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Electronic Properties of Polymethine Compounds. 2. Electron Donor Ability and Relative Stability

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ABSTRACT

A comparative analysis has been carried out for polymethine dyes and heteropolyenes having arbitrary end groups and which absorb in the same spectral region, with respect to their relative stability. To quantify this property, the previously introduced parameter ϕ_0 is used; this characterizes the positions of the frontier energy levels. The dependence of relative stability on compound type and end-group topological indices (Φ_0) is studied. A single stable form is shown to exist for polymethine dyes ($\Phi_0 = 45°$) and two forms for polyenes ($\Phi_0 = 0°$ or $90°$).

1 INTRODUCTION

In the authors' previous paper[1] the frontier energy levels of linear polymethine systems (LPMS) **1** were analyzed in detail, with respect to the dependence of their positions on the type and topology of end groups (EG). The symmetric LPMSs were shown to be naturally divided into two types, viz. polymethine dyes (PMD) and heteropolyenes (HP), differing distinctly in the position of their energy gap with respect to the Fermi level for the π-electrons. Unsubstituted PMDs, as odd linear conjugated hydrocarbons, have their non-bonding level vacant in cationic and filled in anionic polymethines; thus, they behave as unstable compounds. In contrast,

$$G_1—(CH)_m—G_2$$

1

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unsubstituted HPs, which are even conjugated systems, are rather stable, since their frontier levels are symmetrically disposed relative to the Fermi level. Introduction of EGs conjugated with the polymethine chain (PC) radically changes the electron level positions. As a result, EGs can notably affect the stability of PMDs and HPs.[1-4] To characterize the positions of the frontier levels, the authors have recently suggested a new parameter, viz. electron donor ability ϕ_0. This parameter, as well as EG topological indices, enables a study to be made on the effect of LPMS type and constitution on the relative stability of such compounds.

2 THE RELATION BETWEEN ELECTRON DONOR ABILITY AND RELATIVE STABILITY OF LPMS

In this study, we assume that an LPMS is stable provided it has a closed stable electron shell, i.e. bonding levels are double-filled and antibonding levels are vacant. The stability will be referred to as a relative one here, since it implies comparison of systems with the same energy gaps, i.e. PMDs and HPs absorbing in the same spectral region. This approach is of most importance concerning the practical applications of these compounds as coloured substances. Molecules with their highest occupied molecular orbital (HOMO) disposed rather high are characterized by a marked reactivity to electrophiles and oxidizing agents; and vice versa, the LPMSs, which have their lowest unoccupied molecular orbital (LUMO) disposed rather low, are sensitive to nucleophiles and reducing agents. From this point of view, the maximum relative stability is typical of compounds having their frontier levels symmetrically disposed with respect to Fermi level ε_F, i.e. to the non-bonding π-level.

For the relative stability to be estimated quantitatively though very approximately, the parameter ϕ_0 is quite appropriate, since it is related to the energies of HOMO (ε'_g) and LUMO (ε'_e):[1]

$$\phi_0 = 90^\circ \frac{\varepsilon'_e - \varepsilon_F}{\varepsilon_e - \varepsilon_g}$$

or

$$\phi_0 = 90^\circ \frac{x_e}{x_e - x_g} \tag{1}$$

where $x_i = (\varepsilon'_i - \alpha)/\beta$, $\varepsilon_F \equiv \alpha$ is the energy of the Fermi level or the Coulomb integral of the carbon atom in terms of the Hückel model, and β is the resonance integral.

A study of a vinylogous series of model LPMSs with arbitrary EGs shows that with lengthening of the PC, the electron donor ability ϕ_0 (see eqns (1)) tends to a constant value, depending only on the type of compound and the topology of EGs.[1] By taking account of the Kupmans theorem and the linear relation between the transition energy E_{max} and the calculated energy gap,[5] the electron donor ability can be determined from experimental data. Equation (1) can then be rewritten:

$$\phi_0 = 90^\circ \frac{[-(IP - E_{max}) - \alpha]}{E_{max}} \tag{2}$$

where IP is the ionization potential for an electron on the HOMO level. The energy of the Fermi level was found by the authors from photoelectron and UV spectra. According to parity theorem,[5] the levels of even-alternant hydrocarbons are symmetric relative to the Fermi level, and hence the parameter ϕ_0 for them is 45°. For acenes and helicenes[6] it is found that $\alpha \cong -5{\cdot}60\,\text{eV}$, and much the same values have been obtained for other polycyclic aromatic compounds using spectral data previously reported.[7] This is also typified by the α,ω-diphenylpolyene vinylogous series $Ph(CH{=}CH)_nPh$, ($n = 1$–6); photoelectron and UV spectra[8] reveal that on lengthening PC, the values IP and E_{max} both diminish, and the value $(IP - E_{max}/2)$ characterizing the Fermi level energy remains constant for the whole series.

In addition, it is apparent that the redox potentials also change together with the parameter ϕ_0, giving unambiguous experimental evidence for its actuality.

