Dyes and Pigments **15** (1991) 191–202

Electronic Properties of Polymethine Compounds: 1. Frontier Electron Levels and Electron Donor Ability

A. D. Kachkovski, G. G. Dyadyusha & M. L. Dekhtyar'

Institute of Organic Chemistry, Academy of Sciences of the Ukrainian SSR,
252660 Kiev-94, Murmanskaya 5, USSR

(Received 15 January 1990; accepted 10 April 1990)

ABSTRACT

The relation between frontier MOs (FMOs) and chemical structure of linear polymethine compounds (PMCs) is investigated. A new parameter, the electron donor ability ϕ_0 *of the PMC, is proposed in order to characterize the frontier level disposition in respect to the Fermi level. Based on FMOs' symmetry and molecular function periodicity, a classification of PMCs is developed, viz. polyenes of class A, polymethines of class A, polyenes of class B and polymethines of class B. A relationship between the electron donor ability* ϕ_0 *and the topological indices of the end-groups was observed for polymethine dyes and hetarylpolyenes; moving from polymethines to polyenes with the same end-groups is accompanied by an essential shifting up or down of frontier levels. Theoretical results are illustrated by experimental data.*

1 INTRODUCTION

Several physical and chemical properties of polymethine compounds (PMCs) are determined by the position of their frontier levels (FLs), i.e. the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO). For instance, the ability of a dye to sensitize photomaterials is associated, as a rule, with the FLs' disposition in the sensitizer molecule with respect to the conduction band minimum and the valence band maximum.[1,2] It is the disposition of FLs which determines the donor properties of the dye and the reactivity of its polymethine chain.[3]

Information about the electron levels can be obtained both experimentally (e.g. by measuring ionization potentials, electron affinities, polarographic potentials, transition energies, etc.) and theoretically (by means of quantum chemical calculation).[4]

FL disposition depends mainly upon the nature of end-groups (EGs). To estimate EG influence correctly, one can apply the topological parameter Φ_0.[5-8] This parameter characterizes the relative disposition of FLs and the energy level of a non-bonded $2p_z$-electron of a carbon atom, i.e. the Fermi level (α). The index Φ_0 is strictly related to the topological properties of the dye molecule. This present paper utilizes this parameter in a study of the relation between the FL disposition in PMCs and the chemical structure of their EGs.

2 QUANTUM CHEMICAL MODEL OF POLYMETHINE COMPOUNDS

The general form of a PMC can be represented as follows:

$$\overset{\cdots\cdots\cdots\cdots\cdots\cdots}{G_1{-}(CH)_m{-}G_2}$$

I

with the EGs G_1 and G_2 of an arbitrary chemical structure conjugated with the polymethine chain (PC). Such systems (**I**) can exist as neutral molecules [reduced forms of hetarylpolyenes (HPs) or merocyanines], cations or anions [polymethine dyes (PMD) or dications (oxidized form of HPs)]. We consider here only compounds with a closed electron shell.

It should be mentioned that there are no limitations for compounds **I** concerning the parity of m or of the method of partitioning of the polymethine chromophore. The bonding between EGs and PC can be chosen arbitrarily. That is to say, whatever section of PC is attached to an EG, all the results obtained are similar. Within the Hückel MO approximation, all interactions between non-neighbouring atoms are neglected and the Coulomb and resonance integrals are equal for all the atoms and bonds in the PC. Whilst such a model proves to be rather approximate when applied to polyenes, we nevertheless utilize it here since this approach enables us to deal with HPs and PMDs.

As far as the common PC is concerned ($G_1 = G_2 = CH_2$), an exact solution of the secular equations can be found, viz.

$$x_i = -2\cos\frac{k\pi}{N+1}$$

where $x_i = (\varepsilon_i - \alpha)/\beta$ is the energy of a level in β units with respect to α, N is the number of π-centres and k is a level number.

