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Electronic Properties of Polymethine Systems. Part 4. Vinylene Shift

A. D. Kachkovski and N. M. Kovalenko

Institute of Organic Chemistry, National Academy of Sciences of Ukraine, Murmans'ka 5,
Kiyv 94, 253 660, Ukraine

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ABSTRACT

Features of the electron transitions in a vinylogous series of polymethine dyes and α,ω-disubstituted polyenes are considered. It is shown that the vinylene shift of the longwave length band on chain lengthening by one vinylene group depends on the degree of π-bond equalization within the chromophore. In polymethines with end groups characterized by the highest or lowest basicity, the vinylene shift essentially decreases. In polyenes, the magnitude of the vinylene shift is determined by both the topological indices of residues and the polyene form, neutral or charged. On chain lengthening, the difference between the transition energies in different forms increases regularly. Theoretical conclusions are illustrated by both quantum-chemical calculations and experimental data. © 1997 Elsevier Science Ltd

Keywords: polymethine dyes, polyenes, electron transition, vinylene shift, absorption, fluorescence.

INTRODUCTION

Linear polymethine compounds are characterized by an intense absorption and fluorescence in the UV or near IR spectral region, which is caused by $\pi \rightarrow \pi^*$ electron transitions localized within the lengthened polymethine chromophore or fluorophore. Transition energy depends on the system type (polymethine or polyene), symmetry, chain length and nature of end residues. As a rule, lengthening of the conjugated chain leads the maximum being regularly shifted to longer wavelengths. This work is concerned with a consideration of this spectral effect in linear conjugated systems (LCS).

In previous papers [1–4] it was established that the electronic properties of two types of symmetrical LCS differ essentially from each other. For quantitative estimations of the relative position of the frontier levels, a parameter $_0$ (the so-called 'electron donor ability') was introduced. In the first approximation, it was proposed to characterize the contribution of end groups (EG) by their topological indices $-\Phi_0$ and L. The same approach is used in this paper for the investigation of the dependence the electron transition energy within LCSs on their molecular topology, and in particular on the conjugated chain length.

FEATURES OF ELECTRON TRANSITION IN POLYMETHINES AND POLYENES

Symmetrical LCS′ **1** with arbitrary end groups G

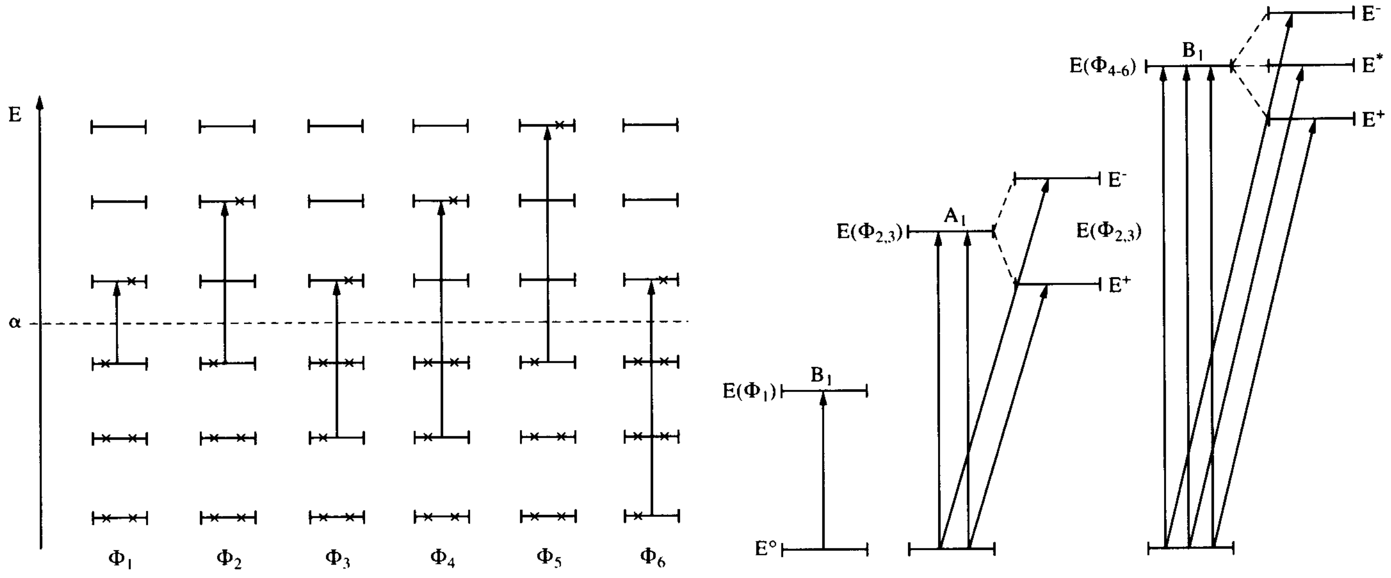
$$\overset{\cdots\cdots\cdots\cdots\cdots}{\mathrm{G{-}(CH)_m{-}G}} \qquad \mathbf{1}$$

can be divided into two types, namely polymethine dyes (PMD) and α,ω-diheterosubstituted polyenes (HP), according to the parity of the number of methine groups in the polymethine chain (PC), differing in the position of their occupied and vacant levels (Figs 1 and 2).

