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Electronic properties of polymethine systems
9: position of soliton level in charged molecules

O.D. Kachkovski*, D.A. Yushchenko, G.O. Kachkovski, N.V. Pilipchuk

Institute of Organic Chemistry, National Academy of Sciences of Ukraine, Murmans'ka Str. 5, 02660 Kyiv 94, Ukraine

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Abstract

The disposition of electron levels in the cations and anions of linear conjugated systems is considered as compared with the pattern neutral molecules. It is found that the injection or removing of an electron causes the so-called "soliton level" to appear in the energy gap and the valence band top and conduction band bottom are shifted considerably up with anions and down with cations, due to the electron–electron interaction in the charged π-systems. The influence of the terminal donor and acceptor groups on both the position of the soliton level and band is modeled by $-NH_2$ and $-CH{=}O$ residues; it is shown that the energetic effect of the donor group is greater in cations while anions are more sensitive to the acceptor groups.

Keywords: Linear conjugated molecules; Polyenes; Polymethine dyes; Molecular levels; Soliton; Quantum–chemical calculation

1. Introduction

Charged or ionic linear conjugated system (LCS), particularly, the stable polymethine dyes exhibit numerous unique electronic and spectral properties and hence continue to find the widest application in the fields related to light conversion, i.e. spectral sensitisation, initiation of polymerization, molecular probes in polymer science and biology, active and passive components for tuneable lasers, non-linear media exploring excited-state absorption (ESA), etc. [1–6]. Polymethine molecules are also the suitable molecules for the development of the new theoretical conceptions and effective quantum–chemical models; the first and the simplest quantum–chemical theories, Hückel molecular orbital theory and "metallic model", were elaborated to explain the deep colour of polymethine dyes containing the extended chain of the methine groups as a main component [7–11].

The interest in charged conjugated molecules has been increased by the discovery that oxyacetylene and other π-electron molecules doped through oxidants or reductants can exhibit high conductivity (see, for example, [12] and references therein). Progress in understanding and design of new materials with required properties has relied predominantly on the principles of solid-state physics, first of all, on the theoretical concepts about the charged defects or solitons in doped conjugated polymers. It was found by numerous investigators that the total charge (positive or negative) in the charged π-electron systems is not delocalized uniformly along the whole polymethine chain but it is distributed at π-centres as a wave of the alternated positive and negative partial charges, i.e. as a soliton (polaron) of the electron or hole type [12–17]. The quantum–chemical calculations show that the charge wave in the linear conjugated molecules is

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* Corresponding author. Fax: +38 44 573 26 43.
E-mail address: iochkiev@ukrpack.net (O.D. Kachkovski).

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of finite size long, approximately 15–17 carbon atoms for unsubstituted polymethine chain [13,14]. Since the polymethine chain is a non-rigid π-electron system (in contrast to, for example, a crystal), the wave of the partial charges raises the corresponding rearrangement of the molecular geometry, primarily, the carbon–carbon bond lengths. It was established that the equilibrium bond lengths are practically equalised in that chain segment where the soliton is located [13]. Also, investigation shows that the nature of terminal groups has a substantial influence on the solitonic charge wave. In the diaminopolymethine cations (Brooker ions or streptocyanines) the centre of the charge wave could be shifted to one of the terminal groups, if the dimension of the soliton is shorter than the length of the total π-electron system. As a result, the symmetry breaking occurs [12–15,17–19] which leads to essential changes in the observable characteristics. Meanwhile, no symmetry breaking appears in neutral polyenes with the same end residues even with comparative great lengthening of the conjugated molecules.

According to the so-called triad theory developed by Daehne and Radeglia [20,21] for conjugated systems (aromatics and linear molecules), there are considerable differences between cyanine dyes containing an odd number of –CH-groups in the chromophore and polyenes with an even number of π-centres which lead to the principal difference in spectral properties. It was found by numerous fundamental investigations (for example, [3,5,6]), that the polymethine chromophore of the symmetrical cyanine dyes is characterised by equalisation of the equilibrium carbon–carbon bond length and the alternation of the positive and negative charges at the carbon atoms in the polymethine chromophore. In contrast, related neutral polyenes demonstrate a considerable alternation of the bond orders (and hence lengths) and an equalisation of an electron density along the polymethine chain.