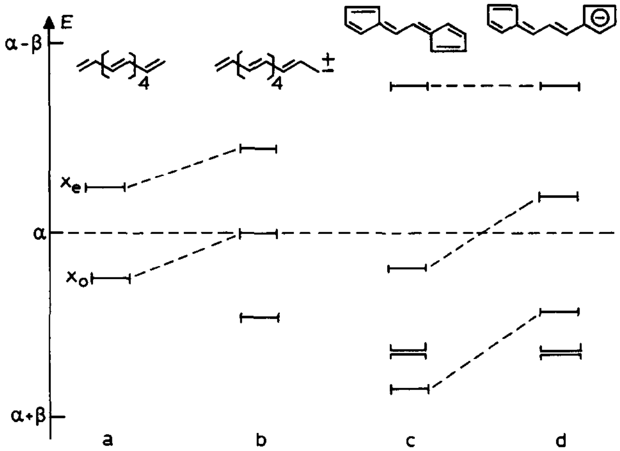


Fig. 1. Frontier levels of hetarylpolyenes (a, c) and polymethine dyes (b, d) with the same double bond number.

The disposition of FLs and levels neighbouring them for even and odd N is shown in Fig. 1(a) and (b). The general solution of secular equations for PMCs of type I concerning FLs and levels close to them was obtained in the approximation of the quasi-long PC, with accuracy up to n^{-1}:[5,6]

$$w_i = \frac{\phi + (m - 2i)(\pi/2)}{m - \theta} \qquad (1)$$

where $x = 2 \sin w$ and i is the number of the MO.

Parameters $\phi = \Phi_1 + \Phi_2$ and $\theta = -(L_1 + L_2)$ express the additivity of the EG influence on the PMC properties. Both parameters can be calculated using coefficients of characteristic polynomials.[5-9] The effective length L represents the lengthening of the free electron path caused by the EG. If a PC section is added to the EG, then the effective length L will increase by a value n, i.e. $L' = L + n$. The second topological parameter Φ characterizes the shift of the MO nodes due to EGs from their initial positions. The change in the electron level disposition due to the influence of the EGs in complex structures is shown in Fig. 1(c) and (d).

3 DISCUSSION

3.1 Electron donor ability of PMC

To represent the FL energies, it is necessary to know their absolute numbers i. However, we face here the problem of determining the number of positive and negative roots of the characteristic polynomial, which is not a trivial task in the general case.[9] Thus, it is necessary to use an intuitive treatment of the chemical structure of a compound.

If a molecule with a closed shell includes $N\pi$-centres, its HOMO number is normally equal to $N/2$ for even N and $(N \pm 1)/2$ for odd N. The effects of heteroatoms, with their electron pairs involved in π-conjugation, can result in an increase of HOMO number. In a general case we can replace $(m-2i)$ in eqn (1) by the variable k; $k=0, 1, -1$, for three w-roots with minimal absolute values.

Since $\sin w \simeq w$, where m is large, the analytical form for ε_k can be represented as

$$\varepsilon_0 = \alpha + \frac{2\phi}{L}\beta; \quad \varepsilon_{+1} = \alpha - \frac{2\phi - \pi}{L}\beta; \quad \varepsilon_{-1} = \alpha - \frac{2\phi + \pi}{L}\beta \tag{2}$$

where $L\,(= m + L_1 + L_2)$ is the total length of the chromophore expressed by the equivalent number of methine groups. Depending on the sign of ϕ, the orbital with ε_0 energy is HOMO ($\phi > 0$) or LUMO ($\phi < 0$). In the case of $\phi = 0$, this orbital is a non-bonding one. The minimal distance between levels is always $w = w_{-1} - w_0 = w_0 - w_{+1} = \pi/L$. Thus, one can obtain, for two neighbouring levels,

$$\phi_{m,i} = \pi\frac{w_i}{\Delta w} - (m - 2i)\frac{\pi}{2} \tag{3}$$

There is a good reason to determine the function $\phi_{m,i}$ within the range of 2π, so that a $4m$ 'quasi-period' can be introduced. For FLs, which are of special interest, eqn (3) can be represented in the following form:

$$\begin{aligned} \phi &= \pi\frac{w_0}{w_0 - w_{-1}} \quad \text{if } w_0 > 0 \\ \phi &= \pi\frac{w_{+1}}{w_{+1} - w_0} \quad \text{if } w_0 < 0 \end{aligned} \tag{4}$$

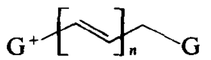
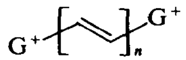
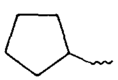
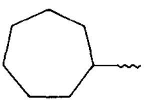
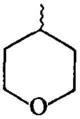
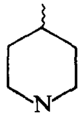
Let ε_e (LUMO energy) always be in the numerator and $\varepsilon_e - \varepsilon_0$ (the difference of LUMO and HOMO energies) the denominator. For additive components, Φ_1 and Φ_2 are equal in the case of a symmetrical PMC, and the parameter ϕ may be substituted by the halved value ϕ_0, which is more convenient, viz.

