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# Electronic properties of polymethine systems 8: geometry and electron structure of radicals

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**Abstract**

The electron distribution and equilibrium molecular geometry of the radicals of the pyridocyanines and their carbo- and hetero-analogues are compared with their original compounds with a closed electron shell. It is found that going from ionic polymethine dyes to their neutral radicals is accompanied by equalizing of the atomic charges in the chain while changes of the CC-bond lengths are minimal. In contrast, the considerable bond length alternation in polyenes decreases radically in their ionic radicals. It is shown that lengthening the chain in the polyene radicals as ionic conjugated systems leads to a shift of the solitonic charge wave and hence to symmetry breaking, in a similar behavior to ionic polymethine dyes with a closed electron shell. A general classification of the linear conjugated systems is proposed.

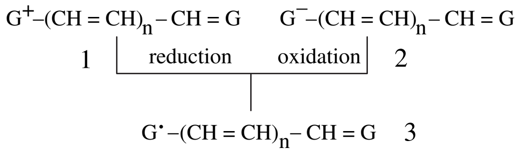
*Keywords:* Polymethine dyes; Radicals; Electron structure; Molecular geometry; Quantum–chemical calculation

## 1. Introduction

The radicals of linear conjugated systems (LCSs) appear upon the electrolytic oxidation and reduction, ionization, as well as when using polymethine dyes or polyenes as photosensitizers, polymerization initiators, etc. [1–5]. Compared with relative stable molecules with closed electron shell the polymethine dye radicals are extremely unstable [1,2]. Polyene radicals exhibit somewhat higher stability than polymethine derivatives with an open shell [3–5].

It has been shown in previous papers [6–8] that two types of stable LCS's with a closed electron shell, polymethine dyes (PMD) and α,ω-heterosubstituted polyenes (HP), differ substantially from each other in many electronic characteristics.

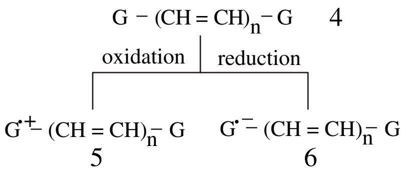
This work is concerned with a consideration of the geometrical and electronic features of the vinylogues series of LCSs with an open electron shell obtained from PMDs and HPs containing the terminal or end groups (EGs) of variable basicity. Only neutral polymethine dye radicals derived from both cationic and anionic PMDs were investigated:



$$G^{+}{-}(CH=CH)_n{-}CH=G \quad 1 \qquad G^{-}{-}(CH=CH)_n{-}CH=G \quad 2$$

$$G^{\bullet}{-}(CH=CH)_n{-}CH=G \quad 3$$

In the case of polyene, two ionic radicals could be generated:



$$G-(CH=CH)_n-G \quad 4$$

$$G^{\bullet +}(CH=CH)_n^{-}G \quad 5 \qquad G^{\bullet -}(CH=CH)_n^{-}G \quad 6$$

The relative stability of both radical forms depends on the basicity of their EGs. In this paper, we have investigated only the more stable radicals.

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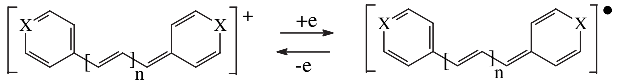
The optimized molecular geometry and electron distribution were calculated by semiempirical AM1 approximation (package HyperChem); the optimization procedure was stopped when reaching energy gradient 0.01 ccal/mol.

## 2. Neutral polymethine dye radicals

The originated PMDs **1**, **2** are ionic conjugated systems. The π-electron system causes the charge (negative or positive, correspondingly) to be localized at the atoms (π-centers) as a charge wave, i.e. as an electron or hole soliton [9–11]. As a result, the total electron densities at the atoms within the polymethine chain (PC) are found to alternate be considerable [2,7,12]. The calculation in the framework of the PPP and CNDO/2 approximations gives the opposite signs of the charges at the neighbouring carbon atoms, the positive and negative charges being approximately equal [7,12]. The AM1 method overestimates the CH-bond polarization results in considerable positive charges at the hydrogen atoms and the higher total electron densities at the carbon atoms within chain (see Fig. 1a). However, the density alternation, $\Delta q_\mu = q_\mu - q_{\mu+1}$ (where $q_\mu$ is the total electron density at the $\mu$th atoms), is found to be similar in any of the standard semiempirical approximations (PPP, CNDO/2, AM1, PM3, etc.).

A typical picture of the electron distribution obtained in the well-known AM1 approximation for unsubstituted polymethine cation (**1**, G ⇒ $CH_2$) is presented in Fig. 1a. One can see that the electron density wave is of a solitonic type (a group soliton). It was shown [10,13,14] that the function $|\Delta q_\mu|$ is more regular and hence is more convenient for an analysis than value $\Delta q_\mu$ (Fig. 1b). An appearance of the soliton in the charged π-electronic system leads to the CC-bond length equalization which is maximum at the soliton center. In contrary, in the soliton ends, the bond length alternation, $|\Delta l_\nu| = |l_\nu - l_{\nu+1}|$ increases regularly (Fig. 1c). Provided the chain is enough long, the solitons (electron density wave and geometrical or topological wave) can be shorter than a conjugated molecule. Calculation of the AM1 and ab initio (STO-6-31G** basis set) approximations gives the half width of the solitonic wave: $1 \approx 7$ [9]. Almost the same magnitude was calculated for the streptocyanines (**1**, $G^+ \Rightarrow H_2N^+{=}CH$, G ⇒ $CH{-}NH_2$). Also, the AM1 calculations predict that the soliton can move to one of the end groups when $n \geq 8$. For the dyes **1** with the more complex, carbo- or heterocycles as end groups, G, the shifting of the center of the charge wave can occur proving even shorter length of the polymethine chain which is caused by the additional increasing of the chromophore due to the extended π-electron system of both end groups. For example, the symmetry breaking appears in the thia- or pyridocyanines upon $n = 5$ [13,14]. Based on these results, we have assumed that two electronic forms of the symmetrical dyes exist in solution: (1) symmetrical form with the soliton in the molecule center; (2) unsymmetrical form with soliton located at the chain end. This assumption enabled us to explain correctly the appearance of the additional wide band in absorption spectrum. The unsymmetrical form has a considerable dipole momentum (15–20 D) and hence is very sensitive to solvent polarity [13,14]. Also, the position and shape of the charge and topological solitonic waves were proved to depend on the basicity of the terminal groups.

