may be considerably lower than 1 eV, i.e. the transitions may be in the near infra-red.

Key words: Substituted polymethines — Energy spectrum of ~ — Complex substituents

1. Introduction

Substituted polymethines are one of the main classes of organic dyes. This justifies the interest towards the theoretical study of their energy spectrum. The latter is determined by two factors: by the length of the polymethine chain and by the type of the substituents $R_1—$ and $R_2—$:

$$R_1—(CH)_N—R_2.$$

In the previous communications [1, 2] it was shown that the width of the energy gap is equal for polyenes [$N=2n$] and polymethines [$N=2n+1$] for [$N\to\infty$]

---

* Second communication: Theoret. Chim. Acta. (Berl.) (1981) 60:185

and is ≈2 eV. Upon substitution in a polymethine chain, "impurity" states may arise in its energy gap, their energy depending on the type of the substituents R_1— and R_2—. These impurity states are responsible for the energy of the longest-wavelength $\pi\pi^*$ transitions.

In the preceding investigations [1, 2] the substituents R are atoms or atomic groups, $-O^-$, $-NH_2$, $-BH_2$, which participate with a single atomic orbital in the system of conjugation. For such substituents the boundary conditions are simple and the problem of determining the energy spectrum of the substituted polymethines has an analytical solution [1, 2]. Of practical interest, however, are those ω,ω'-substituted polymethines, in which the substituents are complex, many-atom π-electron systems [3]. For just such systems the energy of the longest wavelength transitions may be considerably lower than the corresponding energy for polymethines with simple substituents. In the works of Sens [4] and Drexhage [5], as well as in the work of Ishchenko [6], the synthesis of ω,ω'-substituted polymethines is reported, for which the energy of the longest-wavelength transitions is much lower than the energy of the corresponding merocyanines - oxonoles and cyanines with the same number of C-atoms in the polymethine chain.

Some recent studies [4, 5] give rise to the general question about the lower boundary of the electron transition energy for an infinite polymethine with complex substituents, i.e. whether the energy of the longest-wavelength transition $\Delta\varepsilon_\infty$ $[N \to \infty]$ converges towards a non-zero value or $\Delta\varepsilon_\infty \neq 0$. When the substituents are atoms [N, O], as with the cyanines, oxonoles and merocyanines, the lower boundary for the excitation energies $\Delta\varepsilon_\infty \approx 1$ eV [2]. For complex substituents, however, it is possible that the energy of the electron transition is less than 1.0 eV. In the paper of Schäfer and Lüttke [7], the lower boundary for the electron transition energy is set at 0.73 eV ($\lambda_{\max} = 1700$ nm). To find a more general answer to this problem which is important for synthetists who seek substances absorbing in the infrared is the main objective of the present investigation.

Another aim of this study is to find criteria which allow an estimation to be made for the transition energies of polymethines with many-atom substituents.

2. Model for substituted polymethines

The energy gap ΔE_∞ of any one-dimensional system with a given topology is determined by two factors: geometry and electron correlation [8, 9]

$$\Delta E_\infty = \sqrt{\Delta_{\text{corr}}^2 + \Delta_{\text{geom}}^2}. \tag{1}$$

In the case of polymethines, the geometry component $\Delta_{\text{geom}} = 2|\beta_d - \beta_s|$ [10]. β_s and β_d are the resonance integrals of the single and double bonds in the polymethine chain, respectively.

As in [2], the study of the energy spectrum can be made in the general case, when $\Delta_{\text{geom}} \neq \Delta_{\text{corr}} \neq 0$. For simplicity, we shall assume that the energy gap is determined solely by the geometry factor, i.e.

$$\Delta E_\infty = \Delta_{\text{geom}} = 2|\beta_d - \beta_s| = 2\beta_d|1 - t|. \tag{2}$$

(In (2) and in the expressions that follow we shall consider the resonance integrals positive: $\beta > 0$.)