$$\phi_0 = \frac{\pi}{2}\frac{\varepsilon_e - \alpha}{\varepsilon_e - \varepsilon_0} \quad \text{or} \quad \phi_0 = \frac{\pi}{2}\frac{x_e}{x_e - x_0} \tag{5}$$

This parameter characterizes the position of the PMC energy gap in respect of the Fermi level. Considering the model of equivalent bonds, on lengthening the PC, the FLs tend to the Fermi level (Table 1), whilst their

TABLE 1

FL Energies Calculated in HMO Approximation, and Electron Donor Ability ϕ_0 of the Vinylogous Series of the PMC

G	n	*Polymethines*			*Polyenes*		
							
		x_e	x_0	ϕ_0 (*deg*)	x_e	x_0	ϕ_0 (*deg*)
	0	−0·356	0·618	33			
	1	−0·254	0·504	30	−0·835	0·186	74
	2	−0·198	0·420	29	−0·618	0·145	73
	3	−0·163	0·358	28	−0·492	0·119	72
$\Phi_0 = 27°$	4				−0·409	0·101	72
	5				−0·351	0·087	72
	0	−0·445	0·289	55			
	1	−0·386	0·216	58	−0·145	0·714	15
	2	−0·338	0·174	59	−0·120	0·548	16
	3	−0·299	0·145	61	−0·102	0·445	17
$\Phi_0 = 63°$	4	−0·267	0·125	61	−0·088	0·375	17
	5				−0·078	0·324	17
	0	−0·355	0·400	42			
	1	−0·305	0·298	46	−0·053	0·826	5
	2	−0·266	0·240	47	−0·044	0·625	6
	3	−0·235	0·201	48	−0·037	0·505	6
$\Phi_0 = 44°$	4	−0·210	0·173	49	−0·032	0·425	6
	5				−0·029	0·368	7
	0	−0·594	0·262	62			
	1	−0·504	0·190	65	−0·230	0·737	21
	2	−0·431	0·149	67	−0·184	0·552	22
	3	−0·373	0·123	68	−0·152	0·442	23
$\Phi_0 = 69°$	4	−0·327	0·105	68	−0·113	0·316	24

relative disposition in respect to this level ϕ_0 tends to a constant value which is characteristic of a specific polymethine or polyene vinylogous series. The parameter ϕ_0 depends only on the nature of the EG and the type of PMC (polymethine or polyene), if the EGs are the same. It is apparent from eqn (5) that as ϕ_0 increases the FLs gradually increase, accompanied by a decrease of both ionization potential and the polarographic oxidation potential, in contrast to the reduction potential. Thus, ϕ_0 increases with the PMC donor characteristics and may thus be used in the context of electron donor ability. In PMC with a stable electron shell, where $x_e > 0$ and $x_0 < 0$, the parameter ϕ_0 is always positive, lying within the interval (0°; 90°). Since the unsymmetrical PMCs can be considered as derivatives of the parent symmetrical PMC, ϕ_0 can also be used as characteristic of the FL disposition for unsymmetrical PMCs. Generally speaking, this parameter holds true for any molecule, and can be easily calculated through the energies of the FLs according to eqn (5).

3.2 Classification of PMCs

As far as eqn (3) is a 'quasi-periodic' function with its 'quasi-period' equal to $4m$, it is possible to distinguish four types of PMC and to propose a general classification of them.

It is known that linear conjugated systems can belong to two vinylogous series which have different spectral properties, i.e. polymethines and polyenes.[10] In the polymethines, lengthening of the PC leads to a linear shift of the first absorption maximum, viz. $\lambda_{\max,n} = \lambda_0 + Vn$, where n is the number of vinylene groups in the PC; $V \simeq 100\,\text{nm}$ is the so-called vinylene shift. In contrast, polyenes show a lowering of the vinylene shift with increase in PC length, the $\lambda_{\max,n}$ tending to a certain limiting value.