In this paper, the pyridocyanines and their carbo- and hetero-analogues **7** were used:



X = CH, $NCH_3$, O, S

**7c** **7r**

The dye cations **7c** are convenient as model compounds for the investigation of the influence of end groups on the electron structure of the polymethine chain: the electron donor strength of these residues could be modified by changing the only nature of the heteroatoms X upon the same topology of the end groups. As a rule, the polymethines studied experimentally contain the substituents in 2, 6 positions: $CH_3$, $C(CH_3)_3$, Ph, Th [15].

The basic properties could be estimated quantitatively by their topological parameter $\Phi_o$, which is connected with the shift of the frontier MO nodes with respect to their positions in the unsubstituted conjugation chain [6,12]. For the molecules with the stable electron shell, an index $\Phi_o$ is positive and lies in a range $0° \leq \Phi_o \leq 90°$. The calculated magnitudes for the dyes studied are equal: 0° (X = CH), 76° (X = $NCH_3$), 44° (X = O), 36° (X = S) [15].

Fig. 2a demonstrates the charge alternation, $|\Delta q_\mu|$, in the polymethine chain of the vinylogues series of the dyes **7c** while Fig. 3a shows the corresponding function for the bond length alternation, $|\Delta l_\nu|$. One can see that symmetry breaking occurs upon $n \geq 6$ for the pyrylocyanines (X = O); $n \geq 5$ for the pyridocyanines (X = $NCH_3$); $n \geq 3$ for the thiapyrylocyanines (X = S) while the α,ω-diphenylpolymethine cations (X = CH) keep their symmetrical electron structure and molecular geometry, independently on the chain length.

The addition of an electron into the π-electron system of the dyes **7c** and hence going from PMD ions to their neutral radicals **7r** should be accompanied by the redistribution in the charges at the carbon atoms within the polymethine chain. In the neutral radicals of the α,ω-diphenylpolymethines as odd alternant

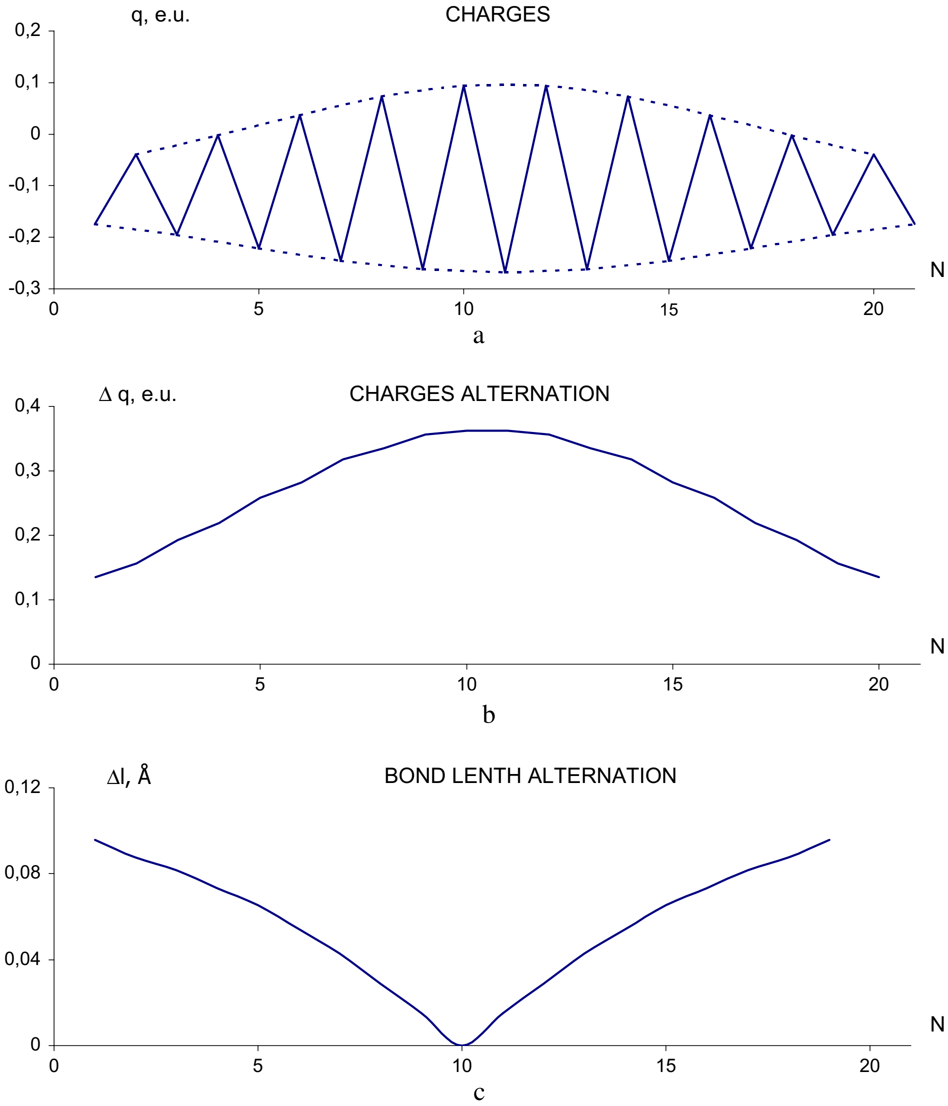
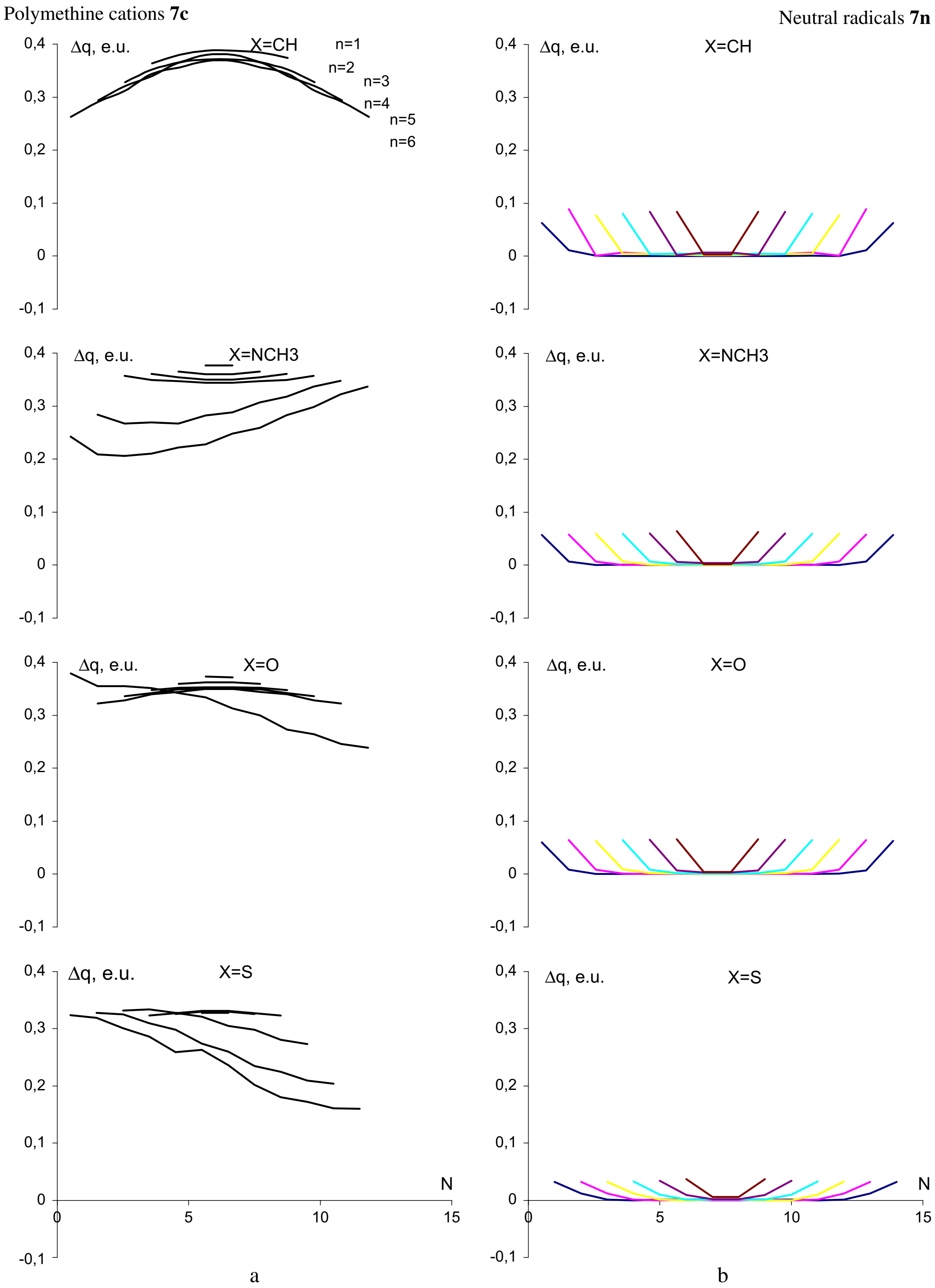