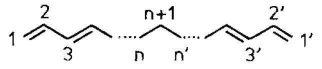
The choice of model with alternation in the bond lengths does not restrict the generality of the treatment. As in (2), for an appropriate parametrization, the same results could be obtained in the general case, too, i.e. when $\Delta_{\mathrm{corr}} \neq 0$. The considered model with alternation also has the advantage of being more visual and allowing the application of substantially simpler formalism.

If we assume the experimental value $\Delta E_{\infty} = 2.25$ eV [11] and $t = 0.719$ [2], we obtain from relation (2) $\beta_d = 4.0036$ eV, $\beta_s = 2.8786$ eV. If the relationship between the resonance integrals and the distance is calculated according to formula [10] $\beta(R) = \beta(R_0) \exp \alpha(R - R_0)$ [$\alpha = 3.2195$], then $\beta(R_0) = \beta_0 = 3.39$ eV. It follows from these values of the parameters that the energies in the energy gap of an infinite polymethine chain are within the interval:

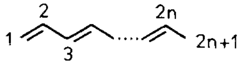
$$-0.3319\beta_0 = -|\beta_d - \beta_s| \leq E \leq |\beta_d - \beta_s| = 0.3319\beta_0.$$

Since only the odd polymethines ($N = 2n + 1$) are of practical interest [3], those will be treated below. However, the transition energy can be easily evaluated for the substituted polyenes ($N = 2n$) as well. The latter have the same gap but no NBMO.

Two structures: a symmetric (S) - C_{2v}, and a non-symmetric (A) one are possible for the non-substituted polymethines, as well as for polymethines symmetrically substituted with two end groups R ($N = 2n + 1$):



S

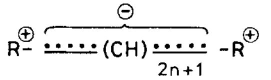


A

For large values of n the energy spectra of non-substituted polymethines for both forms: (S) and (A), are identical [12]; however, they differ relative to the electron density distribution in the non-bonding MO [NBMO].

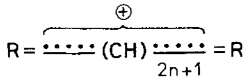
Since model (S) is more adequate than model (A) for describing both non-substituted and ω,ω'-disubstituted polymethines, all further considerations are carried out in terms of model (S).

All the polymethines discussed in the paper are cationic systems. The charge distribution (with conservation of the symmetry C_{2v}) between the polymethine chain and the substituents can be represented as follows:



$$R^{\oplus}-\overbrace{\cdots(CH)_{2n+1}\cdots}^{\ominus}-R^{\oplus}$$

(S-1)

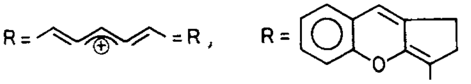


$$R=\overbrace{\cdots(CH)_{2n+1}\cdots}^{\oplus}=R$$

(S-2)

In the first case, (S-1), the two substituents have a positive charge each, while the polymethine chain bears the negative charge (anionic odd alternant hydrocarbon). The NBMO of the polymethine chain is doubly occupied. Polymethines 4 studied in a previous work [6] belong to this type (see Sect. 4).

In the second case, (S-2), neutral substituents are attached to a polymethine chain of positive charge; so, the NBMO is vacant. Here belongs the class of pyrilocyanines [4, 5], e.g. the cyanine:



1

The two fragmentation models are nearly equivalent.

3. Method and derivation of the main relations

Let us denote with $\{\Psi_k\}$ the MO's of the polymethine chain, with $\{\Psi_i\}$ and $\{\Psi_j\}$ the MO's of the substituents R_1 and R_2 of the ω,ω'-substituted polymethine, and with $\{E_k\}$, $\{E_i\}$, $\{E_j\}$ their corresponding energies. In the LCMO approximation, the MO's of the substituted polymethine may be represented as follows:

$$\Phi_p = \sum_k C_{pk}\Psi_k + \sum_i C_{pi}\Psi_i + \sum_j C_{pj}\Psi_j \tag{3}$$

and the energy matrix will take the form:

$$Q = \left|\begin{array}{cc|c} \boldsymbol{R}_1 & \boldsymbol{O} & \\ \boldsymbol{O} & \boldsymbol{R}_2 & \boldsymbol{W} \\ \hline \multicolumn{2}{c|}{\tilde{\boldsymbol{W}}} & \boldsymbol{P} \end{array}\right| . \tag{4}$$