However, the simple triad theory is based on the topological (Hückel) approximation and does not take into consideration any electron–electron interaction. Also, this concept cannot correctly explain the alternation of the positive and negative charges in cationic cyanine dyes as well as the symmetry breaking in the relatively long dyes absorbing in near IR region. Hence, the deep colour of polymethines dye cations or anions cannot be explained adequately by this concept, although one could connect the low transition energies with an existence of so-called soliton (polaron) levels positioned in the forbidden band.

This paper presents the results of the quantum–chemical study of the dependence of the position of the solitonic level of the type of linear conjugated molecules and nature of the terminal groups as well as comparing the positions of the valence and conductive bands in the neutral and charged π-electron systems.

2. Objects and methodology

As objects, the linear conjugated systems with the simplest model terminal groups have been studied:

(1) Ions of following polymethine dyes:

$H_2C^+{-}(CH{=}CH)_n{-}CH{=}CH_2$	**1c**	(Pm–C–n)
$H_2C^-{-}(CH{=}CH)_n{-}CH{=}CH_2$	**1a**	(Pm–C–na)
$H_2N{-}(CH{=}CH)_n{-}CH{=}{}^+NH_2$	**2**	(Pm–N–n)
$O^-{-}(CH{=}CH)_n{-}CH{=}O$	**3**	(Pm–O–n)

(2) Neutral radicals of the polymethine dyes:

$H_2C^{\cdot}{-}(CH{=}CH)_n{-}CH{=}CH_2$	**4**	(Pm–Cr–n)
$H_2N{-}(CH{=}CH)_n{-}CH{=}{}^{\cdot}NH_2$	**5**	(Pm–Nr–n)
$O^{\cdot}{-}(CH{=}CH)_n{-}CH{=}O$	**6**	(Pm–Or–n)

(3) Neutral polyenes:

$H_2C{=}CH{-}(CH{=}CH)_n{-}CH{=}CH_2$	**7**	(Pe–C–n)
$H_2N{-}(CH{=}CH)_{n+1}{-}NH_2$	**8**	(Pe–N–n)
$O{=}CH{-}(CH{=}CH)_n{-}CH{=}O$	**9**	(Pe–O–n)

(4) Ion-radicals of the polyenes:

$H_2C^{+\cdot}{=}CH{-}(CH{=}CH)_n{-}CH{=}CH_2$	**10c**	(Pe–Cr–nc)
$H_2C^{-\cdot}{=}CH{-}(CH{=}CH)_n{-}CH{=}CH_2$	**10a**	(Pe–Cr–na)
$H_2N^{+\cdot}{-}(CH{=}CH)_{n+1}{-}NH_2$	**11**	(Pe–Nr–n)
$O^{-\cdot}{=}CH{-}(CH{=}CH)_n{-}CH{=}O$	**12**	(Pe–Or–n)

The equilibrium geometry of molecules and an electron distribution at atoms within the polymethine chain in the ground state were optimized by the AM1 approximation (Package HyperChem); the procedure of the optimization stops when the energy gradient reaches 0.01 kcal/mol.

3. Molecular levels in the topological (Hückel) approximation

Traditionally, the solitonic level for the doped polymer conjugated chain (polyacetylenes, polythiophenes, polyphenylenevinylene, etc.) is presented as an impurity level or dopant-induced state in the gap between the conductive band and valence band that is schematically depicted in Fig. 1 (see, for example [16] and references

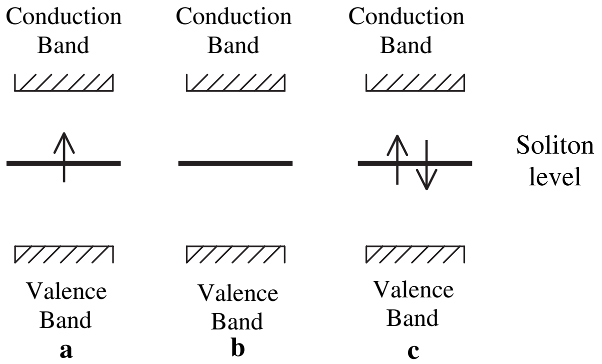

Fig. 1. Soliton level as midgap.