We have previously shown that the bond orders and lengths in the PC of symmetrical PMDs are appreciable equalized. Its result, the closest to the Fermi level (no-bonding level of π-electrons) are disposed approximately at equal distances. The first excited state is mainly described by the ϕ_1 configuration (Fig. 1a). If the function Ψ_p^* of the pth excited state is presented by expansion in the basic set of electronic configurations ϕ_i so that: $_p^* = \Sigma T_{ip}\phi_i$, it was then found that for the usual PMDs $T_{11} > 0.9$. This permits the use of the one-configuration approximation with reasonable accuracy.

In symmetrical polymethines with closed shell, the ground state is totally symmetric $-A_1$. Since the frontier MO (FMO), as the neighbouring orbitals, are of opposite symmetry, the configuration ϕ_1 is antisymmetrical (B_1), so that the first transition could be written as: $A_1 \rightarrow B_1$, and the transition momentum, μ_1 is directed along the polymethine chromophore.

The next two transitions concern the configurations ϕ_2 and ϕ_3 (Fig. 1a). Both transitions involving MOs of the same symmetry are symmetrical: $A_1 \rightarrow A_1$. In the first approximation, the energies of ϕ_2 and ϕ_3 are degenerate. Configurational interaction results in the splitting of the degenerated states (Fig. 1b) to two new states, which were named by Pariser [5] as plus and minus states, Ψ^+ and Ψ^-: $\Psi^+ = (\phi_2 + \phi_3)/\sqrt{2}$; $\Psi^- = (\phi_2 - \phi_3)/\sqrt{2}$. Their



(a)

(b)

Fig. 1. Electron levels and single excited configuration ϕ_i (a), and the states and transitions (b) in polymethines.

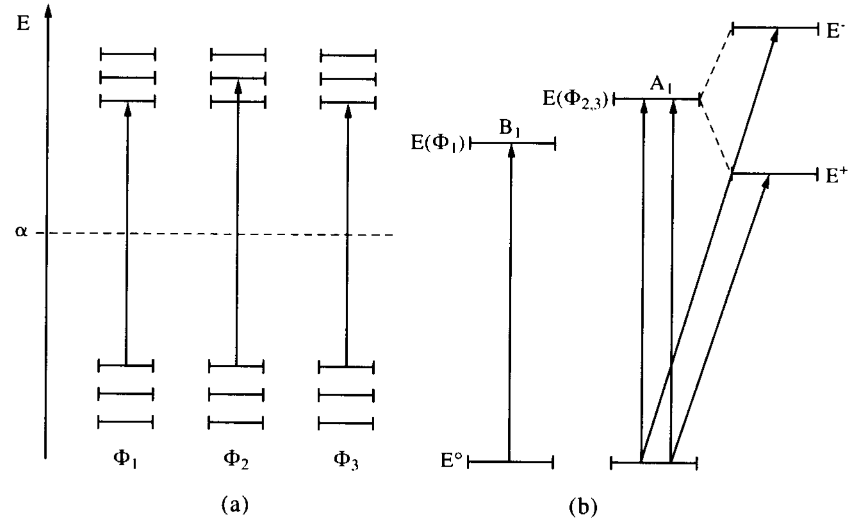


Fig. 2. Electron levels and single excited configuration ϕ_i (a), and the states and transitions (b) in polyenes.

energies are: $E^+ = E^0 + h$ and $E^- = E^0 - h$, where $h = <\phi_2|H|\phi_3>$ is the energy of the configurational interaction. For PMDs, the splitting energy $2h$ is relatively low, and hence the energy of the second and third transitions are considerably higher than the first transition energy.