The matrices $\boldsymbol{R}_1$, $\boldsymbol{R}_2$ and $\boldsymbol{P}$ are diagonal and their matrix elements are equal to:

$$r_{ii} = E_i - E, \qquad r_{jj} = E_j - E, \qquad p_{kk} = E_k - E.$$

The elements of the submatrix $\boldsymbol{W}$ represent the interaction between the AO's of the substituents and the MO's of the polymethine.

The expansion of the determinant, det Q, leads to wieldy and simple expressions when the substituents R_1 and R_2 are atoms - a case which was treated in a previous communication [2]. In the general case, the expansion of det Q leads to a complex unwieldy polynom, from the study of which no conclusion can be made in the general case about the energy spectrum of the substituted polymethine.

For many-atom substituents the following two general conclusions about the energy spectrum of the substituted polymethine can be made:

(i) For $n \rightarrow \infty$ the energy spectrum of the polymethine chain is not changed by the substituents. This follows directly from the perturbation theory. The matrix elements contributing to the second order correction to the energy are equal to:

$$h_{ik} = \langle \Psi_i | h | \Psi_k \rangle = C_{ir} C_{k_{1(N)}} \tilde{\beta}.$$

C_{ir} is the coefficient of the AO of the rth atom of the ith MO of the substituent, whereas $c_{k1(N)}$ is the coefficient of the 1(N)th AO of the kth MO of the polymethine chain. When $n \to \infty$, $c_{k1(N)} \to 0$ and the correction to the energy of the kth MO of the polymethine chain is equal to:

$$\Delta E_k^{(2)} = \sum_k^m \frac{h_{ik}^2}{E_k - E_i} \xrightarrow{n\to\infty} 0$$

(m is a finite integer).

However, in the general case the correction to the MO energies of the substituent is non-zero (see Eq. (10)).

(ii) In the cases when the substituents have elements of symmetry, some general and exact (within the used approximation) conclusions can be made. If the substituents R belong to the symmetry group C_{2v}, the MO's can be classified into symmetric Ψ^S and antisymmetric Ψ^A, relative to the plane perpendicular to the molecular plane. If the atom r of the substituent R, which is connected with the polymethine chain, lies in the plane σ, the coefficients C_r^A of the atomic orbital φ_r of the antisymmetric MO's are equal to zero. This means that E_i^A, the energies of the substituents R which correspond to the antisymmetric MO's, do not change on connection to the polymethine chain. Their position relative to the energy spectrum of the non-substituted polymethine chain can be directly determined.

If one of the substituents: R_1 or R_2 or both, have an MO of energy $E_{i(j)}^A$ satisfying the condition

$$|E_{i(j)}^A| < |\beta_d - \beta_s| = 0.3319\beta_0 \tag{5}$$

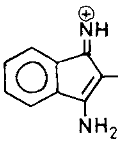
the antisymmetric MO falls within the energy gap.

For finite polymethines Eq. (5) takes the form:

$$|E_{i(j)}^A| < |E_g| \tag{6}$$

where E_g is the frontier MO (but not the non-bonding, NBMO, for the odd polymethines) of the polymethine chain.

For example, the MO energies of substituent 2


2

(in β_0 units) are

$$E_i^S = -2.504;\ -1.762;\ -1.000;\ -0.526;\ 0.922;\ 1.870$$

$$E_i^A = -1.775;\ -1.000;\ 0.186;\ 1.360;\ 2.228.$$

The energy of the LUMO ($E_7 = 0.186\beta_0$) satisfies condition (5) and lies in the energy gap.

If only states Ψ^A are located in the energy gap, those will be responsible for the longest-wavelength transitions in the substituted polymethine.