therein). It is assumed that the chain length is infinite and the solitonic level is positioned in the middle of the energy gap. Also, the position of the impurity level does not depend on its occupancy, i.e. the molecule could be ionic (positive or negative) and neutral as well as having a closed or open electron shell. At the same time, the spectrum of molecular levels in the real conjugated systems, oligomer or molecules containing only some −CH-units in the chain, should be sensitive to the molecule length, constitution of the terminal groups and the occupancy of the electron shell.

Molecular topology could be mathematically correctly taken into consideration even in the simplest quantum−chemical approximation − Hückel method of Molecular Orbitals (HMO). Provided the lengths of the all carbon−carbon bonds in the π-electron system are totally equalised, the calculated energy levels for series of odd systems (**1**) and even molecules (**7**) are depicted in Fig. 2. One could see that the lengthening of the chain leads the LUMO and HOMO approach each other, so that the distance between them decreases regularly and $\lim(\varepsilon_{\mathrm{LUMO}}-\varepsilon_{\mathrm{HOMO}}) \to 0$. In the odd system (Fig. 2a), the non-bonding level exists while other levels are situated symmetrically with respect to this level (so-called parity theorem [22]). The HMO calculation gives a similar decrease of the energy gap for the even system (Fig. 2b), whereas it is well-known that neutral polyenes exhibit considerable alternation of lengths of the neighbour bond: $\Delta l^{\mathrm{exp}} \approx 0.08$ Å [23]. If this non-equivalency of the carbon−carbon bonds and hence their resonance integrals, $\beta_{\mu\nu}$, were taken into consideration, then HMO calculation results in the increase of the energy gap as shown in Fig. 2c. However, the original Hückel approximation without any additional special perfections (for example, alternation of resonance integrals, $\beta_{\mu\nu}$, or Coulomb integral, α_μ) does not predict the energy gap for the infinite conjugated chain, but gives the asymptotic decrease in the distance between the highest occupied and lowest vacant levels, which can be written as an analytical expression; $\Delta\varepsilon = (N+1)^{-1/2}\sin[\pi/2(N+1)]$ where N is the number of −CH-units (more correctly, π-centres) in the conjugated molecule [22]. The spectrum of electron levels for any linear polymethine chain was found to lie in a restricted interval: $\alpha + 2\beta \geq \varepsilon_{\mathrm{i}} \geq \alpha + 2\beta$.

Another disadvantage of the Hückel method as a topological model is the neglect of the electron−electron interaction. As a result, the same levels are obtained upon calculation of neutral molecules, their cations or anions, as well as related radicals with an open electron shell. Thus, the topological (Hückel) approximation is imperfect for the correct investigation of the solitonic levels, although, the modified Hückel model was used to develop the soliton concept [24,25]. However, the recent approximation taking explicitly into consideration an electron interaction gives more correct results.

4. Solitonic level in unsubstituted linear conjugated systems

As a preliminary, we consider the level bands for initial neutral molecules: the classical polyenes **7** with even number of CH-groups in the chain and with the closed electron shell as well as the polymethine radicals **4** containing an odd number of −CH-units. Their vacant and occupied electron levels are situated closely to energy gap and are shown in Fig. 3. Lengthening of the polymethine chain leads to a regular decrease in the distance between the highest occupied level and the lowest vacant level, similar to the Hückel levels (compare with Fig. 2). However, taking this into account the electron interaction gives two principal differences: (1) in contrast to the energy level spectrum obtained in the HMO approximation, there is no non-bonding level in the odd π-system; (2) the energy