In polyenes, dependence of the electron transitions on the molecular topology is more complicated due to the bond alternation within the PC. As a result, energetic levels of HPs and PMDs with nearly equal chain length diverged considerably in their positions. Comparing Fig. 1 and Fig. 2 shows that the distance between the frontier levels in the polyene increases while the distances between each of the frontier levels and the one nearest to it, decreases. On PC lengthening, this tendency is further enchanced, and the electron levels make up bands, so that, in limit, the energetic gap depends only on the resonance integrals of double β_d and single β_s bonds: $E_\infty = 2|\beta_d - \beta_s|$ [6, 7]. Thus, the electron transition from HOMO to LUMO, ($A_1 \rightarrow B_1$) in HPs has always greater energy than the transition in the corresponding PMDs with the same EGs containing an even shorter chain (see, for example [8]).

On the other hand, the excitation in HPs is accompanied by relatively large changes of the bond lengths within the PC. This is why the observed absorption bands were rather broad, with pronounced vibrational structure, unlike the relative narrow bands in the spectra of PMDs.

An additional problem exists. This concerns the nature of the first S_1 and the next transitions S_i in the spectra of HPs. It is seen from Fig. 2 that the energies of the symmetrical configurations ϕ_2 and ϕ_3 are close to the energy of the ϕ_1 (Fig. 2b), in contrast to the case with PMDs (Fig. 1b). If the distance between the electron levels in the bands is small enough, while the configurational interaction is, in contrast, relatively great, then the energy of one of the splitting states of symmetry A_g can be lower than the energy of the antisymmetrical state B_u [9, 10]. This forbidden excited state A_g, as the lowest excited state in α,ω-diphenylpolyenes, has been experimentally detected by two-photon spectroscopy [11, 12].

Introducing EGs leads the electron levels to be shifted down or up depending on both the polyene form and the topological index ϕ_0 [2]. Also, the distances between the levels in both level bands can be substantially changed, especially if the energies of local levels of the complicated terminal groups proved to be closed to band energy. As a rule, this leads to a decrease in the distance between the frontier levels, while the energies of the higher configurations ϕ_2 and ϕ_3 increase. Additionally, the degeneracy of the configurations ϕ_2 and ϕ_3 is removed, and the interaction between them also decreases. Therefore, in these HPs, the lowest excited state S_1 is of symmetry B_u and the antisymmetrical transition $A_g \rightarrow B_u$ takes place. This transition is characterized by great momentum, which results in the color of substituted polyenes. In many cases, the next transition with energy close to the first transition

TABLE 1
Spectral Data of Azaanalogues of PMDs **4** (in nm)[20]

n	$X = S$		$X = \text{-}CH = CH\text{-}$	
	λ_{max}	V	λ_{max}	V
0	375		422	
1	484	109	471	49
2	553	69	518	47

energy is rather intense, as is observed, for example, in the reduced polyenic form [13].

VINYLENE SHIFT

PMDs **2** and HPs **3** containing the same EGs but differing by the number of vinylene groups in the PC form a vinylogous series. It was initially observed by Koenig [14] that lengthening of the chromophore in the symmetrical dyes **2** by successive attachment of vinylene groups shifted the absorption maxima to regularly longer wavelengths. The spectral shift per one vinylene unit is traditionally called by vinylene shift:

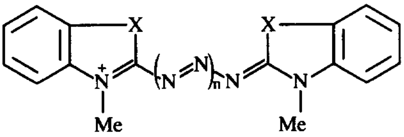
$$G^{+}{-}(CH{=}CH)_n{-}CH{=}G \qquad G{-}(CH{=}CH)_n{-}G$$

2 **3**

$$V = \lambda_{n+1} - \lambda_n \tag{1}$$

Thus, the value V is the additive contribution of one vinylene group, the PC topological unit, in the total molecular characteristic λ_n. Koenig established that the vinylene shift is approximately 100 nm and is maintained on PC lengthening. Further investigations showed that the parameter V slightly depends on the nature of the nuclei [6, 15–19]. Symmetrical PMD series have been proposed as a no-convergent series, in contrast to the convergent series of unsymmetrical dyes and polyenes in which the vinylene shift decreases regularly [16].

Similar longwave band shift is observed in the spectra of PMD azaanalogues **4** [20]. However, the vinylene shifts presented in Table 1 are rather lower. Naturally, fluorescence bands behave similarly on PC lengthening. It has been found that the magnitudes of the vinylene shift obtained from absorption and fluorescence spectra of symmetrical PMDs are essentially equal [21–23].