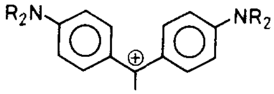
For polymethines ($N = 2n+1$) disubstituted with substituent 2, the energy of the longest-wavelength $\pi\pi^*$ transition is determined by the vacant antisymmetric MO of the substituents. The energy of the transition will be equal to:

$$\Delta\varepsilon = 0.186\beta_0. \tag{7}$$

The transition energy is lower than the energy of the longest-wavelength transition in 2, which is equal to: $0.186\beta_0 + 0.526\beta_0 = 0.712\beta_0$. For the selected value of $\beta_0 = 3.39$ eV, $\Delta\varepsilon = 0,712.3,39 = 2.41$ eV, whereas $\Delta\varepsilon_{\exp} = 2.71$ eV [13]. For this parametrization the transition energy for the substituted infinite polymethine will be equal to $\Delta\varepsilon_\infty = 0,186.3,39 = 0.63$ eV.

Using solid state theory terminology, the levels satisfying conditions (5), i.e. those lying within the energy gap, are impurity-local levels. The transitions from these levels to other levels from the same fragment with antisymmetric MO's, are strictly localized within the fragments *R*.

Within the framework of the tight-binding approximation in Hückel π-electron approximation, the position of the local levels with energy $E^A_{i(j)}$ in the energy gap is exact. It is possible, however, that the energy of the symmetric MO-$\Psi^S_{i(j)}$ also satisfies condition (5). Such is the case, for example, of the substituent derived from Michler's Hydrol blue 3:



3

where the LUMO is symmetric and its energy amounts $\alpha + 0,1635\beta_0$ ($\alpha_N = \alpha - \beta_0$; $\beta_{CN} = \beta_0$).

In this case the symmetric MO's of the substituents interact with the MO's of the polymethine. As a result, their energies are changed (see Eq. (10)). An analogous case occurs when the substituent does not have the specified symmetry elements, e.g. it belongs to the symmetry group C_{1h}, like for example substituent 1.

For complex substituents, such as 1, 2 and 3, the exact calculation of the impurity level energies in the spectrum of an infinite polymethine [$N \to \infty$] is not available in the general case. For finite values of N, the eigenvalues of the matrix defined by Eq. (4) can be obtained by a direct numeric diagonalization.

The eigenvalues of the matrix *Q*, for $N \to \infty$, can be found simply, but approximately, in the following way: if we assume that every MO of the substituent interacts with the MO's of the polymethine chain, independently of the interaction of the other MO's of the same or another substituent, Eq. (3) transforms into equations of the form:

$$\Phi_p = C_{pi}\Psi_i + \sum_k C_{pk}\Psi_k. \tag{8}$$

To each MO of the fragments (except for the antisymmetric Ψ^A, if these exist) an equation of type (8) is juxtaposed, respectively, an energy matrix of the form:

$$\begin{vmatrix} E_i - E & d_1 & d_2 & d_3 & \cdots & d_N \\ d_1 & E_1 - E & 0 & 0 & \cdots & 0 \\ d_2 & 0 & E_2 - E & 0 & \cdots & 0 \\ \cdots & & & & & \\ d_N & 0 & 0 & 0 & \cdots & E_N - E \end{vmatrix} \tag{9}$$

where

$$d_k = \langle \Psi_i | H | \Psi_k \rangle = C_{ir} C_{k_{1(N)}} \tilde{\beta} = C_{ir} C_{k_{1(N)}} \eta \beta_0 .$$

C_{ir} is the coefficient of the AO of the rth atom of the ith MO in the fragment, which is connected to the 1st or the Nth atom of the polymethine chain, and $\tilde{\beta} = \eta\beta_0$ is the resonance integral between these two AO's. The expansion of the characteristic determinant of the matrix (9) leads to the equation:

$$E - E_i + \sum_k^N \frac{d_k^2}{E - E_k} = 0 \tag{10}$$

its solution described in [2].