For systems having close electron shells, the parameter ϕ_0 has only positive values lying within the interval:

$$0^\circ \leq \phi_0 \leq 90^\circ \tag{3}$$

An LPMS can be regarded as a relatively stable one provided that its value ϕ_0 satisfies the above inqualities.

It was shown previously[1] that the parameter ϕ_0 is directly related to the zeroth-order topological index Φ_0 of EGs calculated through the free terms of characteristic polynomials for the EG and its residue with one atom removed.[1-3] Although in principle LPMS molecules can be divided into the PC and EGs arbitrarily, the division is usually effected so that Φ_0 meets the condition: $0^\circ \leq \Phi_0 \leq 90^\circ$.[2,3] Using the equal-bond approximation, one can obtain the following expressions for symmetric PMD and HP:

$$\Phi_0 = \lim_{m \to \infty} \phi_0 \quad \text{(PMD)} \tag{4}$$

$$\Phi_0 = \lim_{m \to \infty} \phi_0 \pm 45^\circ \quad \text{(HP)} \tag{5}$$

(The sign in eqn (5) is positive if HOMO numbers coincide for PMD and HP, and negative if it is not the case.) Equations (4) and (5) indicate that PMD and HP with the same EGs should differ substantially in the positions of their frontier levels and hence in their relative stability.

Hereafter we consider in detail the effect of chain length and EG topology on LPMS stability, based on eqns (3)–(5).

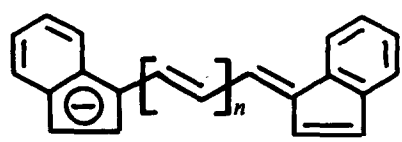
3 DISCUSSION

3.1 Symmetric polymethines

Unsubstituted polymethines containing N π-centres can exist in two forms: electron-excessive (**2**) and electron-deficient (**3**) with $(N+1)$ and $(N-1)$ π-electrons, respectively.

$$H_2C{=}CH{-}(CH{=}CH)_n{-}CH_2^- \qquad H_2C{=}CH{-}(CH{=}CH)_n{-}CH_2^+$$
2 **3**

Both forms have a non-bonding level, filled for the electron-excessive form ($x_g = 0$) and vacant for the electron-deficient form ($x_e = 0$). On going from one form to the other, the HOMO number changes by 1, accompanied by a 90°-change of the parameter ϕ_0. When end groups are introduced into the PMD molecule, the levels are shifted so that one of the forms becomes stabilized and the other becomes destabilized (since its electron donor ability no longer meets condition (3)). If PMD contains EGs with $\Phi_0 = 45°$, then their frontier levels are symmetric with respect to the Fermi level, and $\phi_0 = 45°$ (see eqn (4)). With lengthening PC, the LUMO energy decreases while the HOMO energy increases, these levels however remaining symmetric relative to the Fermi level. As an example, the energies of frontier levels for dyes **4** with their EGs having $\Phi_0 = 45°$ are presented in Fig. 1.



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It is apparent that as the PC lengthens, the HOMO level shifts upwards, which implies decrease in the absolute stability. At the same time, the relative stability is not affected, keeping maximum among the compounds with the same energy gap.

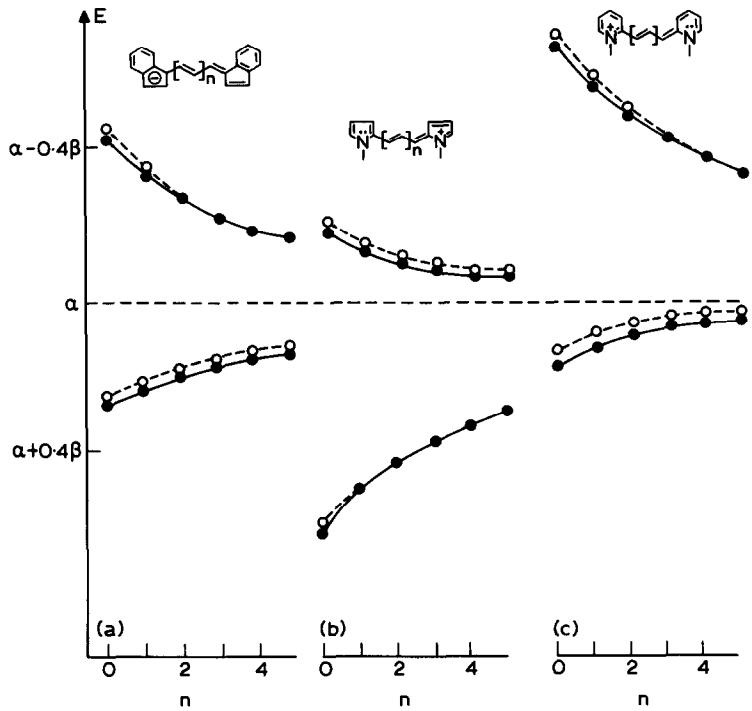


Fig. 1. Frontier level energies for polymethines calculated in standard HMO approximation (———) and with resonance integral self-consistency (– – – –) versus chain length.