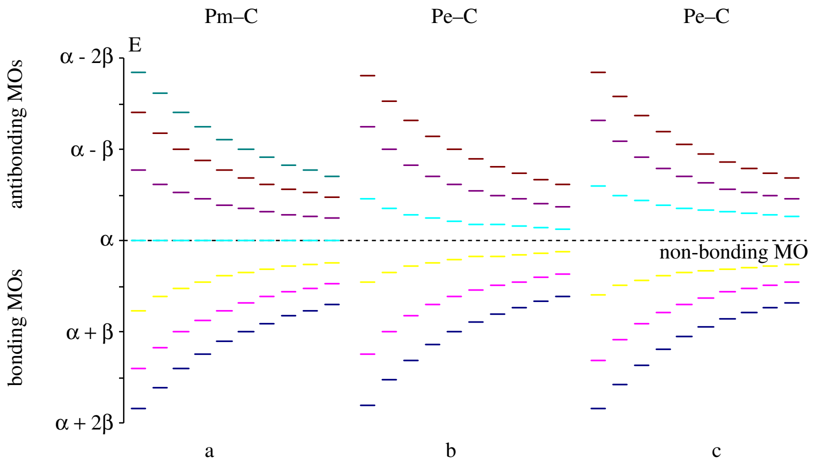

Fig. 2. Electron levels calculated in Hückel approximation: (a) polymethines **1c** (**1a**, **4**); (b) polyenes **7** with the equalized CC-bond lengths; (c) polyenes **7** with the alternated CC-bond lengths.

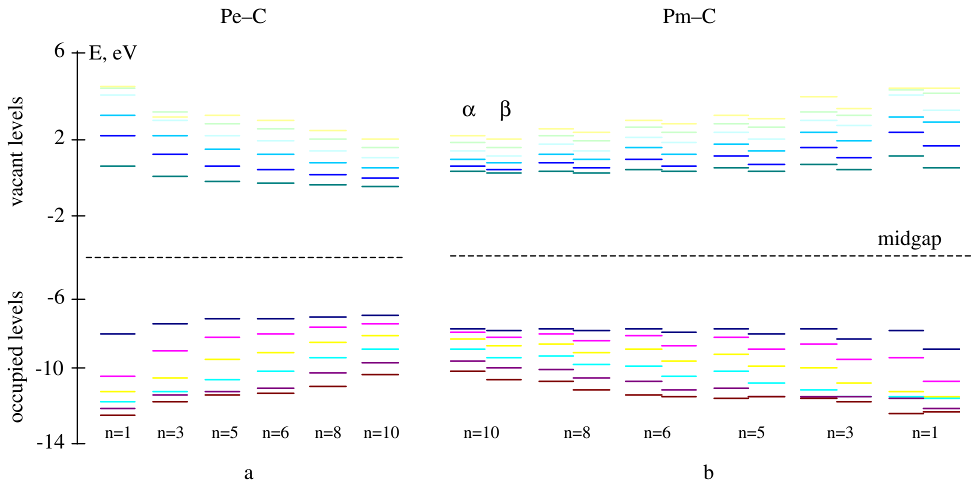

Fig. 3. Electron levels calculated in AM1 approximation: (a) neutral polyenes **7**; α and β are the corresponding spin-orbitals; (b) neutral polymethine radicals **4**.

gap, Δ, does not tend to zero, but approaches asymptotically to a constant magnitude: provided $n = 10$, the AM1 calculation results in $\Delta = 6.66$ eV for polyene; $\Delta(\alpha) = 8.11$ eV and $\Delta(\beta) = 8.15$ eV for the α-spin-orbitals and β-spin-orbitals of the polymethine radicals.

Also, as seen from Fig. 3a and b the midgaps for the polyenes and polymethine radicals with the relative long chain coincides practically: $\varepsilon_{1/2} = -4.44$ eV (polyene **7**, $n = 10$); $\varepsilon_{1/2}(\alpha) = -4.39$ eV and $\varepsilon_{1/2}(\beta) = -4.47$ eV (radical **4**, $n = 10$). There exists a considerable energy gap in the polymethine radical **4**, in spite of the equalisation of carbon–carbon bond lengths [25]. The AM1 calculation of the model polyenes with totally equalised lengths of bonds in the chain gives the relatively considerable energy gap, $\Delta = 5.29$ eV when $n = 10$ and $\Delta = 4.86$ eV when $n = 20$, which is quite opposite to the HMO calculation (Fig. 2b). Thus, the appearance of the considerable energy gap between the valence and conductive bands is mainly caused by an electron interaction in the neutral π-system acting as an insulator. Going from conjugated molecules with the comparative long chain to the more shorter vinylogs is accompanied by decrease in density of the electron levels near the bottom of the conductive band and to top of the valence band, as well as by increase of the difference in the energies of the α- and β-spin-orbitals in the neutral polymethine radicals **4**.