We now present a classification of the symmetric PMCs, based on the symmetry of their FLs, as previously proposed for PMDs.[11]

Considering the π-electron antisymmetry, symmetrical PMC can be considered as belonging to the C_{2v} point group; more precisely, HP molecules have C_2 symmetry. However, in HMO approximations which neglect non-neighbouring interactions, C_{2v} symmetry can be considered for both the PMD and the HP. The axis/plane of symmetry passes through the central bond/atom if m is even/odd. If the PC is rather long, HOMO and LUMO are of different symmetry types, a_2 and b_2, and the first excited state proves to be of ${}^1B_1$ symmetry, the x-axis going along the chain.

Let us consider four PMCs in which m varies from 1 to 3. No other limitations concern the EGs, with the exception of their chemical identity. In the case of odd values of m, EGs differ by the number of electrons, taking account of their classical structural formulae:

$$H_2N^+{=}CH{-}CH{=}CH{-}NH_2 \leftrightarrow H_2N{-}CH{=}CH{-}CH{=}N^+H_2$$
$$O{=}CH{-}CH{=}CH{-}O^- \leftrightarrow O^-{-}CH{=}CH{-}CH{=}O$$

Nonetheless, it should be kept in mind that the distribution of the electron density is even in a real molecule of a symmetric PMC.

Lengthening of the PC by one methine group results in an additional π-level in the energy spectrum of the PMC. If its energy is higher than that of the Fermi level and the PMC has a stable electron shell, then the number of occupied MOs and the symmetry of the FMOs stay unchanged.

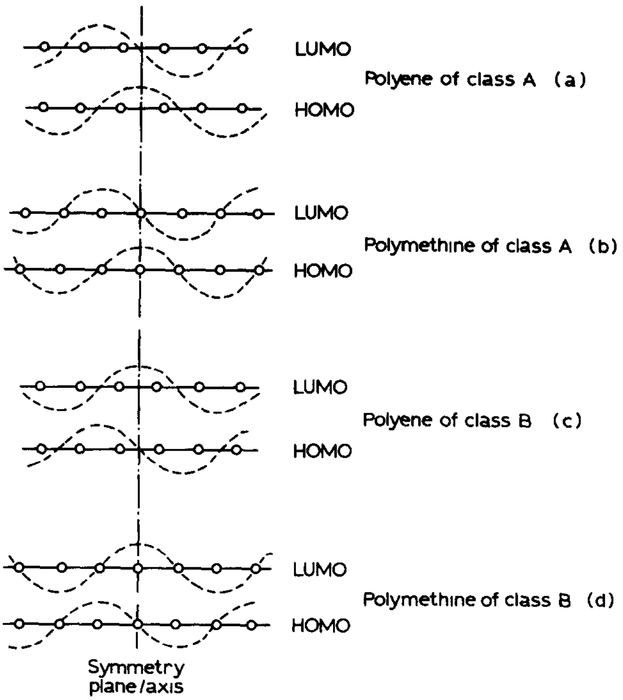


Fig. 2. Frontier MO fragments in the middle of the polymethine chain of a PMC.

Contrary to this, the additional binding level results in the addition of two more electrons in order to satisfy the criterion of the closed electron shell. The position of the additional level depends upon the nature of the EGs.

If the PC length increases by two methine groups and one electron pair is added, two more levels appear in the energy spectrum, viz. bonding and antibonding, the FLs exchanging by their symmetry types.

Therefore, four types of PMC exist. To classify them strictly we shall select the EGs so that LUMO is antisymmetrical at $m = 0$.

(1) Polyenes of class A: m is even and the plane of symmetry passes through the central bond. LUMO is antisymmetrical and HOMO is symmetrical. The shape of FMOs in the centre of the PC is shown in Fig. 2(a). HOMO coefficients on the central atoms are of the same sign and hence HOMO contributes positively to the order of the central bond. The latter is doubled if a PMC of this class is represented in the classical form:

$$G{=}CH{-}(CH{=}CH)_{2n}{-}CH{=}G \qquad G = G \text{ if } m = 0$$

(2) Polymethines of class A: m is odd and the symmetry plane passes through the central atom. LUMO is antisymmetrical and HOMO is

symmetrical (Fig. 2(b)). HOMO has its maximum on the central atom, which accounts for the high electron density localized here in the ground state. The central atom is conjugated with the EG in the donor form, as the classical structural formula indicates:

$$\mathrm{G^{+}{-}(CH{=}CH)_{\mathit{n}}{-}CH{=}(CH{-}CH)_{\mathit{n}}{=}G}$$

or

$$\mathrm{G^{+}{-}(CH{=}CH)_{2\mathit{n}}{-}CH{=}G}$$

(3) Polyenes of class B: *m* is even; LUMO is symmetrical and HOMO is antisymmetrical (Fig. 2(c)). The general formula is

$$\mathrm{G{-}(CH{=}CH)_{\mathit{n}}{-}(CH{=}CH)_{\mathit{n}}{-}G}$$

or

$$\mathrm{G{-}(CH{=}CH)_{2\mathit{n}}{-}G}$$

(4) Polymethines of class B: LUMO is symmetrical and HOMO is antisymmetrical (Fig. 2(d)). There is a node of HOMO on the central atom and consequently an electron deficiency in the ground state. The central atom is conjugated with the EG in the acceptor form:

$$\mathrm{G^{+}{-}(CH{=}CH)_{\mathit{n}}{-}CH{=}CH{-}CH{=}(CH{-}CH)_{\mathit{n}}{-}G}$$

or

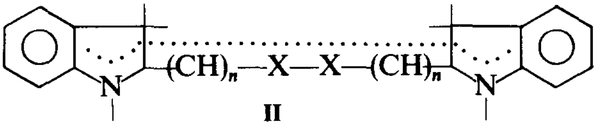
$$\mathrm{G^{+}{-}(CH{=}CH)_{2\mathit{n}+1}{-}CH{=}G}$$

Thus, polymethines and polyenes differ in respect of the location of the plane of symmetry and this is accompanied by differences in the electron density distribution over the atoms and bonds. The FMO coefficients are much the same for neighbouring atoms. They have opposite signs if the MO node lies on the bond between them. As with polymethines, the nodes of their FMOs in the middle part of the chain prove to be located on the atoms, and the orbital coefficients are negligibly small in these positions.

Classes A and B of polymethines and polyenes become distinguishable only provided that the PC is perturbed, this perturbation causing opposite spectral effects. It is possible to vary the electronegativity of the atoms, as well as the energy of their interaction. According to perturbation theory, the change of transition energy is proportional to the change of electron density on the atom/bond when the corresponding Coulomb/resonance integral is varied. The sign of the electron density change is governed by the position of the FMO nodes. Based on the perturbation theory, the Förster–Dewar–Knott rule was formulated concerning the shift of the first absorption maximum in PMDs.[12–14] The generality of this rule has been studied[15] with consideration of the nature of the EG. For instance, substitution of the central methine group by a more electronegative atom (e.g. nitrogen) causes a hypsochromic shift of the first maximum for the polymethines of the A class, as opposed to a bathochromic shift for those of B class.

Similarly, the spectral shift rule for HPs was demonstrated, provided that the transition in question is $^{1}A_{1} \rightarrow {}^{1}B_{1}$. Since the MO nodes in polyenes are located in the middle of the bonds, varying their resonance integrals proves to be more effective in this case, rather than the Coulomb integrals of the atoms. According to perturbation theory, the spectral effect is $\Delta\lambda = -2\,\Delta p_{\mu\nu}\,\partial\beta_{\mu\nu}$. The central bond of polyenes belonging to the A class is loosened on excitation, since the HOMO coefficients on the central atoms are of the same sign in contrast to the LUMO, so that $\Delta p_{\mu\nu} = C_{e\mu}C_{e\nu} - C_{0\mu}C_{0\nu} < 0$. At the same time, $\Delta p_{\mu\nu} > 0$ for the central bond of the B class of polyenes. Therefore, a perturbation of the middle bond length results in opposite effects for polyenes of different classes.

To illustrate this, diazasubstitution in the indopolyenes **II** can be considered. Their first transition is sure to be a polymethine one. Spectral parameters of these compounds are given in Table 2.



II

X = —CH—, —N—

Since the absolute values of the FMO coefficients are practically equal, polyenic spectra will be almost insensitive to variations of the electronegativities of the atoms. It is the difference between the resonance integrals β_{NN} and β_{CC} which influences the transition energy initially. Since $\beta_{NN} < \beta_{CC}$, diazasubstitution leads to bathochromic effects for a polyene of class A, and hypsochromic shifts for class B. There are two alternative ways for changing the class of a PMC: firstly, lengthening the PC by one vinylene group, and secondly, changing the HOMO number by one. The latter can be obtained by oxidation of the neutral polyene into a dication, or vice versa. As Table 2 shows, the proposed rule is in agreement with the experimental data;[16] the sign of the spectral effect is determined by the class of HPs.