Thus, the problem of determining the change in the energy of the ith orbital of the fragment R is reduced to the problem of a monosubstituted polymethine with an effective atom $-X$ of Coulomb integral

$$\alpha_X = \alpha + h\beta_0 = E_i .$$

For symmetric ω,ω'-disubstituted polymethines of type R—(CH)$_N$—R, following the method described in [2] for determining the energies of the impurity levels, we obtain the equations:

$$E\left\{ h\beta_0 + E - \eta^2 \beta_0^2 C_{ir}^2 \frac{2E}{\pi} F(E) \right\} + \eta^2 \beta_0^2 C_{ir}^2 C_0^2 = 0 \tag{11}$$

$$h\beta_0 + E - \eta^2 \beta_0^2 C_{ir}^2 \frac{2E}{\pi} F(E) = 0. \tag{11a}$$

In the above equations C_0 is the AO coefficient of the atom bonded to the substituent in the NBMO. For polyenes the NBMO is absent, and for symmetric odd polymethines $C_0^2 \approx t^n = (\beta_s/\beta_d)^n$ [2]. The function $F(E)$ is equal to [$N \to \infty$]:

$$F(E) = \int_0^{\pi/2} \frac{\sin^2 \operatorname{arctg} \dfrac{\sin\omega}{e(\omega) - \cos\omega}}{E^2 - (\frac{1}{4}\Delta E_\infty^2 + 4\beta_0^2 \cos^2\omega)}\, d\omega$$

where

$$e(\omega) = \sqrt{(1-t)^2 + 4t\cos^2\omega}.$$

When $n \to \infty$, $C_0 \to 0$, and Eq. (11) has a root $E = 0$. In addition to this root which corresponds to the unperturbed NBMO, Eqs. (11)-(11a) have two equal roots, their value depending on h, which correspond to two degenerate impurity states, belonging to different irreducible representations: B_1 or A_2, respectively.

In the case $n \to \infty$, the NBMO of a substituted symmetrical polymethine chain is not changed (see Sect. 3(i)). Then the matrix elements of the transition from the impurity level Φ_p to the NBMO of a polymethine chain with $4m+3$ AO's will look like (see the expressions for the MO's in Appendix I and II):

$$\begin{aligned}\langle\Psi_0(B_1)|X|\Phi_p\rangle &= C\left\langle\Psi_0(B_1)|X|\sum_k \frac{d_{2k+1}}{E_{2k+1}-E_p}\Psi_{2k+1}(A_2)\right\rangle \\ &= \sqrt{2}\, CE_p\tilde{\beta}C_{ir}(R_2+R_d)\sqrt{\frac{s^2-1}{s^{2m}-1}} \\ &\quad \times \sum_{l=0}^{m}\sum_{k=0}^{m}(-s)^l[2(m-l)+1]\frac{C_{2k+1,1}C_{2k+1,2l+1}}{E_k^2-E_p^2} \qquad (12)\end{aligned}$$

with

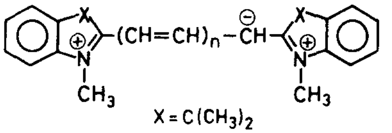
$$s = (\beta_d/\beta_s) \neq 1.$$

In the above expression R_s and R_d stand for the bond length in the polymethine chain.

The analysis of Eq. (12) shows that the asymptotic case ($m \to \infty$) leads to a finite value of the transition matrix element, depending strongly, however, on: $\tilde{\beta}$, E_p and c_{ir}.

4. Comparison with experiment

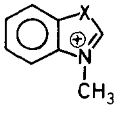
The absorption spectra of the polymethines of the type ($S-1$) with substituent 4



4

have been studied by Ishchenko et al. for $n = 1, 2, 3, 4, 5$ [6]. Using the method of Padé [15] for the asymptotic value [$n \to \infty$] of the energy of the longest-wavelength $\pi\pi^*$-transition, one obtains the values 0.82 eV (solvent CH_2Cl_2) and 0.66 eV (solvent C_2H_5OH).