Fig. 1. Atomic charges, $q$ (a), alternation of charges, $\Delta q$ (b) and alternation of CC-bond lengths, $\Delta l$ (c) in the chain of polymethine cation $H_2N^+{=}CH{-}(CH{=}CH)_{10}{-}NH_2$, so that carbon atoms or CC-bond is numbered by N.

hydrocarbons, the unpaired electron occupies the non-bonded MO (NBMO) which has its nodes in odd positions of the chain. As a result, an additional electron is located at the atoms with an electron density deficiency so that electron densities should be equalized along whole chain. On the other hand, the product $C_{\mathrm{NBMO},\mu}C_{\mathrm{NBMO},\mu+1}$ for the NBMO as a contribution in the total π-bond order, $p_{\mu\nu}$, is equal to zero for any two neighbouring atoms, and hence the bond order should not be changed upon going from the cationic dye molecule to its neutral radical. In the first approximation, one could suppose that CC-bond lengths should remain unchanged too, according to the known relation: $\Delta l_{\mu\nu}$ (Å) $= 0.17\Delta p_{\mu\nu}$ [9]. A similar picture appears to remain approximately correct also for the heterocyclic end groups ($X = NCH_3$, O, S).

The calculated amplitude of the alternation of the electron density at the carbon atoms, $|\Delta q_\mu|$, and the CC-bond lengths, $|\Delta l_\nu|$ in the chain of the dye radicals **7r** are depicted in Fig. 2b and Fig. 3b, respectively. It is seen that the atomic charge is totally equalized, in contrast to the related PMD cations, only for the pairs of the atoms positioned nearest to terminal groups, the amplitude $|\Delta q_\mu|$ is not equal to zero.