An unsymmetrical PMC can be constructed as the derivative of

TABLE 2

Spectral Data of Hetarylpolyenes II[16]

n	*X*	*Reduced form*			*Oxidized form*		
		Class	λ_{max} (*nm*)	$\Delta\lambda$ (*nm*)[a]	*Class*	λ_{max} (*nm*)	$\Delta\lambda$ (*nm*)[a]
1	CH	A	410		B	450	
1	N	A	464	+54	B	382	−68
2	CH	B	435		A	454	
2	N	B	387	−48	A	492	+38

[a] $\Delta\lambda$ is calculated with respect to the unsubstituted compound.

symmetrical parent compounds. If the EG parameters differ slightly, two initial polymethines of the same class are combined to give a polymethine; otherwise, in the case of different classes, a polyene is formed. Likewise, two symmetrical polyenes of the same class give a polyene, whereas the combination of polyenes belonging to different classes results in the formation of a polymethine. However, the general mode of designing unsymmetrical PMC is outside the scope of this paper and requires more detailed discussion.

3.3 Electron donor ability and topological parameter Φ_0

The parameter ϕ in eqn (1) characterizes the influence of EGs upon the position of the FLs. It is an additive value, viz. $\phi = \Phi_1 + \Phi_2$. The components are directly related to the topology of the EGs and can be calculated through the coefficients of the characteristic polynomial:[6-9]

$$\tan \Phi = -q_0/r_0 \qquad (6)$$

where q_0 is a free term of the polynomial Q concerning the EG and r_0 is that for minor R, corresponding to the residue of EG without the atom connected with the PC. If a methine group from the PC is added to an EG, its value will change by $\pi/2$, so that $\Phi' = \Phi - \pi/2$. This is due to the invariance of eqn (1) with respect to the method of formal partitioning of a PMC molecule. However, in order to be a convenient estimate of donor ability, this parameter has to be unequivocal and positive. As proposed earlier,[6-8] Φ is calculated for the EGs of polymethine chosen so that a symmetric monomethine dye belongs to class A. In this case, the polynomials Q and R correspond to the acceptor and donor forms respectively of an EG. The parameter Φ_0 calculated on this basis then estimates the ability of an EG to transfer the π-electron density excess on the PC, whereby it can be called the electron donor ability of an EG. Its physical meaning resembles that of empirical EG parameters,[17-19] such as the Brooker 'basicity' or 'ADBS' calculated through deviations of unsymmetrical dyes,[17] as well as electron donation also found from the spectra of unsymmetrical dyes.[19] In contrast to these empirical parameters, Φ_0 is calculated theoretically by means of eqn (6) and lies within the interval (0°; 90°).

The electron donor ability of a PMC (ϕ_0) and the parameter Φ_0 of an EG can be readily related through eqns (1) and (5), giving, for symmetrical PMDs,

$$\Phi_0 = \lim_{m \to \infty} \phi_0 \qquad (7)$$

Thus, Φ_0 characterizes both EGs simultaneously. The following expression is true for unsymmetrical PMDs, provided that the accuracy of the quasi-long PC approximation is sufficient:

$$(\Phi_{01} + \Phi_{02})/2 = \lim_{m \to \infty} \phi_0 \tag{8}$$

The transformation of PMDs into HPs can be regarded as the inclusion of a methine group into one of the EGs, thus permitting a simple interrelation between ϕ_0 and Φ_0:

$$\Phi_0 = \lim_{m \to \infty} \phi_0 \pm \pi/4\,; \qquad (\Phi_{01} + \Phi_{02})/2 = \lim_{m \to \infty} \phi_0 \pm \pi/4 \tag{9}$$

The sign in eqn (9) depends upon the form of HP (neutral or dicationic), i.e. the HOMO number and the PMC class.

On the basis of eqns (7)–(9), it can be concluded that PMDs and HPs with the same EGs differ radically in the disposition of their FLs. Polyenic FLs are shifted up or down by almost half of the energy gap when compared with PMDs. Calculation of the FL disposition in the HMO approximation gives the same result, if the resonance integrals β are taken as equal (see Fig. 1 and Table 1).

