Linear Conjugated Systems Bearing Aromatic Terminal Groups. XIV.[1] On the Electronic Spectral Regularity of α,ω-Diarylpolyenes

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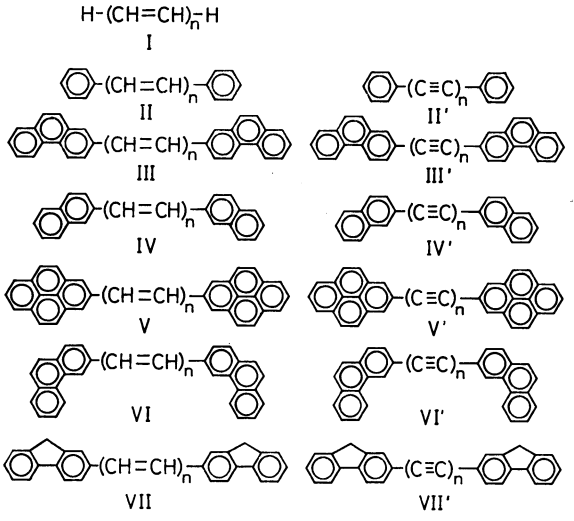
The bathochromic shift of the longest wavelength absorption maxima (λ) of several series of polyenes along with the increase in number of ethylenic double bond (n) can be expressed excellently by the empirical formula $\lambda=An^x+B$. The value of x varies from 0.5 to 0.8 $[0.5\leq x\leq 0.8]$ depending on the nature of terminal groups and the position of linking of polyene chain to terminal aryl nucleus, being $x=0.5$ in the case of parent polyenes (I) and $x=0.8$ for di(3-phenanthryl)- (VI) and di(2-fluorenyl)polyenes (VII). The linear relationship could be reproduced fairly well by the HMO method using the usual bond-alternation approximation ($\beta_{\mathrm{C=C}}=1.1\,\beta$; $\beta_{\mathrm{C-C}}=0.9\,\beta$; $\beta_{\mathrm{C}\overset{\cdots}{-}\mathrm{C}}=\beta$. $\mathrm{C}\overset{\cdots}{-}\mathrm{C}$ denotes aromatic double bond). The calculation based on a modified bond-alternation approximation ($\beta_{\mathrm{C=C}}=[1+0.5/(n+4)]\beta$; $\beta_{\mathrm{C-C}}=[1-0.5/(n+4)]\beta$; $\beta_{\mathrm{C}\overset{\cdots}{-}\mathrm{C}}=\beta$) which is analogous to that successfully applied to diarylpoly-ynes did not reproduce the spectral regularity of diarylpolyenes. This seems to offer further support for the pertinence of assumption of increasing contribution of cumulenic structure in diarylpoly-ynes along with the increase in n.

The bathochromic shift of the longest wavelength absorption maxima (λ) in the electronic spectra of α,ω-diarylpoly-ynes along with the increase in number of acetylenic bond (n) can be expressed well by the empirical formula $\lambda=An^x+B$, indicating a prominent effect of aromatic terminal groups on the electronic spectral regularity.[3,4] The finding prompted the authors to synthesize various α,ω-diarylpolyenes to reveal the influence of the aromatic terminal groups on the electronic excitation of conjugated polyene chain.[5–9] Five series of α,ω-diarylpolyenes (III, IV, V, VI, and VII) exhibited electronic spectra with well-developed vibrational fine structure. The bathochromic shift could be expressed by the same type of empirical formula. The present paper gives the results of a HMO treatment to reproduce the linear relationship between λ and n^x observed in α,ω-diarylpolyenes.



The empirical formulas are summarized in Table 1 together with those for the corresponding acetylenic analogues. The plots of the reported values of the longest wavelength absorption maxima (λ) of polyenes (I)[10] and those of diphenylpolyenes (II)[11] against $n^{0.5}$ and $n^{0.6}$, respectively, gave straight lines. The empirical formulas for (I) and (II) are also included in Table 1.