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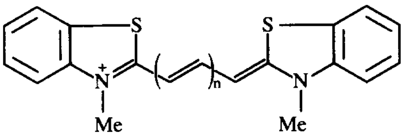

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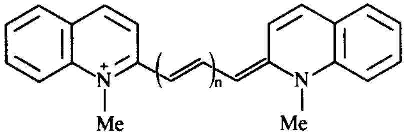

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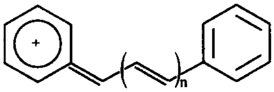

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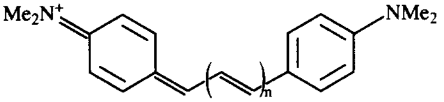

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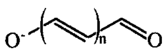

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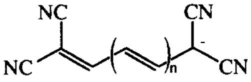

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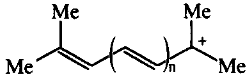

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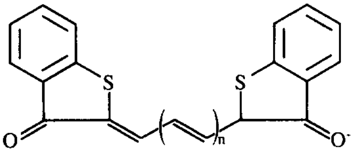

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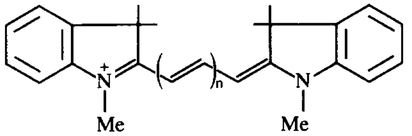

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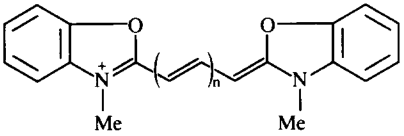

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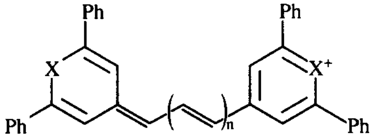

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The simplest treatment of the vinylene shifts is given within the framework of a metallic model: it is lengthening the free electron path. In the HMO approximation, for the rather long PMDs, the value V can be calculated from equation (2):

$$V = hc/\pi|\beta| \tag{2}$$

Unfortunately, calculations of the vinylene shift by standard PPP and all-valence methods give magnitudes more lower than 100 nm, which decreases on PC lengthening [15, 18, 24]. Numerous approaches have been proposed for consistency between the observed and quantum chemical data. It can be seen from formula (2) that the vinylene shift V is directly determined by the resonance integral magnitude $\beta_{\mu\nu}$, which depends on the bond orders $p_{\mu\nu}$. For instance, in the PPP approximation, the effective resonance integral is calculated as: $\beta_{\mu\nu} = \beta_{\mu\nu}{}^0 - 0.5 p_{\mu\nu}\,\gamma_{\mu\nu}$, where $\gamma_{\mu\nu}$ is a two-center integral of an electro-electron interaction, and $\beta_{\mu\nu}{}^0$ is an off-diagonal core integral. Since bond orders within the PC depend on the topological index ϕ_0 [4], the vinylene shift V proved to be sensitive to the EG nature.

VINYLOGOUS SERIES OF POLYMETHINES

It was shown in a previous paper [4] that PMDs are characterized essentially by equalization of bond lengths, and hence their bond orders. Therefore, the vinylene shifts should be relatively large and maintained on passing to higher vinylogous. Experimental data confirm the linear relation between the wave length of the first transition λ_{max} and the number of vinylene groups (**n**) within the PC [14–19, 25, 26]. For illustration, a similar correlation for the vinylogous series of the well-known PMDs **5–12** are presented in Fig. 3. The value V is near 100 nm (except for series **7** and **12**).

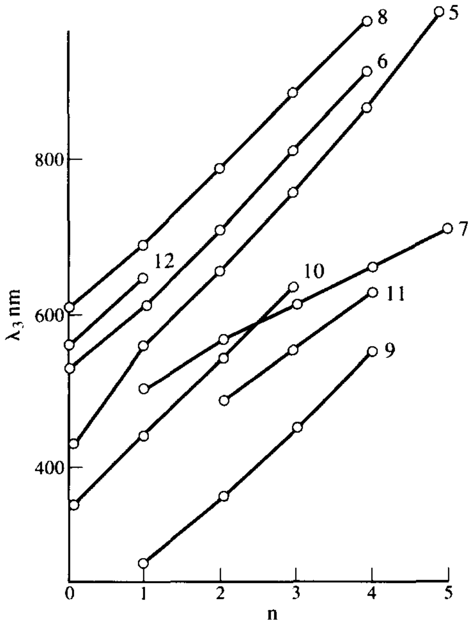


Fig. 3. Dependence of the wavelength of absorption band maximum, λ_{max}, on vinylene groups, n, in PMD **5–12**.

Since in the excited state the bonds within the chromophore are equalized, the vinylene shifts obtained from fluorescence spectra, V^{fl}, are close to them from absorption band maxima V^{ab} [21, 22]. To confirm this conclusion, the spectral data of some cyanine dyes are collected in Table 2.