An electron or hole injection in the π-system and hence conversion of the neutral molecule into the charged ion considerably changes the position of molecular levels. As an illustration, Fig. 4a shows some vacant and occupied levels for the vinylogues series of the polymethine cation **1c** containing the hole soliton. One can see that there appears a solitonic vacant level in the energy gap, closer to the conductive band, so that the distance between this level and the bottom of the band becomes practically unchanged upon chain lengthening. The energy of the

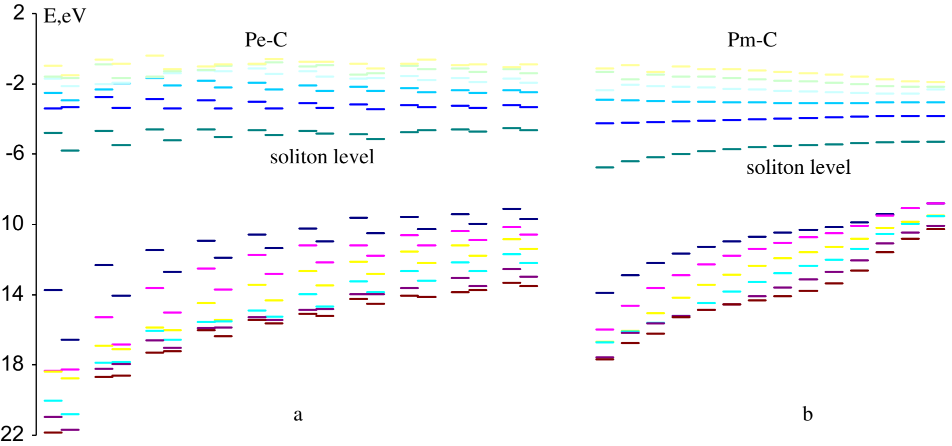

Fig. 4. Soliton level in polyene cation radicals **10c** (a) and in polymethine cations **1c** (b).

HOMO seems to increase regularly while the lowest level in the conductive band keeps its position approximately the same, especially for molecules with long chains.

In the case of the cation radicals **10c** with the open electron shell, there are two solitonic levels, obtained for α-spin and β-spin orbitals (Fig. 4b). Their positions practically coincide for the molecule with the comparative long conjugated chain, although the difference in the energies of the α-MOs and β-MOs becomes significant in the molecules containing one to three vinylene groups.

Similarly, a solitonic level is generated in the polymethine anions **1a** or anionic polyene radicals **11a**, with the impurity level positioned closer to the valence band (Table 1). The disposition of both the bands and solitonic level in the energy gap has been found to be a mirror image, with respect to the corresponding cationic molecules of polyene or polymethine type. Consequently, the results of AM1 calculation confirm qualitatively the theoretical scheme represented in Fig. 1.

At the same time, the calculations in any quantum–chemical approximation taking into consideration the electron–electron interaction suggest that the positions of both the bands and solitonic level in the cationic, neutral and anionic π-systems differ, in principle, in contrast to the simplest scheme in Fig. 1. The main distinctive property is that both the bands turn out to be significantly shifted upon going from neutral molecules to their ionic forms: cations or anions.