The CC-bond lengths prove to be equalized, particularly, in PMD radicals with basic heterocyclic residues when parameter $\Phi_o \neq 0°$. The magnitudes of the bond length are found from calculation to be nearly 1.40 Å which coincides with the CC-bond lengths in the chromophore of the cationic polymethines **7c**. Only at the chain ends, near to the terminal residues, does a relative small alternation of the bond lengths appear, its amplitude, $\Delta l_\nu$, depending on the basicity of the end groups. For example, parameter $\Delta l_\nu$ for the terminal pair of the CC-bonds is practically constant upon lengthening of the chain: 0.020 Å ($X = NCH_3$);

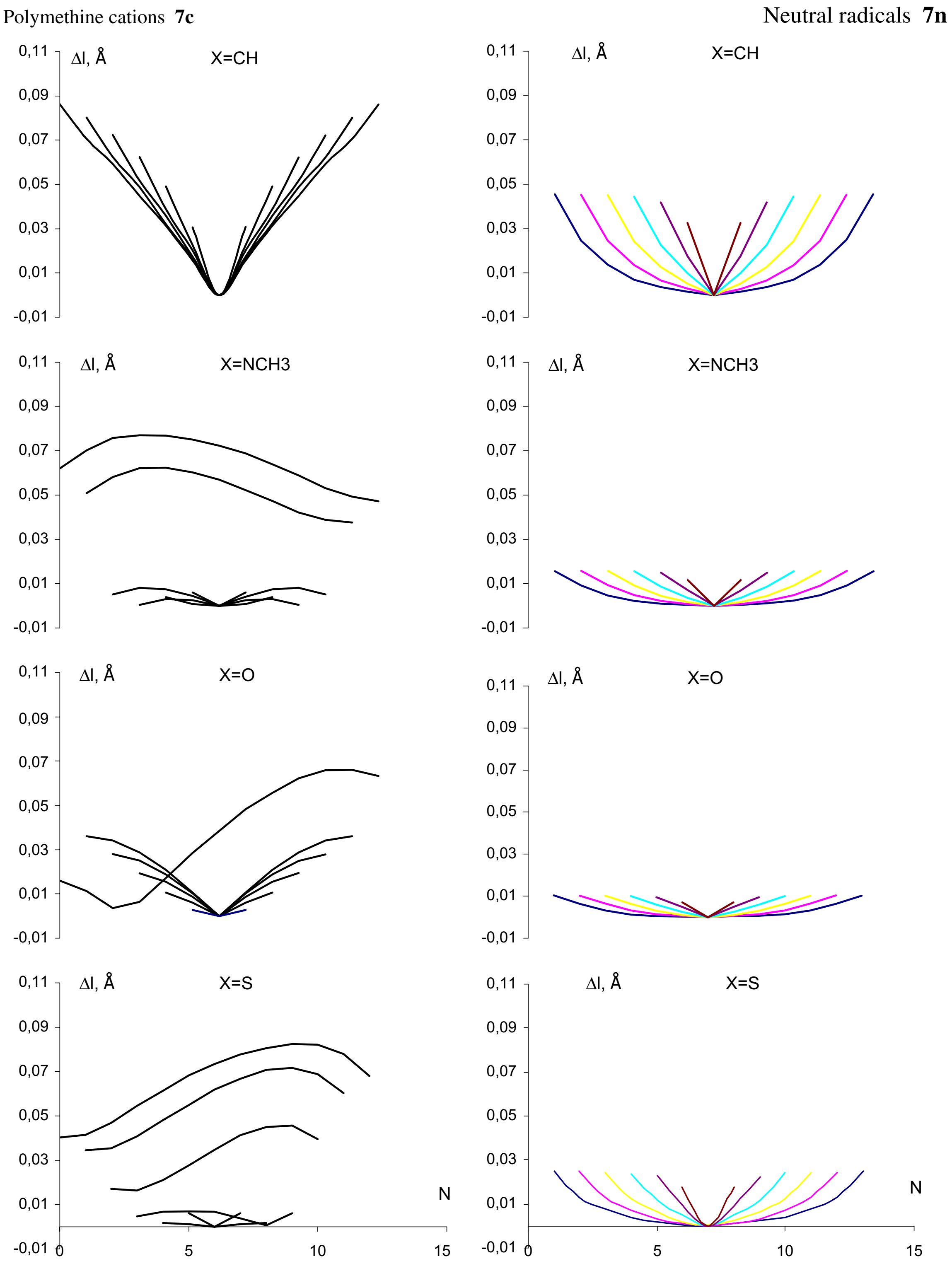

Polymethine cations **7c**

Neutral radicals **7n**

Fig. 2. Alternation of the atomic charges, $\Delta q$, in the chain of the polymethine dyes **7c** (a) and their radicals **7r** (b).

0.016 Å (X = O); 0.026 Å (X = S), while the $\Delta l_v$ value for the α,ω-diphenylpolymethine radicals (X = CH, $\Phi_o = 0°$) reaches the comparative high magnitude: 0.047.

Another main distinction of the neutral radicals from the parent ionic PMDs is the fact that lengthening of the polymethine chain by introducing the vinylene groups does not lead to symmetry breaking even when



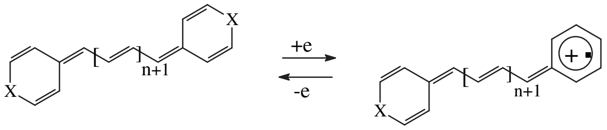
a b

Fig. 3. Alternation of the CC-bond lengths, Δ*l*, in the chain of the polymethine dyes **7c** (a) and their radicals **7r** (b).

$n > 20–30$ or greater, since the PMD radicals are uncharged π-electron systems and hence are not soliton-like waves.

## 3. Ionic polyene radicals

The originated classic polyenes (**4**, G ⇒ CH=CH$_2$) or their α,ω-disubstituted derivatives HPs with closed electron shell are neutral conjugated molecules, in contrast to charged PMD ions. It was established by experimental and theoretical methods that electron density is totally equalized at carbon atoms in the unsubstituted polyenes (see, for example, review [16] and references therein). Although the AM1 calculation gives the partial negative charges at carbon atoms, −0.17, due to the overestimation of the polarization of the C−H bond as referred above. A similar equalization of the electron densities was obtained for the α,ω-diphenylpolyenes (**8n**, X = CH), so that the $|\Delta q_\mu|$ values are practically zero; only at two atoms near to the end groups, there is a small disturbance in the general regularity of the electron density distribution (Fig. 4a).