It has been established that the vinylene shift slightly depends on solvent nature [27, 28]. For illustration, the absorption band maxima of pyrylocyanines and their heteroanalogues **15** measured in both the low-polar dichloroethane and the higher polar nitromethane are presented in Table 3.

Instead of the band maximum λ_{max}, the first band momentum M^{-1} can be used [27, 28]. The value V_M, as seen from the data for dyes **15** presented in

TABLE 2
Spectral Data of Cyanines (in nm)[21]

Dyes	*n*	λ_{max}^{ab}	V^{ab}	λ_{max}^{fl}	V^{fl}
5	1	559		575	
	2	656	97	675	100
	3	762	106	790	115
	4	875	113	910	120
13	1	547		564	
	2	642	95	661	97
	3	742	100	766	105
	4	855	113	900	134
14	1	485		500	
	2	580	95	610	110
	3	682	102	710	100

TABLE 3
Absorbtion Maxima λ_{max}, First Moments M^{-1} and Corresponding Vinylene Shifts (in nm) of Dyes **15** [27,28]

X	*n*	*Solvent CH_2Cl_2*				*Solvent CH_3NO_2*			
		λ_{max}	V	M^{-1}	V_M	λ_{max}	V	M^{-1}	V_M
O	0	555		541		552		539	
	1	686	131	665	124	676	124	658	119
	2	806	120	775	110	798	122	159	101
S	0	630		617		627		615	
	1	762	132	743	126	755	128	731	116
	2	889	127	856	113	879	124	825	94
	3	1016	127	962	106	1000	121	899	74
Se	0	673		663		672		658	
	1	805	132	784	121	795	123	765	107
	2	930	125	898	114	922	127	861	96
	3	1055	125	1007	109	1035	113	931	70

Table 3, is less than the vinylene shifts obtained from the band maxima. This can be explained by the widening of the absorption bands on chromophore lengthening, since the contributions of the higher vibrational transitions increase.

It has been found that some PMDs exhibit a decrease or increase of the first vinylene shift in respect of the value V for the more long dyes [15, 18, 19, 24]. This spectral effect is connected with interaction between the terminal residues within the monomethine PMDs $(n=0)$, which diminishes on PC lengthening. So, a spatial hindrance arising in the quino-2-monomethi-cyanine **6** leads to a bathochromic effect, while similar hiderance is absent within the carbocyanine $(n=1)$. As a result, the first vinylene shift is less than 100 nm: $V=82$ nm $(n=1$ and $0)$, but the values V for next members of the vinylogous serii **6**, are equal, correspondingly: $V=98$ nm $(n=2)$; $V=105$ nm $(n=3$ and $2)$. In PMDs with the sulfur-containing EGs **5** and **12**, the first vinylene shift depends essentially on resonance interaction between sulfur atoms in the dye and the shortest chain considered in detail [29, 30]. If the monomethine dye is of class A, as for example PMD 5 $(n=0)$, then the first shift increases: $V=182$ nm. In contrast, the shortest PMD **12** is of B class, having the opposite symmetry of FMOs, and hence the first shift is found to be considerably lower: $V=65$ mm [30].

As it can be easily seen from Fig. 3, the vinylene shifts for dye series **7** and **11** are rather less than that for other PMDs, independent of the PC length. For the EGs, their topological indices Φ_0, and hence electron donor ability $_0$, reach their limiting magnitudes: 0°. This maximum deviation from the ideal polymethine state leads to bond order alternation from PC center to its ends [4]. As a result, the vinylene shifts have to decrease for the whole vinylogues series. The quantum-chemical methods taking correctly into consideration an electron interaction (PPP or ZINDO/S approximation), predict also a decrease of the value, as for example, in PMDs **11** and **7** (Table 4). It is to be noted that calculated data obtained by the ZINDO/S method proved to be rather lower than the PPP results and experimental values. This is a usual feature of all-valence approximations, which seems to overestimate the resonance interaction [18]. In the case of α,ω-diphenylanions **16**, the parameter φ_0 has other limiting magnitude, 90°. Accordingly to parity theorem, the anions **16**, and cations **7** should have the same transition energies. This theorem is fulfilled only in Hückel and PPP approximations, with accuracy to 1–2 nm. However, both the results and the observed vinylene shifts for the anions **16** are found to be non equal to those for the cations—the experimental values are essentially lower than theoretical ones. Maybe, this is connected with an interaction with solvent molecules (H_2SO_4). It is noted that the quantum calculations gives rather greater values V, near 100 nm, for the polymethines **17** containing also carbocyclic nuclei, but with the no-limiting index: $\phi_0 = 27^\circ$. Thus, decreasing the additive contribution of the PC, V, in wavelength λ_{max} for PMDs of limiting electron donor ability, predicted theoretically is confirmed experimentally. This spectral effect is evidently caused by alternation from the PC center to its ends. As a final example, the polymethines which are MeO-analogues of PMDs **8** with the same bond topology, it is seen from Table 5 that a decrease of the topological index Φ_0 is accompanied by decreasing of the vinylene shifts.