It should be noted that eqns (3)–(5) were derived in terms of an ideal polymethinic model, with C—C bonds equalized, and in applying these formulae to real molecules allowance should be made for possible deviations from the model conditions. PMDs are known to have C—C bonds in their PC equalized, in contrast to polyenes exhibiting bond alternation.[9,10] Calculations of PMDs by the CNDO/2 method, involving geometry optimization, gives bond lengths only slightly differing, all approximating to 1·40 Å.[11–13] There is also experimental evidence for the equalization of C—C bonds in PC of PMDs.[9,13–15] Thus, the equal-bond model fits for polymethines. However, it is necessary to take account of a pronounced alternation of atomic charges in their PC,[9–15] which influences the orbital parameter of the carbon atoms. In the Hückel approximation this effect corresponds to changing the Coulomb integrals of the carbon atoms: their resultant values can be presented as $\alpha_p = \alpha + \delta\alpha_p$, where $\delta\alpha_p = h_p\beta$ is a correction index, p denoting the atomic number in the PC. By assuming h_p to be rather small, it is possible to apply perturbation theory and determine the changes in level energies: $\delta\varepsilon_i = C_{ip}^2 h_p\beta$ (C_{ip} is the coefficient of the ith MO on the pth atom). The change in electron donor ability caused by the changing

positions of frontier levels can be estimated through its derivatives with respect to the Coulomb integrals of chain atoms:

$$\delta\phi_0 = \sum_p \frac{\partial\phi_0}{\partial h_p} h_p\beta$$

$$\frac{\partial\phi_0}{\partial h_p} = a\left[C_{ep}^2\left(\frac{\pi}{2} - \phi_0\right) + C_{gp}^2\phi_0\right] \tag{6}$$

where $a = 1/(x_e - x_g)$.

For systems with a close electron shell satisfying the condition (3), the derivative $\partial\phi_0/\partial h_p$ is always positive. Therefore, the sign of correction to the electron donor ability depends only on the change or sign of h_p in the Coulomb integral. If the PC is rather long, it is possible to take the limiting values for C_{ip}: $C_{ip}^2 \to 1/(n+L)$ and $a = (n+L)/\pi$, where n is the number of vinylene groups in the PC, and L is the first-order topological index of the EG referred to as EG effective length.[1-4] Thus, in an approximate treatment, the derivative $\partial\phi_0/\partial h_p$ is only slightly affected by chain length.

According to eqn (6), the correction δ_{γ_0} depends on electron donor ability alone. First, we can consider the case of the middle electron donor ability ($\phi_0 = 45°$) resulting from introduction of EGs with $\Phi_0 = 45°$ into the PMD molecule. Under this condition, the so-called ideal polymethine state is realized.[9,10,12] All C—C bond orders in the PC are equalized both in the ground state S_0 and in the first excited state S_1. The charges on any neighbouring atoms are equal in absolute value and opposite in sign: $z_p = -z_{p+1}$. The derivative $\partial\phi_0/\partial h_p$ can be found as follows:

$$\partial\phi_0/\partial h_p = \pi \cdot a(C_{ep}^2 + C_{gp}^2)/4 \tag{7}$$

Providing there is a long chain in the LPMS, the value $\partial\phi_0/\partial h_p$ is constant, due to the equality: $C_{ep}^2 + C_{gp}^2 \cong 1/(n+L)$. It is also evident that $h_p = -h_{p+1}$, since the charge absolute values for the neighbouring atoms are the same. Then the contributions of neighbouring atoms to the sum in eqn (6) are mutually compensated, and the total charge of electron donor ability finally vanishes on the summation over the whole chain: $\delta\phi_0 \to 0°$.

To exemplify this, we can consider the calculation data for polymethines **5** having their EGs simulated by heteroatoms X with Hückel parameters: $\alpha_X = \alpha + h_X\beta$; $\beta_{CX} = \eta_{CX}\beta$.

$$[X{=}CH{-}(CH{=}CH)_n{-}\ddot{X}]^+$$

5

In this case the topological parameter Φ_0 depends only on the orbital parameters of the heteroatom X: $\Phi_0 = a\tan(\eta^2/h)$. Calculation involving

Coulomb integrals which are self-consistent relative to the atomic charges in the PC ($n = 1$–7) enables us to conclude that at $\Phi_0 = 45°$ ($h = \eta = 1$), one can neglect the changes in electron donor ability caused by the charge alternation: $\delta\phi_0 \cong 2°$. Thus, the homogeneous alternation has a slight effect on the relative stability of quasi-ideal polymethines.