The values of A, x, and B are dependent on the nature of terminal group and the position of linking of unsaturated chain to terminal aryl system. The fact that the B-values of the polyene series and the poly-yne series are similar is understandable since they formally correspond to the absorption wavelength of hypothetical coplanar biaryls ($n=0$). The trend of variation of A, x, and B was found to be similar in both diarylpoly-ynes[4] and diarylpolyenes. The values of x and B increase with the augmentation of conjugate system in the terminal groups. On the other hand, the values of A decrease along with the increase in x and B. It is to be noted that the increase of x-value with the variation of terminal group accords to the same sequence as that found in diarylpoly-yne series. Diphenylpolyenes (II)[11] exhibit the longest wavelength absorption maxima at longer wavelength (Table 2) as compared with those of corresponding diphenylpoly-ynes (II', $n=1$, 297; $n=2$, 326; $n=3$, 358; $n=4$, 397;

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TABLE 1. ELECTRONIC SPECTRAL REGULARITY OF POLYENES AND POLY-YNES[a)]

R		$R(CH{=}CH)_nR$	n		$R(C{\equiv}C)_nR$	n
H-	I	$\lambda=132.3\ n^{0.5}+\ 39$	3—6			
Phenyl-	II	$\lambda=\ 65.2\ n^{0.6}+253$	1—6	II′	$\lambda=33.0\ n^{1.0}+263$	1—6
2-Phenanthryl-	III	$\lambda=\ 57.9\ n^{0.6}+303$	1—6	III′	$\lambda=13.9\ n^{1.3}+333$	1—6
2-Naphthyl-	IV	$\lambda=\ 45.4\ n^{0.7}+302$	1—6	IV′	$\lambda=15.5\ n^{1.3}+319$	1—6
2-Pyrenyl-	V	$\lambda=\ 44.6\ n^{0.7}+314$	1—6	V′	$\lambda=12.6\ n^{1.4}+327$	1—6
3-Phenanthryl-	VI	$\lambda=\ 30.3\ n^{0.8}+348$	1—6	VI′	$\lambda=10.8\ n^{1.4}+347$	1—6
2-Fluorenyl-	VII	$\lambda=\ 29.5\ n^{0.8}+353$	1—6	VII′	$\lambda=\ 9.0\ n^{1.5}+350$	1—6

a) The spectral data in tetrahydrofuran were used except for I, II, and II′ to which the reported values in isooctane, benzene, and ethanol, respectively, were used.

$n=5$, 431, and $n=6$, 460 nm)[12)] within a limited length of linearly conjugated system ($n=1$—4). This seems to reflect an enhanced electronic interaction of the ethylenic bond with the phenyl group as compared with the acetylenic bond. The value of A can be regarded as a measure of electronic interaction between terminal group and unsaturated function. Therefore, much larger A-values found in various kinds of polyene series indicate that the interaction of ethylenic bond with aromatic nucleus is stronger than that of the acetylenic bond, regardless of the nature of terminal aromatic system.

One of the authors (K. N.) pointed out that the Hückel molecular orbital (HMO) energy difference between the highest occupied and the lowest vacant orbitals (Δm) (in β-unit) and the absorption wavelength (λ) associated with the ^1L_a band can be correlated by the equation[13)]

$$\lambda(^1L_a) = 474(\Delta m)^{-1/2} - 145\ \text{nm} \qquad (1)$$

The electronic spectral regularity of various kinds of α,ω-diarylpoly-ynes could be reproduced satisfactorily by means of the HMO method using Eq. (1). The resonance integrals were assumed as follows [modified bond-alternation approximation, Eq. (2)] considering increasing contribution of dipolar cumulenic structure (VIII) along with the increase of chain length (n):[4,14)]

$$\beta_{C\equiv C} = [1+1/(n+4)]\beta;\ \beta_{C-C} = [1-1/(n+4)]\beta;$$
$$\beta_{C\doteq C} = \beta \qquad (2)$$

Experimental support for this assumption has been obtained by comparing the wave number of spacing of vibrational sub-band of the electronic spectra with that of C≡C stretching vibration in the IR spectra.[4)]

$$\text{Ar-(C}{\equiv}\text{C)}_n\text{-Ar} \longleftrightarrow {}^{+}\text{Ar=(C=C)}_n\text{=Ar}^{-} \longleftrightarrow {}^{-}\text{Ar=(C=C)}_n\text{=Ar}^{+}$$
$$\text{(VIII)}$$

Since the electronic spectral characteristic of linear polyene system has been explained in terms of bond-alternation,[15,16)] we carried out the HMO calculation using the usual bond-alternation model in which the resonance integrals are assumed as follows:

$$\beta_{C=C} = 1.1\beta;\ \beta_{C-C} = 0.9\beta;\ \beta_{C\doteq C} = \beta \qquad (3)$$

(C≐C denotes aromatic double bond.)