TABLE 4

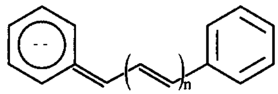
Calculated and Experimental Vinylene Shifts of PMDs Containing Hydrocarbonic EGs (in nm)

			PPP		*ZINDO/S*		*Experiment [18]*	
Dyes	Φ_0	*n*	λ	*V*	λ	*V*	λ_{max}	*V*
11	0°	1	327		257			
		2	403	76	319	62	481	
		3	475	72	378	59	553	72
		4	544	69	432	54	626	73
		5	609	65	482	50		
7	0°	1	498		401		496	
		2	561	63	449	48	557	61
		3	618	57	499	50	612	55
		4	668	50	544	45	663	51
		5	720	52	585	41	711	48
		6	765	45	627	42	755	44
16	90°	1	497		446		535	
		2	561	64	490	44	568	33
		3	617	56	536	46	600	32
		4	668	51	576	40	635	35
17	27°	1	512		465		565	
		2	600	88	529	64	665	100
		3	685	85	597	68		

TABLE 5

Vinylene Shifts of Dyes **8** and Their MeO-analogues (in nm)[32]

n	*Dyes* ***8***, $\Phi_0 = 14^\circ$		*MeO-analogues*, $\Phi_0 = 4^\circ$	
	λ_{max}	*V*	λ_{max}	*V*
0	614		507	
1	705	91	578	71
2	800	95	648	70
3	880	80	717	69
4	980	100	785	68



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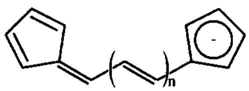

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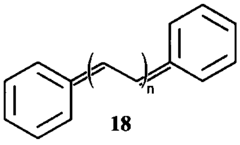

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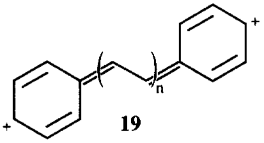

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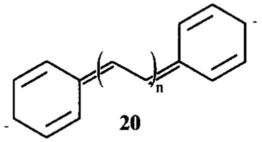

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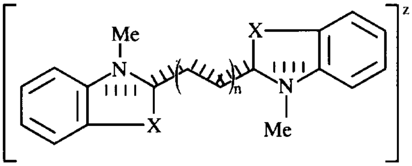
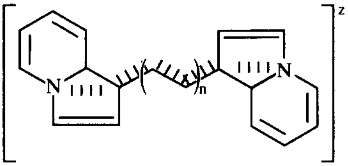


24, X=NMe
25, X=CMe$_2$



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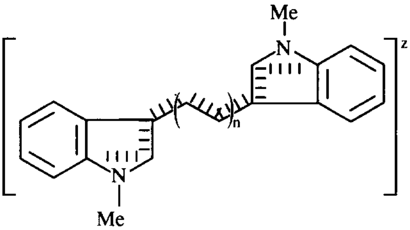

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Naturally, beside the factors involved above, many others can essentially influence the vinylene shift, particularly, an interaction with local transitions [3].

VINYLOGOUS SERIES OF POLYENES

In contrast to PMDs, polyenes form a convergence series, i.e. the observed vinylene shift decreases regularly on PC lengthening. This is mainly caused by considerable bond alternation within the lengthened conjugated chain. It was shown in previous articles [2, 4], that an alternation degree and an ordering of positions of the long and short bonds depends on the polyenic form (electro-deficient, electro-balanced or electro-excessive,) which differ from each other by electron shell occupation. That is why the corrected interpretation of the observed absorption or/and fluorescence bands of HPs proved to be essentially complicated even using modern quantum-chemical modelling. An additional difficulty is connected with the nature of the lowest excited state. For example, it was found from the absorption spectra that the S_1 state in α,ω-diphenylpolyenes **18** is of A_g symmetry [9], due to bond alternation in the equilibrium ground state. However, the equilibrium excited state corresponding to the emitting state is characterized by bond equalization. This results in the lowest excited state (upon its equilibrium geometry) in diphenyl-butadiene (**18**, $n=2$) to be of symmetry B_u [31]. Thus, the bond equalization upon excitation can be accompanied by an inversion of the electron states. Moreover, the ordering of the excited states of different symmetry can change on going to higher vinylogous on PC lengthening. So, in α,ω-diphenylhexatriene and octatetraene, the symmetry A_g is assigned to the lowest emitting state. Because of this, the vinylene shift should be calculated providing the electron transition in two members of vinylogous series are of the same symmetry.