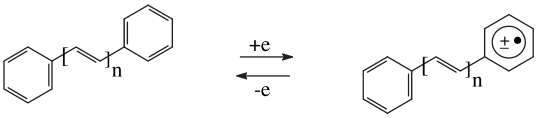
**8n** **8r**
X = CH, NCH$_3$, O, S

Introducing the heterocycles as end groups (X = O, S, NCH$_3$) and hence increasing of the parameter $\Phi_o$ causes the appreciable regular alternation of the electron densities at the carbon atoms near to the terminal groups (Fig. 4a), but the $|\Delta q_\mu|$ magnitude is significantly lower than that in the corresponding PMD cations (compare Fig. 2a). The degree of alternation depends on the nature of heteroatoms and decreases upon moving from the end groups to the chain middle. The maximum magnitude of the value $\Delta q_\mu$ is reached in the polyenes with high basic pyridine residue (X = NCH$_3$).

It is reasonable that this alternation of the atomic charges leads to decreasing of the alternation of the CC-bond lengths in both chain ends (Fig. 5a). Comparing Fig. 2b and Fig. 3b for PMD radicals and Fig. 4a and Fig. 5a for polyenes, one could see that the electron density distribution at the atoms within the chain and the equilibrium molecular geometry (the CC-bond lengths) in neutral linear conjugated molecules are similar, and are independent upon the parity of the number of the CH units (i.e. on the type of LCS: PMDs or polyenes) and on an occupancy of the MOs (closed or open electron shell). Also, the symmetry breaking does not occur upon an arbitrary lengthening of the conjugate chain, which is due to the absence of the charge in the collective π-electron system and hence the absence of the electron or hole soliton.

Taking this conclusion into account, we would expect that going from neutral polyenes **8n** to their charged radicals **8r** should lead to an appearance of the solitonic waves (charge and topological solitons).

At the same time, in the radical of the unsubstituted polyenes or α,ω-diphenylpolyenes (cation **9cr** or anion **9ar**) as even alternant hydrocarbons, the

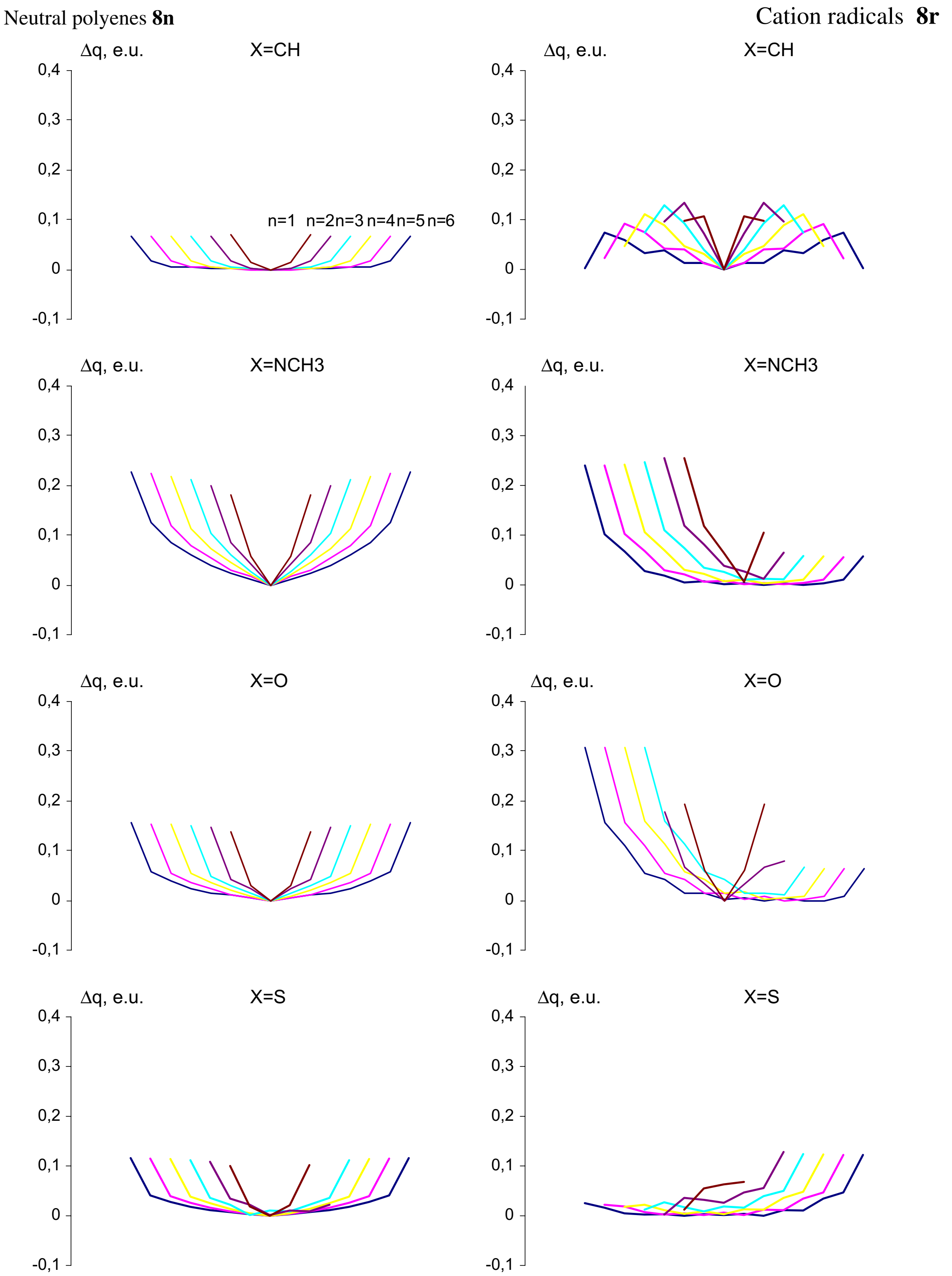


**9n** **9cr, 9ar**

unpaired electron occupies the LUMO or is removed from the HOMO, which have their nodes in the middle of the CC-bonds. The analysis of the contributions of the corresponding MOs in the total electron densities and bond orders (or reducing of the corresponding values in the cation radicals) shows that going from the neutral polyenes to their ionic radicals should be accompanied by equalization of both the atomic charges and the bond length. Hence, the electron distribution in any type of radicals of the symmetrical form of the linear conjugated systems is found to be similar. This theoretical conclusion is confirmed by the results of the quantum−chemical calculations. One could see in Fig. 5b that the $|\Delta l_\nu|$ values decrease sharply for the radical **8r** compared with the corresponding neutral molecules **8n**; only in the chain ends, does the calculation give the regular increase in the amplitude of bond length alternation. At the same time, Fig. 4b demonstrates a small-scale increase of the charge alternation, but its amplitude remains nevertheless significantly lower than the $|\Delta q_\mu|$ values in charged polymethine dyes (compare with Fig. 2a).