For nuclei of a more complex structure, the correction $\delta\phi_0$ resulting from the charge alternation in the PC can increase somewhat. For instance, consideration of the Coulomb integral self-consistency, relative to the charges in the chain of dyes **3**, results in the HOMO increasing to some extent, whereas LUMO remains practically unchanged (see Fig. 1(a)). The corresponding change in electron donor ability is much the same for the whole series: $\delta\phi_0 \cong 4°$, as expected from analysis of eqn (7).

When the electron donor ability ϕ_0 deviates from its middle value the charge alternation is no longer homogeneous. In the case of the nuclei having high electron donor ability (with $\Phi_0 > 45°$) the negative charges in the PC predominate over the positive charges; the opposite effect is observed if $\Phi_0 < 45°$. Thus, the sign of the correction is different for high- and low-electron-donor nuclei introduced into the PMD.

When an electron donor ability of a PMD is minimum, the derivative depends only upon the HOMO coefficients:

$$\partial\phi_0/\partial h_p = \pi \cdot a \cdot C_{ep}^2/2 \tag{8}$$

The unsubstituted polymethine cations **3** serve as a specific illustration of this regularity. Their HOMO is a non-bonding MO and has its non-zero coefficients only in odd positions: $C_{ep}^2 = 1/(2n+4)$. The positive charges on odd atoms are equal to $1/(n+2)$ and, correspondingly, the corrections to their Coulomb integrals $h_p\beta$ are negative. It can then be concluded that $\delta\phi_0 < 0°$, i.e. the dependence of the atomic orbital parameters on the charge alternation results in a lowering of electron donor ability, so that both frontier levels fall below the Fermi level; this leads to $\phi_0 < 0°$ and an even greater destabilization of the PMD molecule. The calculations in the Hückel approximation, with self-consistent Coulomb integrals, show that both frontier levels shift, giving finally: $\phi_0 = -14° - -13°$ (with n varied from 0 to 6).

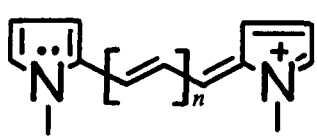
In the case of maximum electron donor ability ($\phi_0 = 90°$), its derivative is determined by the LUMO coefficients:

$$\partial\phi_0/\partial h_p = \pi \cdot a \cdot C_{gp}^2/2 \tag{9}$$

This is the case for polymethine anions **2**. Being a non-bonding MO, LUMO has its non-zero coefficients only on odd atoms charged negatively, so that $h_p\beta > 0$. Consequently, $\delta\phi_0 < 0°$, i.e. the electron donor ability decreases under the influence of charge alternation. The calculation with

self-consistent Coulomb integrals shows that both frontier levels rise and the electron donor ability ϕ_0 is equal to 103–104° (at n varied from 0 to 6).

If the EGs have a medium (non-extreme) value of the topological index Φ_0, the effect of charge alternation in the PC on the electron donor ability is not so pronounced as in the above cases. Figures 1(b) and (c) show the frontier levels of the vinylogous dye series **6** and **7** and it is evident that, of the two frontier levels, the one closer to the Fermi level is more sensitive to the alternation effect. As a result, the electron donor ability of dyes **7**, which have rather basic nuclei ($\Phi_0 = 76°$), increases further ($\delta\phi_0 \approx 4$–$8°$ at $n = 0$–6), whereas that of dyes **6** containing nuclei of low basicity ($\Phi_0 = 19°$) decreases ($\delta\phi_0 = 3$–$5°$).



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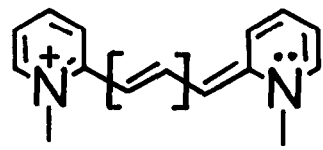

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Thus, consideration of the influence of π-electron distribution on orbital parameters leads to growing asymmetry in the disposition of the frontier level with respect to the Fermi level, i.e. a decrease in the relative stability of the polymethines.

As follows from eqns (1), on going from one form of long-chained PMD to another, the electron donor ability changes by 90°. The calculated values ϕ_0 for both forms of model PMD with nuclei of various basicity (see Table 1)

TABLE 1

Electron Donor Ability (in degrees) of Model Dyes: $[X—(CH—CH)_4—CH—X]^z$

α_X	*Form*	z	*STD*		*SC*		$\delta\phi_0$
			ϕ_0	Δ	ϕ_0	Δ	
$\alpha_X = \alpha + 0{\cdot}2\beta$	EE	+1	79	—	85	—	6
	ED	+3	−11	90	−22	107	−11
$\alpha_X = \alpha - 0{\cdot}2\beta$	EE	−3	101	—	112	—	11
	ED	−1	11	90	5	117	−6
$\alpha_X = \alpha + 2\beta$	EE	+1	27	—	17	—	−10
	ED	+3	−66	93	−93	110	−26
$\alpha_X = \alpha - 2\beta$	EE	−3	157	—	183	—	26
	ED	−1	63	94	73	110	10
$\alpha_X = \alpha$	EE	−1	90	—	103	—	13
	ED	+1	0	90	−13	116	−13