Among the MO's of fragment 4 (with $\alpha_N = \alpha - \beta_0$, $\beta_{CN} = \beta_0$)

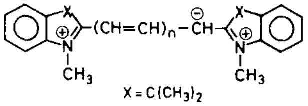


$C_r = 0.778$

only the LUMO is of interest ($E_5 = \alpha + 0.5017\beta_0$). It is the only MO bringing about roots via Eq. (11) that lie within the energy gap. These roots are (with $\eta = 1$, $\beta_0 = 3.39$ eV):

$$E_1 = \alpha; \qquad E_2 = E_3 = \alpha + 0.70 \text{ eV}.$$

Table 1. Dependence of the experimental (λ_{exp}) - [6] and the extrapolated ($N \rightarrow \infty$) values of the wavelength (in nm) of the longest wave $\pi\pi^*$ singlet-singlet transitions on the length of the polymethine chain (n) for polymethines of the type



The asymptotic values of λ ($n \rightarrow \lambda$) are obtained within the Pade [15] approximation

n	$\lambda_{\mathrm{exp}}{}^{a}$	$\lambda_{\mathrm{exp}}{}^{b}$	$\lambda_{\mathrm{exp}}{}^{c}$
1	550	545	312
2	652	640	416
3	758	742	519
4	865	850	626
5	980	958	734
∞	1501 (0, 82 eV)	1877 (0, 66 eV)	1170 (1, 06 eV)

[a] Solvent CH_2Cl_2

[b] Solvent C_2H_5OH; in the case of DMSO solvent the obtained λ_∞ values are practically the same

[c] Experimental values [16] for the polymethincyanines $(CH_3)_2\overset{+}{N}{=}CH-(CH{=}CH)_n-N(CH_3)_2$

The NBMO is doubly occupied and the vacant impurity levels corresponding to the roots E_2 and E_3 lie above the NBMO. Thus, the asymptotic value of the energy of the longest-wavelength transition will be equal to $\Delta\varepsilon_\infty = 0.70$ eV [$n \rightarrow \infty$], whereas the experimental values are 0.66-0.82 eV (Table 1).

To the remaining MO's there correspond roots E_0 according to Eq. (11), which lie on the boundary of the energy gap: $E \approx \alpha \pm |\beta_s - \beta_d|$.

5. Discussion

It follows from the above, that for complex substituents the impurity levels E_p may be located in the whole range of the energy gap of the polymethine chain:

$$\alpha - |\beta_d - \beta_s| < E_p < \alpha + |\beta_d - \beta_s|.$$

This means that the energies of the $\pi\pi^*$-transitions from or to the impurity levels lie within the range determined by the width of the energy gap:

$$0 < \Delta\varepsilon_\infty < E_\infty$$

for odd polymethine chains, and

$$0 < \Delta\varepsilon_\infty < \tfrac{1}{2}E_\infty$$

for even polymethine chains.

The above inequalities, in which $\Delta E_\infty = 2.25$ eV [11] is the width of the energy gap of the infinite polymethine, hold for intra gap electron transitions, i.e. transitions between levels within the energy gap or between them and the boundary levels of the conductivity band or the valence band.

Condition (13) may also be valid for the energies of some local transitions, which occur within the fragments themselves.

Inequality (13) should be interpreted in the following way: upon an increase of N, the asymptotic value of the longest-wavelength electron transition energy lies within the range [0–2.25 eV] (or 0–1.25 eV). For specific substituents it may be less than 0.5 eV.

This result, as well as all the conclusions and considerations in this paper, are valid in the approximation of Born-Oppenheimer. All estimates in this work concern energies of direct-vertical electron transitions, for which the absorption of the photon is not connected with absorption or release of a phonon.