It was established earlier [17] that, in contrast to the comparative equalization of the total charges, there is a considerable alternation of the α- and β-components, $q_\mu^\alpha$ and $q_\mu^\beta$, of the total electron density, $q_\mu$, in the chain. The amplitudes of the density alternation of the electrons with opposite spins are approximately equal while their phases are opposite.

As one would expect, for polyene radicals as charged π-electron systems containing the donor or acceptor end groups ($\Phi_o \neq 0°$), the symmetry breaking occurs upon chain lengthening with the exception of derivatives of the polyenes with alternant terminal residues ($\Phi_o = 0°, 90°$). It is seen in Fig. 4b and Fig. 5b that the crucial length of the chain for the symmetry breaking depends on the basicity of the heterocyclic residue. The calculation predicts that



a b

Fig. 4. Alternation of the atomic charges, Δ$q$, in the chain of the polyenes **8n** (a) and their radicals **8r** (b).

geometrical soliton and electron density wave are shifted from the center of the molecule in the ionic polyene radicals **8r** even upon the shortest chain; only the ion-radicals of the α,ω-diphenylpolyenes ($\Phi_o = 0°$) keep their symmetry.

## 4. Spin density distribution

In addition to electron densities and bond orders (and hence bond lengths), an electron structure of the conjugated radicals can be characterized by the

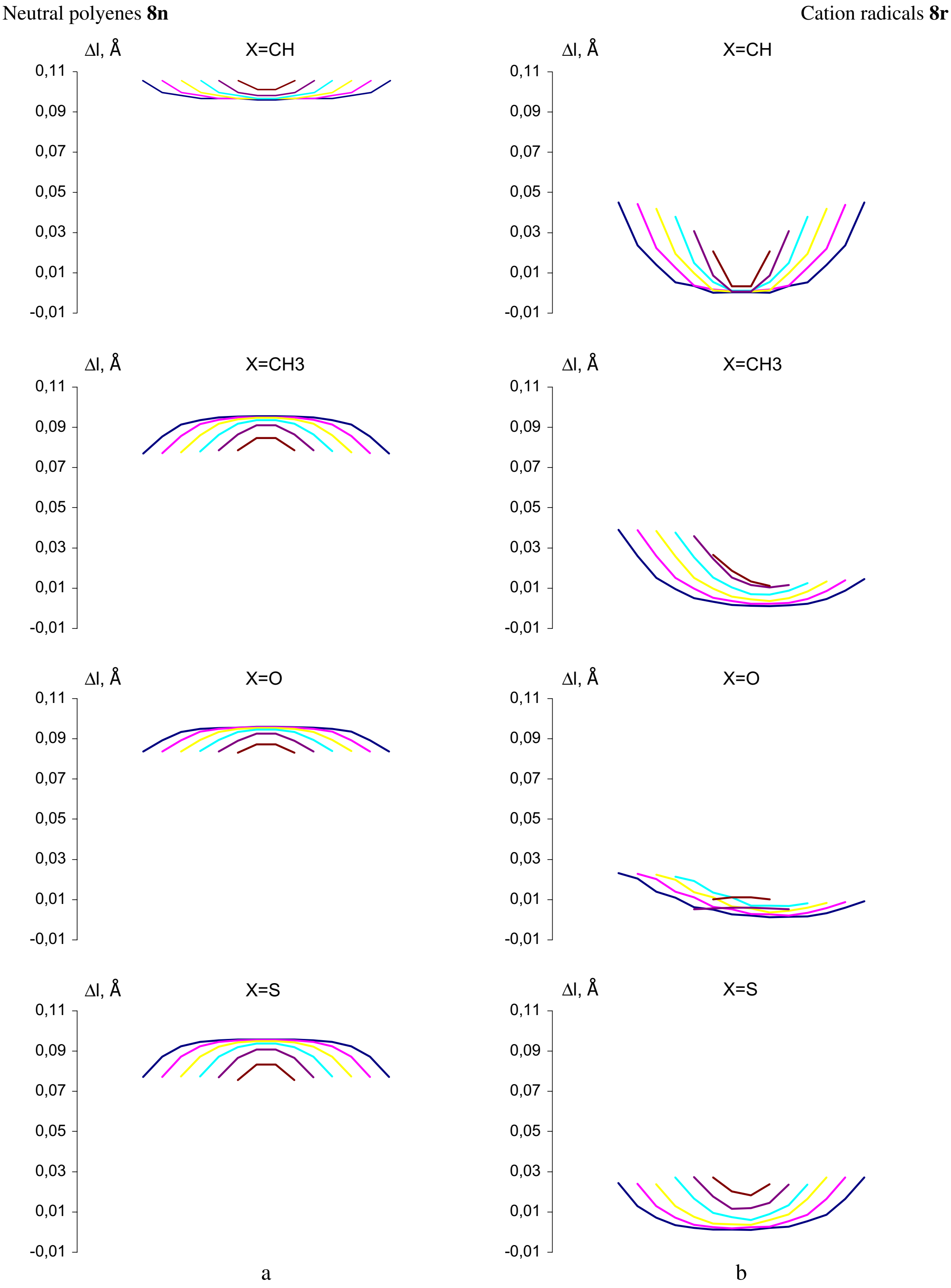


Fig. 5. Alternation of the CC-bond lengths, Δ*l*, in the chain of the polyenes **8n** (a) and their radicals **8r** (b).