STD, Calculation in standard HMO approximation; SC, calculation with self-consistency of Coulomb integrals; Δ, electron donor ability difference of two forms; $\delta\phi_0 = \phi_0$ (STD) $- \phi_0$ (SC); EE, electron-excessive; ED, electron-deficient.

confirm that this rule is essentially valid. However, if charge alternation is taken into account, the difference in electron donor ability between two PMD forms is found to be greater than 90°, reaching its maximum for unsubstituted PMD ($X{=}CH_2$). Thus, an essential conclusion can be made: only one PMD form is stable. At the same time, for cases of extreme donor ability, with one of the frontier levels being non-bonding, two low-stability forms are possible. Symmetric PMDs are, in fact, known to exist in the single ionic form,[16-18] whereas α,ω-diphenylpolymethines exist in the rather unstable cationic and anionic forms.[19]

Nevertheless, it should be noted that more stringent analysis of PMD stability requires consideration of some other factors, in particular the dependence of the π-electron Fermi level on the total charge of the polymethine system, etc.

3.2 Symmetric polyenes

Three forms are possible for unsubstituted polyenes containing N π-centres: viz. electron-balanced **8** with N electrons, electron-excessive **9** with $(N+2)$ electrons, and electron-deficient **10** with $(N-2)$ electrons.

$$H_2C{=}CH{-}(CH{=}CH)_n{-}CH{=}CH_2$$
8

$$H_2C^-{-}(CH{=}CH)_{n+1}{-}CH_2^-$$
9

$$H_2^+{-}(CH{=}CH)_{n+1}{-}CH_2^+$$
10

The electron-balanced form has its frontier levels disposed symmetrically relative to the Fermi level, i.e. $\phi_0 = 45°$. The same is characteristic of polyenes containing EGs with the extreme Φ_0 values, i.e. 0° or 90° (see eqn (5)). Provided such level disposition exists, the so-called ideal polyenic state is realized, and the disposition is distinguished by π-uncharged carbon atoms and the most pronounced π-bond order alternation in the PC.[9,10] Such systems are the most stable ones among polyenes with the same energy gap.

In terms of the equal-bond model, two other polyenic forms should be unstable since their values ϕ_0 differ by 90° from that for the electron-balanced form; as a result, both frontier levels are bonding in the electron-deficient form **10** or antibonding in the electron-excessive form **9** (see eqns (1)).

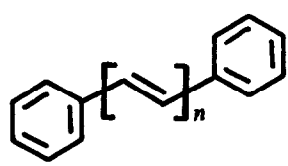
If EGs with some other Φ_0 values are introduced into the HP, the symmetric frontier level disposition is broken for the electron-balanced

form, hence lowering the relative stability of the molecule. According to formulae (3) and (5), only one polyenic form should be stable, providing an equal-bond model. However, the special case is $\Phi_0 = 45°$ for introduced EGs, when two polyenic forms having $\phi_0 = 0°$ and 90° are stable to the same degree. Nevertheless, it is essential that symmetric polyenes exhibit notable C—C bond length alternation, stabilizing bonding MOs and destabilizing non-bonding ones.[20-22] The bond alternation necessarily implies varying the resonance integrals when calculating HPs. Presenting these parameters as $\eta_{pq}\beta$, and taking η_{pq} as the variation parameter, with rather small changes $\delta\eta_{pq}$ it is possible to estimate the change in electron donor ability by means of its derivatives with respect to η_{pq}:

$$\delta\phi_0 = \sum_{p,q} \frac{\partial\phi_0}{\partial\eta_{pq}} \delta\eta_{pq}$$

$$\frac{\partial\phi_0}{\partial\eta_{pq}} = -2a\left[C_{ep}C_{eq}\left(\frac{\pi}{2} - \phi_0\right) + C_{gp}C_{gq}\phi_0\right] \tag{10}$$

It follows that the derivative $\partial\phi_0/\partial\eta$ as does $\partial\phi_0/\partial h_p$ depends on the electron donor ability being almost indifferent to the chain length. It practically vanishes for polyenes of middle electron donor ability $\phi_0 = 45°$. Consequently, the resonance integral alternation causes no changes in the electron donor ability ϕ_0 although the frontier levels taken by themselves are shifted substantially. As an illustration, we can consider the frontier level energies for the α,ω-diphenylpolyene vinylogous series **11** (see Fig. 2(a)).



11

It can be seen that taking account of bond alternation, and thus using the resonance integral self-consistency with respect to bond orders, the energy gap, although increased, maintains a symmetric disposition relative to the Fermi level. Therefore, ϕ_0 remains at 45°, irrespective of alternation amplitude and chain length. According to eqn (5), the frontier levels behave likewise for any HP containing EGs with Φ_0 equal to 0° or 90°. Thus, among HPs with the same energy gap, the most stable are those containing either EGs with the extreme values of the topological index Φ_0, or no EGs at all.