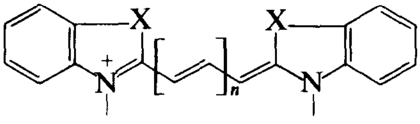
Experimental data for HOMO and LUMO positions can be obtained by means of polarographic investigations. Some reduction potentials, depending linearly upon LUMO energy ($E_{1/2}^{\text{red}} = \varepsilon_e + \text{const}$), are given in

TABLE 3

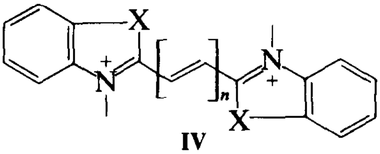
Reduction Potentials $E_{1/2}^{\text{red}}$ (V) of Hetarylpolyenes **III** and Polymethine Dyes **IV**

X	Φ_0 (*deg*)	*n*	*Polyenes* **III**	*Polymethines* **IV**
CMe_2	45	0	−0·06	
		1	−0·06	−1·00
		2	−0·03	−0·87
		3	−0·05	−0·48
S	48	0	−0·17	−1·52
		1	−0·19	−1·13
		2	−0·14	−0·94
		3	−0·17	−0·80
CH=CH	66	0	−0·25	−1·10
		1	−0·16	−1·08
		2	−0·13	−0·93
		3	−0·13	−0·81
NMe	72	0		−0·91
		1		−0·76
		2		−0·69
		3		−0·62

Table 3. They pertain to vinylogous series of cationic PMDs (**III**) and corresponding dicationic HPs (**IV**).



III



IV

Comparison of the corresponding vinologues clearly shows that the polyenic HOMO lies considerably higher than the polymethine HOMO, in good agreement with our conclusions, even though the difference in energy gap is neglected.

To provide the stable electron shell, the electron donor ability ϕ_0 of the PMC should lie within the interval (0°; 90°), as well as the parameter Φ_0 of the EGs. Hence HPs with EGs having $\Phi_0 > 45°$ are stable in the oxidized form, whereas the reduced form is preferable for polyenes with the EGs having $\Phi_0 < 45°$.

The influence of the general molecular charge on the position of the Fermi level is of value for strict analyses of PMCs. However, it is possible to use eqns (7)–(9) to treat the polyene stability quantitatively in considering the effects of various EGs.

REFERENCES

1. Mees, C. E. K. & James, T. H., *The Theory of the Photographic Process*, ed. T. H. James. Macmillan Co., New York, 1972.
2. Shapiro, B. I., *Uspechi Nauchn. Photogr.*, **21** (1982) 79.
3. Fabian, J., Hartmann, H. & Tyutyulkov, N. N., *J. Signal AM*, **4** (1976) 101.
4. Tani, T., *J. Photogr. Sci.*, **19** (1971) 161.
5. Dyadyusha, G. G. & Kachkovski, A. D., *Ukrain. Khim. Ẑurn.*, **41** (1975) 1176.
6. Dyadyusha, G. G. & Kachkovski, A. D., *Ukrain. Khim. Ẑurn.*, **44** (1978) 948.
7. Dyadyusha, G. G. & Kachkovski, A. D., *Theoret. Experim. Khim.*, **15** (1979) 152.
8. Dyadyusha, G. G. & Kachkovski, A. D., *J. Signal AM*, **13** (1985) 95.
9. Dyadyusha, G. G. & Ushomirski, M. N., *Theoret. Experim. Khim.*, **21** (1985) 268.
10. Dähne, S. & Leupold, D., *Ber. Bunsen.*, **70** (1966) 618.
11. Dyadyusha, G. G., *Ukrain. Khim. Ẑurn.*, **30** (1964) 929.
12. Förster, T., *Z. Phys. Chem.*, **48** (1940) 12.
13. Dewar, M. J. S., *J. Chem. Soc.* (1950) 2329.
14. Knott, E. B., *J. Chem. Soc.* (1951) 1024.
15. Kachkovski, A. D., *Structure and Colour of Polymethine Dyes*. Naukova Dumka, Kiev, 1989.
16. Hünig, S. & Linhart, A., *Ann.* (1975) 2116.
17. Brooker, L. G. S., *Rev. Mod. Phys.*, **14** (1942) 275.
18. Platt, J. R., *J. Chem. Phys.*, **25** (1956) 80.
19. Il'chenko, A. Y., *Ukrain. Khim. Ẑurn.*, **42** (1976) 162.