distribution of the spin density at the atoms within the polymethine chain. Traditionally, the spin density is quantitatively calculated as a difference of the α- and β-components ($q_\mu^\alpha$, $q_\mu^\beta$) of the total electron density: $\rho_\mu = q_\mu^\alpha - q_\mu^\beta$ [1–5,17]. For example, the spin distribution in the neutral α,ω-diphenylpolymethine radicals as well as in the α,ω-diphenylpolyene cation and anion radicals with the same comparative long chain $(n = 6)$ is presented in Fig. 6. There is a considerable alternation of the spin densities, $\rho_\mu$, at carbon atoms, the amplitude

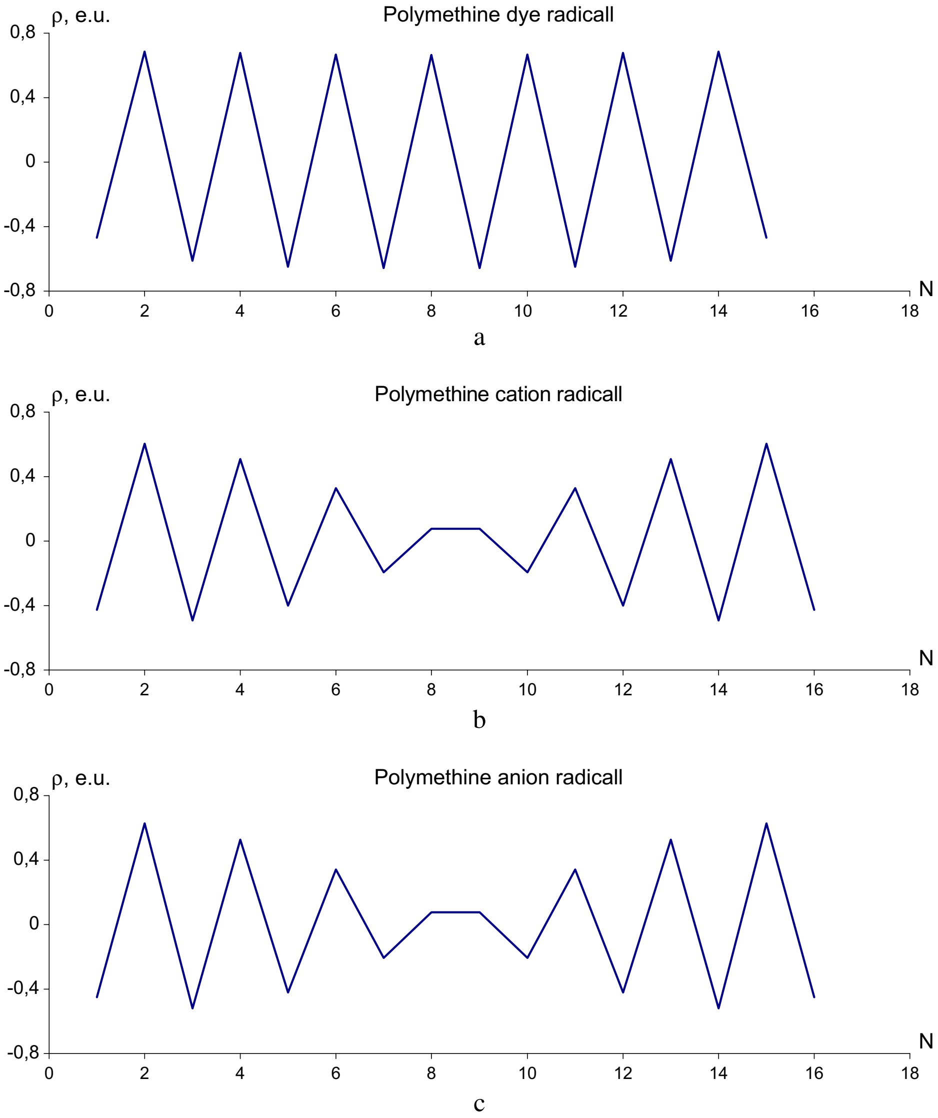


Fig. 6. Spin densities, $\rho$, at the carbon atoms in the chain of the neutral polymethine radical **7r**, X = CH, $n = 6$ (a), and the corresponding polyene ion radicals, **9cr** (b) and **9ar** (c).

of the alternation was kept approximately equal for any pair of the neighbouring atoms. In contrast to neutral polymethine radicals, the spin density alternation in the related ionic polyene radicals decreases regularly from the terminal groups to the chain middle. The $\rho_\mu$ values for both polyenic forms (cationic and anionic) are seen in Fig. 6b and c.

It is appropriate to introduce the function $|\Delta\rho_\mu| = |\rho_\mu - \rho_{\mu+1}|$ for the quantitative estimation of the degree of spin density alternation, similar to the functions $|\Delta q_\mu|$ and $|\Delta l_\mu|$ used above. Fig. 7 represents the dependence of the $|\Delta\rho_\mu|$ values on the position of the atom in the chain for the neutral polymethine radicals **7r** and cationic polyene radicals **8r**.

The $|\Delta\rho_\mu|$ value for neutral PMD radicals is practically the same ($\approx$1.30), independent of the length of the chain and the basicity of the terminal groups. In contrast, the amplitude of the spin density alternation is strongly sensitive to the nature of the heteroatoms, X, and the number of the vinylene groups, $n$, in the ionic polyene radicals.

As one could expect, the replacement of $>$CH group by heteroatoms and hence increase of the electron donor ability $\Phi_0$ of the end groups in the ionic polyene radicals is accompanied by the symmetry breaking of the spin density wave (Fig. 7b) caused by the shift of the center of the soliton. One can see in Fig. 7b that the lengthening of the chain also leads to the regular increase in the degree of alternation of the spin densities so that the $|\Delta\rho_\mu|$ value tends to the asymptotic magnitude: $\approx$1.30, similarly the $|\Delta l_\mu|$ value in the neutral polyenes **8n** tends to the same limit of magnitude.