In this paper, we deal only with electron transitions of symmetry $A_g \rightarrow B_u$ that have relatively great transition momentum and correspond to the observed longwave maxima in the absorption spectra.

It can be seen from Table 6 that the vinylene shifts of the polyenes **18** are essentially lower than those of the corresponding PMDs **7**, **16**. It has also been established that different HP forms with the same vinylene group number and with the same EGs, but with a different number of π-electrons, are considerably different in their absorption region. So, for example, the relative low stable polyene cations **19** and anions **20** are colored deeper than the corresponding vinylogs of the neutral electron-balanced form **18**

TABLE 6

Spectral Data (in nm) of α,ω-Diphenypolyenes and their Corresponding Ions[18]

	18		***19***		***20***	
n	λ_{max}	*V*	λ_{max}	*V*	λ_{max}	*V*
1	306				508	
2	334	28			565	57
3	358	24			637	72
4	384	26	571		685	48
5	403	19	621	50	714	29
6	420	17	678	57	746	32

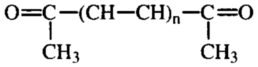
(Table 6). Comparing the observed wavelengths of both charged polyenic forms shows that the anions have lower transition energies than the corresponding cations, although the paring theorem predicts the same energy gaps for both forms. Perhaps this is caused by different experimental conditions.

An investigation of spectral data shows the lowest vinylene shifts to be observed for the most stable electron-balanced polyenic form containing the EGs with limit topological index Φ_0, ie. for the ideal polyenic state, as it is for HPs **18**. In this case, the value V decreases most sharply on PC lengthening. In two other polyenic forms, the electron-deficient and electron-excessive, the bond alternation amplitude decreases somewhat, and the $A_g \rightarrow B_u$ transition energies are found to be rather lower and the vinylene shifts in corresponding series increase.

Introducing EGs with an index Φ_0 not equal to the limit magnitudes leads the ideal state structure to be disturbed and the bond alternation degree to decrease, while the electron densities at carbon atoms arise. Because of this, the vinylene shifts should increase in the HPs with such EGs. As the simplest illustration, there are presented the spectral data of unsubstituted polyenes **21** ($\phi_0 = 90°$) and conjugated α,ω-diketones **22** ($\phi_0 = 76°$) in Table 7.

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

21

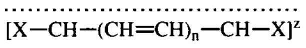


$O{=}\underset{CH_3}{C}{-}(CH{-}CH)_n{-}\underset{CH_3}{C}{=}O$

22

Comparison of the corresponding wavelengths shows that the vinylene shifts for the diketones **21, 22** are essentially greater, and even reach the relatively high value of 50 nm.

Now, let us consider the dependence of the vinylene shift on the topological index ϕ_0 in different forms. Some calculated results of the model HPs with the simplest terminal groups **23** are listed in Table 8.



$[X{-}CH{-}(CH{=}CH)_n{-}CH{-}X]^z$ $z = 0, \pm 2$

23

TABLE 7
Spectral Data (in nm) of Vinylogous Series of HPs **21** and **22**[18]

n	*21*		*22*	
	λ_{max}	V	λ_{max}	V
1	256		228	
2	289	33	278	50
3	317	28	328	50
4	343	26	351	33
5	366	23	380	29
6	384	18	406	26

TABLE 8

Wavelengths of Transitions in Excited State B_u in HPs **23** (nm)

		PPP					*ZINDO/S*				
CH-X	*n*	*(N+2) form*		*N form*		Δλ	*(N+2) form*		*N form*		Δλ
		λ	*V*	λ	*V*		λ	*V*	λ	*V*	
	1	349		255		94	332		238		94
CH-CH$_2$	2	417	60	292	37	125	379	47	275	37	104
$\phi_0 = 90°$	3	473	56	321	29	152	424	45	306	31	118
	4	528	55	345	24	183	464	40	331	25	133
	5	577	49	364	19	213	500	36	353	22	147
	6	621	44	380	16	241	535	35	372	19	163
	1	314		264		50	262		218		44
CH-O	2	382	68	300	36	82	314	52	263	45	51
$\phi_0 = 76°$	3	442	60	329	29	115	361	47	300	37	61
	4	498	56	354	25	144	404	43	331	31	73
	5	548	50	373	19	175	443	39	357	26	86
	6	595	47	388	15	207	478	35	377	20	101
	1	297		283		14	241		235		6
CH-NH$_2$	2	337	40	342	39	−5	280	39	290	55	−10
$\phi_0 = 34°$	3	369	32	399	57	−30	310	30	342	52	−32
	4	394	25	451	52	−57	336	26	389	47	−53
	5	413	19	497	46	−84	358	22	430	41	−72
	6	428	15	537	40	−109	376	18	468	38	−92
	1	241		297		−56	227		235		−8
CH-OH	2	282	41	357	60	−75	266	39	290	55	−24
$\phi_0 = 18°$	3	315	33	421	64	−106	297	31	343	53	−46
	4	341	26	480	59	−139	325	28	390	47	−65
	5	362	21	535	55	−173	348	23	433	43	−85
	6	379	17	563	48	−204	367	19	473	40	−106