Electron donor ability is extremely sensitive to bond alternation if the HP contains nuclei of middle basicity ($\Phi_0 = 45°$). The parameter ϕ_0 then takes

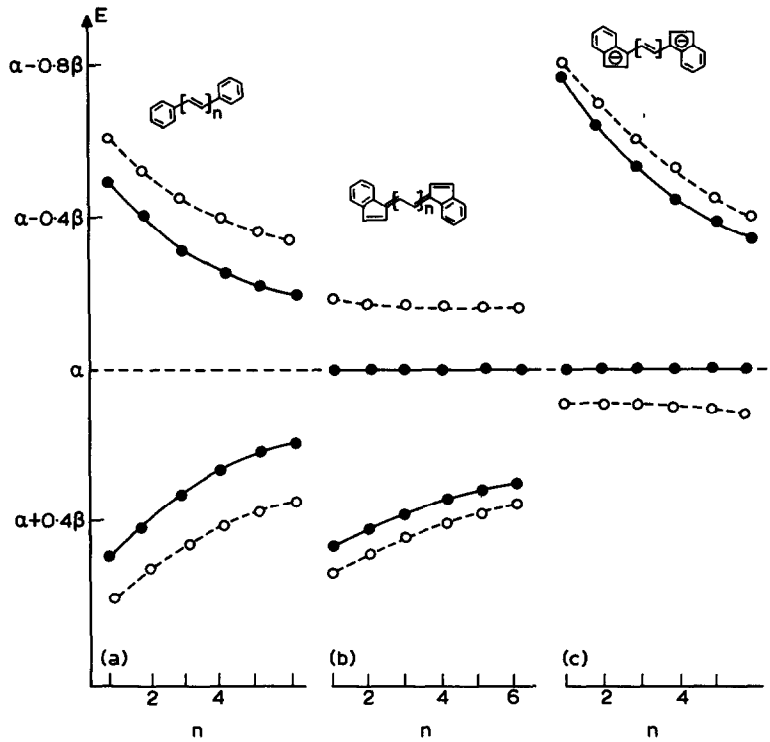


Fig. 2. Frontier level energies for polyenes calculated in standard HMO approximation (———) and with resonance integral self-consistency (– – – –) versus chain length.

on the extreme values, 0° or 90°, depending on the polyene form, and one of the frontier levels becomes non-bonding (see eqn (5)). We can exemplify using two possible cases, (a) and (b), as follows:

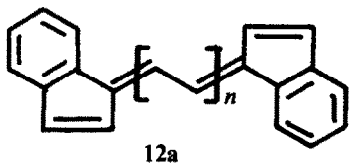
Case (a). LUMO is a non-bonding MO; $\phi_0 = 0°$: in this case the derivative depends only on LUMO coefficients:

$$\partial\phi_0/\partial\eta_{pq} = -2a\pi C_{ep}C_{eq} \tag{11}$$

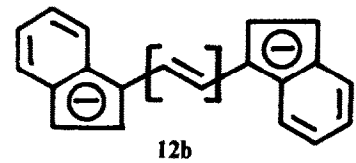
For a bond with increased order, the resonance integral should be increased in absolute value: $\partial\eta > 0$. For the pth and the qth atoms, having their LUMO coefficients opposite in sign, we obtain: $\partial\phi_0/\partial\eta_{pq} < 0$, and $\delta\phi_0 > 0$, in accord with eqn (10). For a bond with a lowered order, it is necessary to decrease the absolute value of its resonance integral. Nevertheless, since the signs of the LUMO coefficients on the neighbouring atoms are the same, $\partial\phi_0/\partial\eta_{pq}$ is positive, and $\delta\phi_0 > 0$, as in the above case. Thus, bond alternation in low-electron donor HPs results in an increase in the electron donor ability of the molecule to rise.

As further confirmation, the frontier level positions for the polyenic

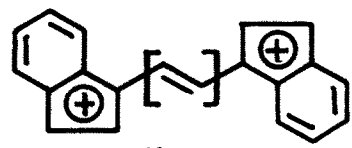
vinylogous series **12a** in the electron-balanced form are presented in Fig. 2(b).



12a



12b



12c

It can be seen that the resonance integral self-consistency causes an essential change in level energies, the LUMO undergoing the stronger shift as the MO is disposed closer to the Fermi level. The resultant electron donor ability increases: $\phi_0 = 23$–$30°$ (at $n = 1$–6), and this type of polyenic form should be a relatively stable one.

Case (b). HOMO is a non-bonding orbital; $\phi_0 = 90°$; here, the derivative depends only on HOMO coefficients:

$$\partial\phi_0/\partial\eta_{pq} = -2a\pi C_{gp}C_{gq} \tag{12}$$

As the product of HOMO coefficients on any two neighbouring atoms in the PC ($C_{gp}C_{gq}$) is opposite in sign to that of LUMO, the derivatives $\partial\phi_0/\partial\eta_{pq}$ for all bonds should also change their signs relatively to case (a), taking on negative values. Thus, the electron donor ability decreases ($\delta\phi_0 < 0$) under the influence of bond alternation.