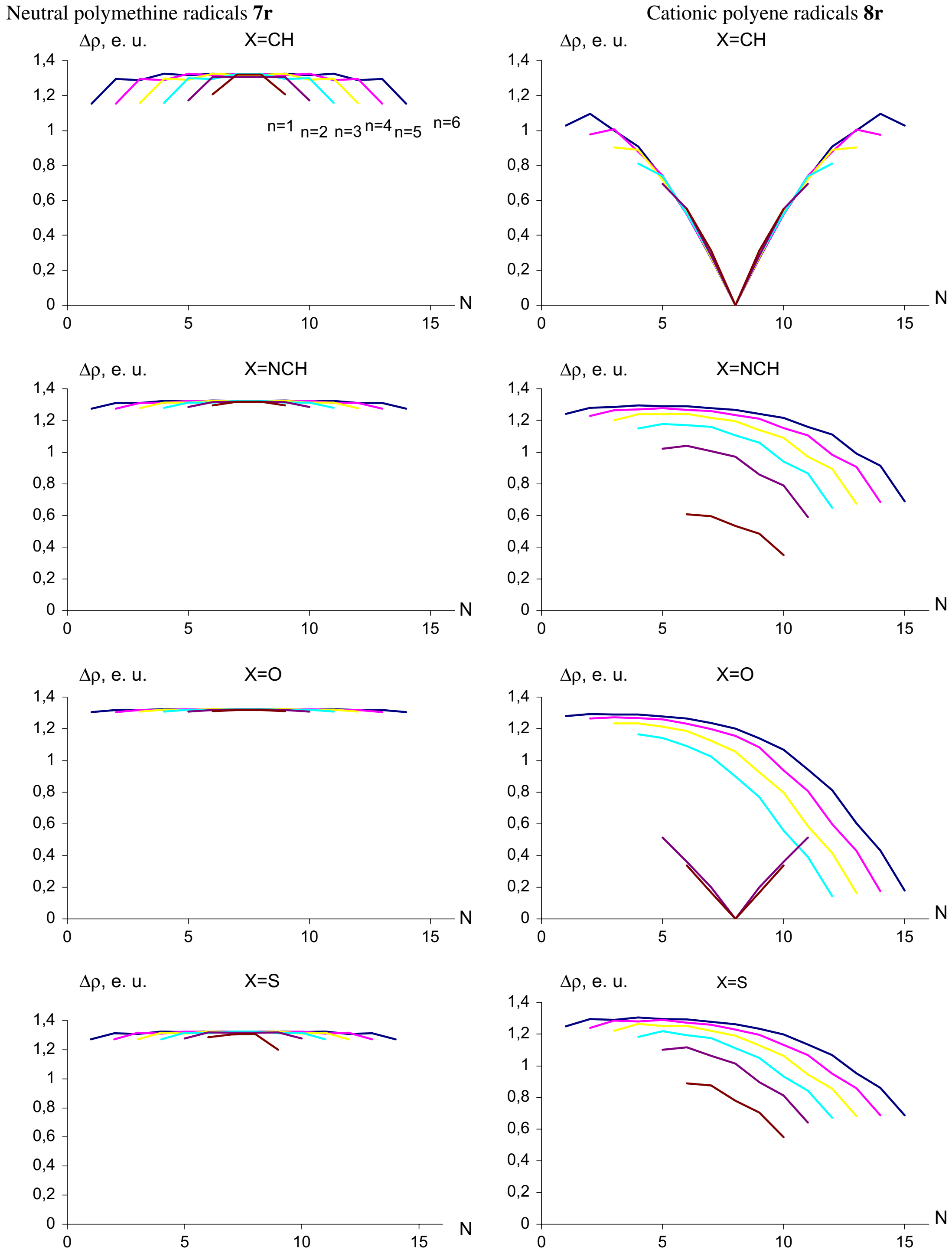


Fig. 7. Alternation of the spin densities, Δ*ρ*, in the chain of the polymethine radicals **7r** (a) and polyene radicals **8r** (b).

## 5. Conclusion: a general classification of the symmetrical linear conjugated systems

Traditionally, symmetrical linear conjugated molecules are divided into two types: polymethine dyes and polyenes, which essentially differ from each other in their chemical and spectroscopic properties [2,12,18]. Regarding an electron structure, they are distinguished by atoms and bond occupancies: PMDs exhibit a considerable alternation of electron densities at the carbon atoms and an equalization of the π-orders of the carbon–carbon bonds (and their lengths) in the chain while polyenes are characterized by an equalization of electron densities at the atoms and considerable

$[R\text{-}(CH)_m\text{-}R]_z$ , z=0, ±1

| | Even Systems (Polyenes) | | Odd Systems (Polymethine Dyes) | |
|---|---|---|---|---|
| Neutral | **Closed Electron Shell** | | **Open Electron Shell** | |
| | EDW | - | EDW | - |
| | BOW | + | BOW | - |
| | SDW | - | SDW | + |
| | Symmetry Breaking | + | Symmetry Breaking | - |
| Ionic | **Open Electron Shell** | | **Closed Electron Shell** | |
| | EDW | - | EDW | + |
| | BOW | - | BOW | - |
| | SDW | + | SDW | - |
| | Symmetry Breaking | + | Symmetry Breaking | + |

Fig. 8. A general classification of the linear conjugated systems. EDW is an electron density wave; BOW is a bond order wave; SDW is a spin density wave.

alternation of the π-bond orders (bond lengths). However, this simplest classification includes only π-systems with a closed electron shell.

We would propose a generalized way to unify the linear conjugated systems that also takes into consideration the molecules with open shell. Thus, the symmetrical LGSs can be neutral and ionic, and contain the odd or even number of the π-centers (carbon atoms) in their polymethine chain. As a result, they are divided into four types, which differ from each other by the following properties: an appearance or absence of the electron density wave (EDW), bond order wave (BOW), spin density wave (SDW) and breaking or remaining of the symmetry of the corresponding waves upon lengthening of the chain. Generally, the proposed classification can be pictorially presented by the convenient scheme demonstrated in Fig. 8.

It is seen from this scheme that SDWs appear, of course, only in the molecules with the unpaired electron while the symmetry breaking is possible only in the charged conjugated π-systems, i.e., in systems generating solitons, independently whether the electron shell is closed or open.

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