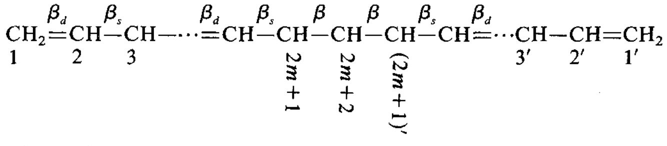
Denoting the energy of the phonon in the infinite polymethine by $h\omega_q$, the energies of the indirect transitions (i.e. of those transitions, where along with the absorption of a photon, a phonon is absorbed or released) will be equal to [14]:

$$h\omega = \Delta\varepsilon \pm h\omega_q.$$

For direct electron transitions, the energy of which is low (i.e. $\Delta\varepsilon < 0.5$ eV) the transition energy becomes comparable with that of the phonons. In this case one can speak of electron transitions only conditionally.

Appendix I

The MO's of a polymethine with $4m+3$ AOs



$$\mathrm{\underset{1}{CH_2}\overset{\beta_d}{=}\underset{2}{CH}\overset{\beta_s}{-}\underset{3}{CH}-\cdots\overset{\beta_d}{=}CH\overset{\beta_s}{-}\underset{2m+1}{CH}\overset{\beta}{-}\underset{2m+2}{CH}\overset{\beta}{-}\underset{(2m+1)'}{CH}\overset{\beta_s}{-}CH\overset{\beta_d}{=}\cdots\underset{3'}{CH}-\underset{2'}{CH}=\underset{1'}{CH_2}}$$

could be written as

$$\psi_{2k+1}(A_2) = \sum_{l=0}^{2m+1} c_{2k+1,1(2)} - 1/2(\varphi_l + \varphi_l') + c_{2k+1,2m+2}\varphi_{2m+2}$$

$$\psi_{2k}(B_1) = \sum_{l=1}^{2m} c_{2k,l(2)} - 1/2(\varphi_l - \varphi_l').$$

If the orbital coefficients of the polymethine chain are:

$$c_{2k+1,\mu} = A_k \sin(\omega_k \mu + \varphi)$$

taking into account the boundary conditions. (For the sake of simplicity we consider only MOs belonging to the irreducible representation A_2; by the same manner we can obtain the expressions for the MOs belonging to the representation B_1)

$$\pm c_{2k+1,1} e(\omega_k) + \beta_d c_{2k+1,2} = 0$$

$$\pm c_{2k+1,2m+2} e(\omega_k) + \sqrt{2}\,\beta c_{2k+1,2m+1} = 0$$

with

$$e(\omega_k)=\sqrt{(\beta_d-\beta_s)^2+4\beta_s\beta_d\cos^2\omega_k}=\beta_d\sqrt{(1-t)^2+4t\cos^2\omega_k}$$

$$0\le\omega_k\le\pi/2$$

is obtained ($\beta<0$; $\beta_d<0$):

$$\omega_k+\varphi=\operatorname{arctg}\frac{\mp\beta_d\sin\omega_k}{e(\omega_k)\pm\beta_d\cos\omega_k}=p(\omega_k)$$

$$(2m+2)\omega_k+\varphi=\operatorname{arctg}\frac{\pm\sqrt{2\beta\sin\omega_k}}{e(\omega_k)\pm\sqrt{2\beta\cos\omega_k}}=q(\omega_k)$$

(sign upper refers to the bonding MOs and the down sign to the antibonding ones).

For the orbital coefficient we have

$$c_{2k+1,2l+1}=\sqrt{\frac{2}{2m+1}}\sin[(2l+1)\omega_k+\varphi]$$

$$=\sqrt{\frac{2}{2m+1}}\sin\left\{\frac{2l+1}{2m+1}[q(\omega_k)-p(\omega_k)]+p(\omega_k)\right\}.$$