The situation is typified by the polyenic electron-excessive form **12b** having the maximum ϕ_0 value. It is apparent from Fig. 2(c) that the resonance integral self-consistency results in the repulsion of the calculated frontier levels, but unlike the previous case HOMO is shifted more than LUMO, thus lowering the electron donor ability: $\phi_0 = 71$–$81°$ (at $n = 1$–6). It should be noted that on lengthening the PC, the correction $\delta\phi_0$ grows from 9° at $n = 1$ to 19° at $n = 6$. This effect of bond alternation on frontier level energies also permits the second polyenic form **12b** to exist and it is relatively stable. The third electron-difficient form **12c** is unstable since its electron donor ability $\phi_0 = -90°$ does not meet condition (3), and the resonance integral self-consistency implies the unsymmetric solution.

The polyenes **13** containing realistic, but simple, nuclei X were also studied in more detail:

$$[X—(CH—CH)_n—X]^z$$

13

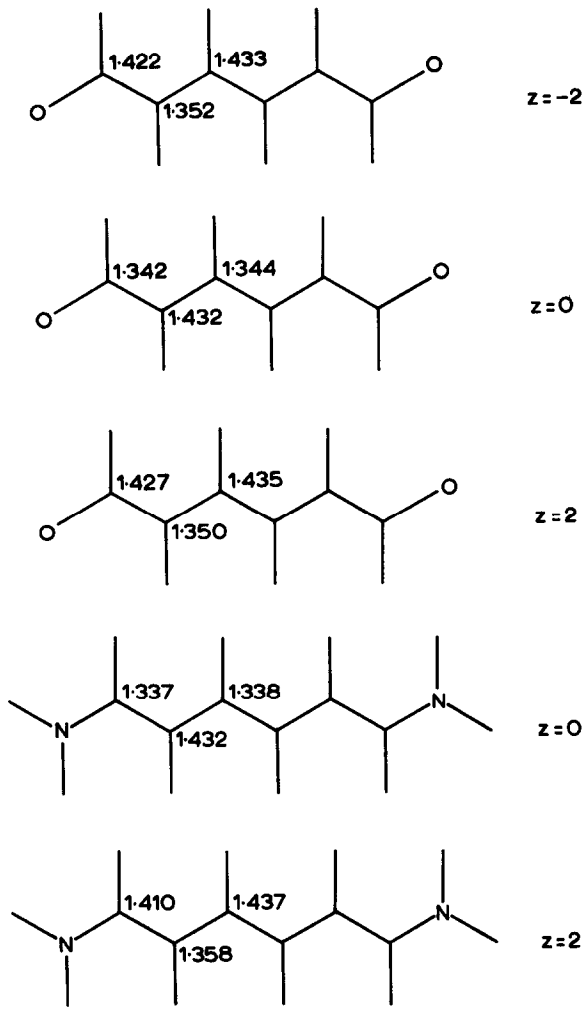


Fig. 3. Optmized C—C bond lengths (in Å) of polyenes **13** calculated in CNDO/2 approximation.

By means of the CNDO/2 method, the equilibrium geometry was calculated for diketones (X = —CH—O) and diaminopolyenes (X = —CH—NH_2) in various forms. It was found that for high-basic diketones, all three forms are relatively stable and for middle-basic diaminopolyenes, only two forms, the electron-balanced and electron-excessive ones, should exist (the electron-deficient form permits no self-consistent symmetric solution). Figure 3 demonstrates the calculated optimized C—C bonds in the PC. It is essential that on going from one form to another, the longer bonds are replaced by the shorter ones, and vice versa. The amplitude of bond length alternation is much the same for the considered molecules: $\Delta l = 0{\cdot}05$–$0{\cdot}10$ Å,

TABLE 2

Electron Donor Ability (in degrees) of Model Polyenes [X—CH—(CH—CH)$_5$—CH—X]^z, Calculated in HMO Approximation with Alternating Resonance Integrals: $\beta_d = 1{\cdot}15\beta$, $\beta_s = 0{\cdot}85\beta$

α_X	Φ_0	*Form*	*STD*		*SC*		$\delta\phi_0$
			ϕ_0	Δ	ϕ_0	Δ	
$\alpha_X = \alpha$	0	$N+2$	101	—	91	—	−10
		N	45	56	45	46	0
		$N-2$	−11	56	−1	46	10
$\alpha_X = \alpha + 6\beta$	9	$N+2$	47	—	48	—	1
		N	2	45	12	36	10
		$N-2$	−181	183	Asymm.	—	—
$\alpha_X = \alpha + 4\beta$	14	$N+2$	48	—	49	—	1
		N	8	40	17	32	9
		$N-2$	−175	183	Asymm.	—	—
$\alpha_X = \alpha + 2\beta$	27	$N+2$	52	—	53	—	1
		N	20	32	27	26	7
		$N-2$	−156	176	Asymm.	—	—
$\alpha_X = \alpha + 0{\cdot}5\beta$	63	$N+2$	71	—	75	—	4
		N	37	34	39	36	2
		$N-2$	−64	101	Asymm.	—	—
$\alpha_X = \alpha + 0{\cdot}2\beta$	79	$N+2$	86	—	92	—	6
		N	42	44	43	49	1
		$N-2$	−29	71	Asymm.	—	—