Remarks: Δλ[(N + 2) form]−λ[N form]; in calculations, all $\pi \rightarrow \pi^*$ single excited configuration were used; PPP: geometry optimize in molecular mechanic approximation; ZINDO/S: geometry optimized in ZINDO/1 approximation.

If HPs contain the nuclei with an increased index, $\phi_0 > 45°$, then the electron-balanced form is more stable, and hence has the greater energy gap, while the lower stable electron-excessive form exhibits the lower transition energy. This situation is reached within polyenes ($\mathrm{CH}\overset{\cdots}{-}\mathrm{X}\rightarrow\mathrm{CH}\overset{\cdots}{-}\mathrm{CH_2}$) and diketones ($\mathrm{CH}\overset{\cdots}{-}\mathrm{X}\rightarrow\mathrm{CH}\overset{\cdots}{-}\mathrm{O}$). On chain lengthening, the difference between the calculated wavelengths for the different polyenic forms increase regularly. It is also seen from Table 8 that the vinylene shift is markedly conditioned by both the polyenic form and the EG nature. As expected, calculation of HPs with high basic residues results in the greater value V for the low stable (N + 2) form.

In the reverse case of HPs with the low topological index, $\phi_0 < 45°$, the frontier levels are shifted down, which is accompanied by stabilization of the electron-excessive form and by destabilization of the electron-balanced form. As a consequence, the (N + 2) form should have the greater transition energy. Comparison of calculated data for the both forms of HPs with amino-groups ($\mathrm{CH}\overset{\cdots}{-}\mathrm{X}\rightarrow\mathrm{CH}\overset{\cdots}{-}\mathrm{NH_2}$) and oxy-groups ($\mathrm{CH}\overset{\cdots}{-}\mathrm{X}\rightarrow\mathrm{CH}\overset{\cdots}{-}\mathrm{OH}$) shows a good accordance with following conclusion: providing the numbers of vinylene groups within the PC of different forms are equal, the longer wavelength is obtained for the low stable N form. On passing to higher vinylogs, the difference between the wavelengths for the different polyenic forms increases. Also, the vinylene shift is found to be greater for the electron-balanced form.

TABLE 9
Absorption Band Maxima of Different Form of Polyenes **24–27**

HP	ϕ_0	*n*	*(N + 2) form, z = 0*		*N form, z = +2*		$\Delta\lambda$
			λ_{max}	*V*	λ_{max}	*V*	
24[33]	76°	1	405		329		76
		2	428	23	351	22	77
	45°	1	370		406		−36
		2	410	40	430	24	−20
25[13]		3	435	25	454	24	−19
		4	461	26	485	31	−24
		5	482	21	514	29	−32
	40°	1	413		459		−46
26[34]		2	430	17	497	39	−67
		3	444	14	526	29	−82
		4	465	21	554	28	−89
	27°	0	310		448		−138
27 [35]		1	337	27	486	38	−149
		2	359	22	522	36	−163
		3	385	26	535	13	−150
		4	410	25	575	40	−165
		5	423	13	613	38	−190

Theoretical conclusions concerning the influence of EG characteristics on the transition energies for different polyenic forms is confirmed not only by quantum-chemical calculations but also by experimental data. In Table 9, the maxima of the long wavelength absorption bands for HPs **24–27** with relatively complex terminal groups are presented. It is seen that the stable dications of polyenes **24** nondeeply colored, while the unstable neutral form is characterized by a more long wavelength absorption. In contrast, in the case of HPs with low basic β-indol nuclei **27**, the more deeper color is observed for the dications as the lower polyenic form.

If HPs include EGs with a composite branched conjugated system, the lowest electron transition could be localized within terminal nuclei [3]; the behavior of the long wavelength band on PC lengthening differs significantly from the examples considered above.

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