From the condition: $\beta_s c_{2l+1}+\beta_d c_{2l-1}=0$ and from the normalisation condition respectively, for the NBMO we obtain

$$\psi_{2m+2}(B_1)=\psi_0(B_1)=\frac{1}{\sqrt{2}}\sum_{l=0}^{m}b_{2l+1}(\varphi_{2l+1}-\varphi'_{2l+1})$$

with

$$b_{2l+1}=\sqrt{\frac{s^2-1}{s^{2m}-1}}(-s)^l$$

$$s=\beta_d/\beta_s\ne 1.$$

Appendix II

If we denote by E_p the energy of the impurity leve in the gap (solution of the Eq. (10)), it follows from (9) that coefficients c_{pk} in representation (8) will be

$$c_{pk}=C=-c_{pi}\frac{d_k}{E_k-E_p}.$$

From the normalization condition we obtain (see Eq. (8)):

$$C=\left\{1+\sum_k^n\frac{d_k^2(E_k^2+E_p^2)}{(E_k^2-E_p^2)^2}+\frac{c_1^2(\mathrm{NBMO})c_{ir}^2\beta^2}{E_p^2}\right\}^{-1/2}$$

$$\xrightarrow{n\to\infty}\left\{1+c_{ir}^2\beta^2\frac{4}{\pi}\frac{c_1^2(\omega)[E^2(\omega)+E_p^2]}{[E^2(\omega)-E_p^2]^2}\,d\omega\right\}^{-1/2}$$

$$=\{1+c_{ir}^2\beta^2S\}^{-1/2}$$

where: $E^2(\omega)=1/4\Delta E_\infty^2+4\beta_0^2\cos^2\omega$, and (see Appendix I)

$$c_1^2(\omega)=\frac{2}{2n+1}\sin^2\operatorname{arctg}\frac{\beta_d\sin\omega}{e(\omega)+\beta_d\cos\omega}.$$

For values of E_p in the range: $0\le E_p\le 1.0$ eV, integral S above varies in the range: $0.220=S=2.494$ ($t=0.719$; $\beta_0=3.39$ eV; $\Delta E_\infty=2.25$ eV). Hence, the expression for the impurity level MO becomes:

$$\Phi_p=C\left[\psi_i-\sum_k\frac{d_k}{E_k-E_p}\psi_k\right].$$

References

1. Tyutyulkov N, Petkov J, Polansky OE, Fabian J (1975) Theor Chim Acta 38:1
2. Tyutyulkov N, Dietz F, Fabian J, Mehlhorn A, Tadjer A (1981) Theor Chim Acta 60:185
3. Fabian J, Hartmann H Light absorption of organic colorants (1980) Springer, Berlin Heidelberg New York
4. Sens B (1984) Cyaninfarbstoffe mit elektronischer Absorption im infraroten Spektralbereich. Dissertation, Universität Siegen
5. Kopainsky B, Qiu P, Kaiser W, Sens B, Drexhage KH (1982) Appl Phys B29:15
6. Ischchenko AA, Derevjanko NA, Zubarovski VM, Tolmachev AI (1984) Theor Exp Khimii (USSR) 20:443
7. Schäfer FP, Lüttke W (1983) Laser und Optoelektronik 2:127
8. Tyutyulkov N (1975) Int J Quantum Chem 9:683
9. Tyutyulkov N, Polansky OE, Fabian J (1975) Z Naturforsch 30a:1308; (1977) 32a:490
10. Longuet-Higgins HD, Salem L (1959) Proc Roy Soc A251:172
11. Marrell JN (1963) The theory of the electronic spectra of organic molecules. Wiley, New York p 72
12. Tyutyulkov N, Kanev I, Polansky OE, Fabian J (1977) Theor Chim Acta 46:191
13. Freimanis Ya F, Vanag Ya G (1961) Zh Obshtei Khimii (J Gen Chem) (USSR) 31:1945
14. Davidov AC (1976) Solid state theory, Moscow, Nauka, chapt VIII
15. Johnson RSC (1973) In: Graves-Morris PR (ed) Pade approximants and their application. Academic Press, London, p 53
16. Malhotra SS, Whiting MC (1960) J Chem Soc (Lond.) 3812