SC, Calculation with self-consistency of resonance integrals; Asymm., asymmetrical.

so that short bonds are 1·33–1·36 Å while long ones are 1·42–1·44 Å, being rather slightly dependent on the electron donor ability and the total polyene charge, i.e. on the polyenic form. As was shown for the vinylogous polyenes **13**, the lengths of C—C bonds in the PC are practically independent of the number n of vinylene groups in the PC.

Thus, for the approximate estimates to be effected, it is possible to carry out the calculation of polyenes involving only two values of resonance integrals, one for lowered and the other for increased bond order, equal to $(1-t)\beta$ and $(1+t)\beta$, respectively (β denoted the standard resonance integral for C—C bond in the PC, 1·39 Å long, and $t = 0{\cdot}15$ is the acceptable correction for the ascertained alternation degree).

The electron donor abilities for polyenes **13** were calculated, with the varied resonance integrals (see Table 2). It is apparent that in the general case, two forms are stable, and when Φ_0 assumes its extreme values (at X = —CH_2), three forms exist. Transition from one stable form to another is accompanied by change in electron donor ability, though much less than

90°, a value which is expected in terms of an equal-bond model. It also follows from Table 2 that the calculation with varied resonance integrals leads to rather small corrections $\delta\phi_0$.

The results obtained show the polymethines to have, as a rule, a single stable form, which is due to bond order equalization in their PC. For polyenes, at least two forms should exist, because of notable bond order alternation. On going from one form to the other, the position of the long and short bonds within the PC changes.

Introduction of EGs stabilizes PMDs, the most stable being those with nuclei having middle electron donor ability ($\Phi_0 = 45°$). In contrast to these, the most stable polyenes contain nuclei with the extreme values of this topological parameter ($\Phi_0 = 0°$ or 90°); in this case all three forms are relatively stable.

REFERENCES

1. Kachkovski, A. D., Dyadyusha, G. G. & Dekhtyar, M. L., *Dyes and Pigments*, **15** (1991) 191.
2. Kachkovski, A. D., *Structure and Colour of Polymethine Dyes.* Naukova Dumka, Kiev, 1989 (in Russian).
3. Dyadyusha, G. G., Kachkovski, A. D. & Dekhtyar, M. L., *J. Mol. Struct.*, **217** (1990) 195.
4. Dyadyusha, G. G. & Kachkovski, A. D., *J. Signal AM*, **13** (1985) 95.
5. Streitwieser, A., *Molecular Orbital Theory.* John Wiley, New York, 1963.
6. Olenband, S. & Schmidt, W., *J. Am. Chem. Soc.*, **97** (1975) 6633.
7. Clar, E. & Schmidt, W., *Tetrahedron*, **31** (1975) 2263.
8. Hudson, P. S., Ridyard, I. & Neil, A., *J. Am. Chem. Soc.*, **98** (1976) 1126.
9. Dähne, S., *Z. Chem.*, **10** (1970) 168.
10. Dähne, S., *Science*, **199** (1978) 4334.
11. Steiger, Th. & Radeglia, R., *J. Prakt. Chem.*, **326** (1984) 145.
12. Dyadyusha, G. G., Repyakh, I. V. & Kachkovski, A. D., *Theoret. Experim. Khimia*, **20** (1984) 398 (in Russian).
13. Slominski, Yu. L., Popov, S. V., Repyakh, I. V. *et al. Theoret. Eksperim. Khimia*, **23** (1987) 687.
14. Kulpe, S., Zedler, A., Dähne, S. & Nolte, K.-D., *J. Prakt. Chem.*, **315** (1973) 865.
15. Zeimer, B. & Kulpe, S., *J. Prakt. Chem.*, **317** (1975) 199.
16. Brooker, L. G. S., *Rev. Mod. Phys.*, **14** (1942) 275.
17. Platt, J. R., *J. Chem. Phys.*, **25** (1956) 80.
18. Kiprianov, A. I., *Colour and Structure of Cyanine Dyes.* Naukova Dumka, Kiev, 1979 (in Russian).
19. Hünig, S., In *Optische Anregung organischer Systeme. II Intern.* Farbensymp. Chemie, Weinhein, 1966, p. 184.
20. Schulten, K., Ohmine, I. & Karplus, M., *J. Chem. Phys.*, **64** (1976) 4422.
21. Soos, Z. G. & Ducasse, L. R., *J. Chem. Phys.*, **78** (1983) 4092.
22. Hudson, B. & Kohler, B., *Synth. Methals*, **9** (1984) 241.