Fig. 5 demonstrates the positions of the conductive and valence bands and solitonic level in the energy gap for the comparative long conjugated molecules and molecular ions ($n = 10$), in relation to a π-system type (odd polymethines and even polyenes), a total charge and an occupancy of electron shell (open and closed). One can observe that the removal of an electron and hence a decrease in the total energy of an electron–electron interaction in cations is accompanied, first of all, by a drop in the energy of the valence band (Fig. 5a). In response to changing of the positions of the occupied levels, the bottom of the conductive band is also displaced downwards, the energy level density becoming significantly lower than in the neutral molecules. As a result, one of the vacant levels is separated from conductive band and manifests itself as an isolated or solitonic level, especially, in the system with the long chain (see Fig. 4, too). It is to be noticed that the solitonic level is positioned even lower at 1.03 eV with respect to midgap of the neutral conjugated molecules.

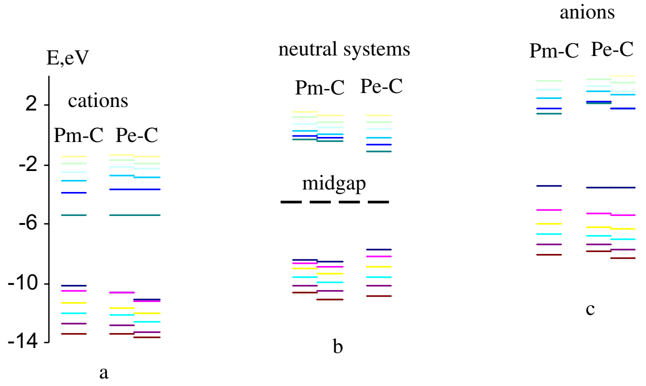

Fig. 5. Position of soliton level and bonds in cation (a), neutral (b) and anions (c), $n = 10$.

There is a good agreement with the parity theorem [22], and the AM1 calculations give the positions of both the bands and the solitonic level for the negatively

Table 1
Energies of solitonic level and bands of dyes **1–12** ($n = 10$)

π-End atom	Type	Dye	Charge	CB bottom		VB top		Solitonic level	
				ε (eV)	Δε (eV)	ε (eV)	Δε (eV)	ε (eV)	Δε (eV)
C	Pm	**4**	0	−0.36	–	−8.49	–	–	–
C	Pe	**7**	0	−1.11	–	−7.77	–	–	–
N	Pm	**5**	0	−0.12	+0.24	−7.95	+0.54	–	–
N	Pe	**8**	0	−0.72	+0.39	−7.27	+0.50	–	–
O	Pm	**6**	0	−0.79	−0.43	−8.79	−0.30	–	–
O	Pe	**9**	0	−1.46	−0.35	−8.14	−0.37	–	–
C	Pm	**1c**	+	−3.92	–	−10.14	–	−5.44	–
C	Pe	**10c**	+	−3.69	–	−10.93	–	−5.40	–
N	Pm	**2**	+	−3.54	+0.38	−9.30	+0.84	−4.91	+0.53
N	Pe	**11**	+	−3.27	+0.42	−9.41	+1.52	−4.56	+0.84
C	Pm	**1a**	–	1.42	–	−5.01	–	−3.41	–
C	Pe	**10a**	–	1.94	–	−5.35	–	−3.56	–
O	Pm	**3**	–	0.79	−0.63	−5.36	−0.35	−3.81	−0.40
O	Pe	**12**	–	1.10	−0.84	−5.62	−0.27	−3.89	−0.33

Remarks: value Δε is calculated with respect to the corresponding unsubstituted compounds. For the radicals with their α- and β-spin MOs: $\varepsilon_i = [\varepsilon_i(\alpha) + \varepsilon_i(\beta)]/2$.

charged ionic molecules **1a** and **10a** (Fig. 5c) as mirror images of the levels for the corresponding cations, **1c** and **10c** (Fig. 5a).

In this case (Fig. 5c), the solitonic level is shifted up, at 1.03 eV, which coincides (within accuracy of calculation) with the corresponding value of the positively charged systems (Fig. 5a).

The first result of the specific electron level (solitonic level) in the energy gap is as follows: the distance between the highest occupied level and the lowest vacant decreases. For comparison, the calculated energy gap in the polymethine cation with 10 vinylene groups is 4.70 eV whereas for the corresponding neutral radical, the distance between the bands is 8.14 eV. The energy of the first electron transition also decreases. Thus, the charged π-system should absorb the light quantum of lower energy and hence usually exhibits a deep colour, in contrast to the neutral conjugated molecules [3,21].

5. Influence of the nature of end groups

It is well-known that introducing terminal groups (both the simplest and complex carbocyclic or heterocyclic residues) causes significant changes in the electron distribution in the chain, equilibrium geometry, position of molecular levels and hence energies of electron transitions [3,5,6,21]. Here we consider the influence only of the simplest donor and acceptor terminal groups containing a single π-centre.

As a donor end group, the $-NH_2$ residue is used in the α,ω-diamino-substituted linear conjugated systems **2**, **5**, **8**, **11**. Such a substituent has a single occupied electron level (a lone electron pair interacting with the main π-system) which is dispoded lower than a valence band top and a solitonic level. While oxonoles **3**, **6** and polyenedications **9**, **12** contain an acceptor $-CH{=}O$ group which has two π-electron MOs, the vacant level are positioned more closer to the conductive band bottom and the corresponding solitonic level. As a result, just the vacant MO of an acceptor effectively causes a shift of two energy bands and solitonic level.

According to the perturbation theory [22], the interaction of any electron level of two π-systems leads repulsion between them, so that an effect (shift of electron levels, $\Delta\varepsilon$) is inversely proportional to the distance between the interacting levels:

$$\Delta\varepsilon = C_{\mathrm{ir}}^2 C_{\mathrm{js}}^2 / \left(\varepsilon_{\mathrm{j}} - \Delta\varepsilon_{\mathrm{i}}\right) \qquad (1)$$

where ε_{j} and $\Delta\varepsilon_{\mathrm{i}}$ are energies of the corresponding MOs while C_{ir} and C_{js} are their coefficients.

The calculated shifts of the solitonic level as well as the boundaries of both bands arose from introducing the donor (NH_2) and acceptor ($-CH{=}O$) groups in the conjugated systems **1**–**12** provided $n = 10$ are given in Table 1.

5.1. Neutral molecules

It was shown above that the energy gap in the neutral polymethine radicals **4** is slightly greater than in polyene **7** (Fig. 3). Consequently, the valence band top in polymethine **4** is situated closer to the donor level while the conductive band bottom is positioned nearer to the vacant acceptor level, in the related polyenes **7**. Table 1 shows that the calculated magnitudes of the shifts, $\Delta\varepsilon$, of both energetic bands are qualitatively in a good agreement with formula (1). So, the shifts of the valence band in the α,ω-diaminoderivatives **5** and **8** (+0.54 and +0.50 eV) are greater than the shifts at the bottom of the conductive bands (+0.24 and +0.39 eV), which is displaced more far from the donor level. Vice versa, the acceptor level in the oxonole radicals **6** effectively affects the conductive band bottom than the valence band (−0.43 and −0.30 eV), although, in the polyenes **9**, interaction with both energetic bands is practically the same.

5.2. Ionic systems

In the first approximation, one could assume that going from neutral molecules to their ions should only slightly influence the positions of the levels of the terminal donor and acceptor groups. On the other hand, the considerable shifting of the electron levels of the conjugated chain in the charged systems to the donor level (in cations) or to the acceptor level (in anions) should be correspondingly accompanied by increasing energetic effects upon introducing the heteroatomic end groups. The analysis of the data in Table 1 confirms this conclusion. The magnitude of the shift of the valence band top reaches the maximum in the cation radicals of the α,ω-diaminopolyenes **11** ($\Delta\varepsilon = -1.52$ eV), and the bottom of the conductive band in anion radicals of the oxygen substituted polyenes **12** prove out to be shifted at 0.84 eV.

It is to be noted that the sensitivity of the solitonic level to heterosubstitution should be intermediate, with respect to both bands, since it is positioned in the energy gap. The calculated data agree perfectly with this assumption.

Thus, the results of the investigation show that going from neutral conjugated systems to their ions is accompanied not only by the appearance of the separated, so-called solitonic level in the energy gap, but by the considerable shifting of both the valence and conductive bands. Additionally, positions of both the bands and solitonic level depend on the nature of the end groups.

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