In the case of di(2-fluorenyl)polyenes (VII), the resonance integral of the central C–C bond linking two benzene rings was assumed to be 0.9β. The observed and calculated values of absorption wavelength are summarized in Table 2. The present calculation reproduced the experimental relationship $\lambda=An^x+B$ except for the constant term B (Fig. 1). In the series of V and VII, calculation gave less satisfactory A-values than those of the other series. However, agreement between experimental and calculated results seems to be rather good in view of the simple treatment based on HMO.

The HMO calculation employing other parameters such as $\beta_{C=C}=1.2\beta$; $\beta_{C-C}=0.8\beta$; and $\beta_{C\doteq C}=\beta$ gave less satisfactory results. The results based on the following modified bond-alternation approximation (Eq.

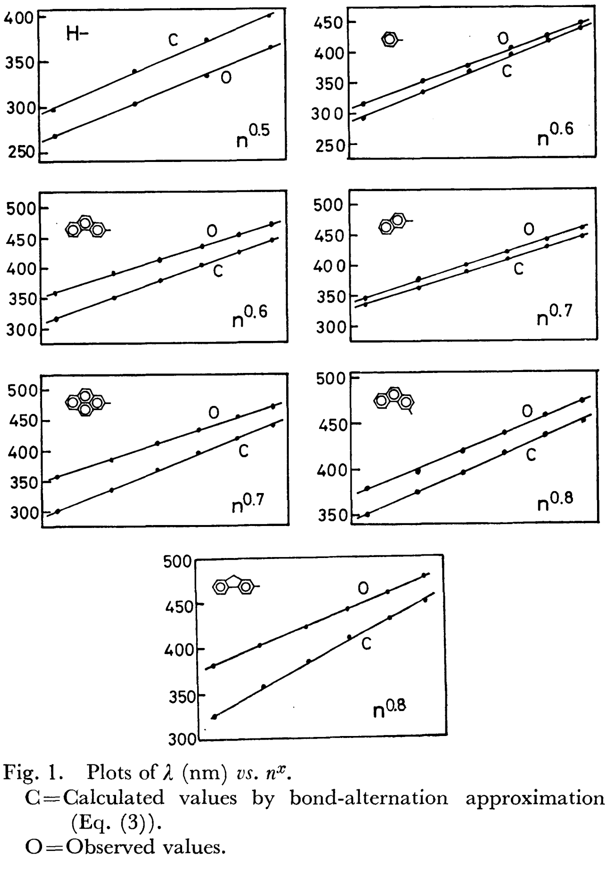

Fig. 1. Plots of λ (nm) *vs.* n^x.
C=Calculated values by bond-alternation approximation (Eq. (3)).
O=Observed values.

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TABLE 2. OBSERVED AND CALCULATED LONGEST ABSORPTION WAVELENGTH OF $R(CH{=}CH)_nR$

R		method	*n*					
			1	2	3	4	5	6
H-	I	Obsd			268	304	334	364
		BA	175	245	298	339	372	399
Phenyl-	II	Obsd	319	352	377	404	424	445
		BA	294	334	367	395	418	438
		MBA	294	339	380	412	452	485
2-Phenanthryl-	III	Obsd	360	392	414	436	455	471.5
		BA	318	351	379	404	425	444
		MBA	318	355	392	427	460	492
2-Naphthyl-	IV	Obsd	347	377	401	423	441	462
		BA	337	362	388	411	431	448
		MBA	337	368	401	434	465	496
2-Pyrenyl-	V	Obsd	359	385	410	431	452	470
		BA	299	336	369	396	419	438
		MBA	299	357	382	418	453	485
3-Phenanthryl-	VI	Obsd	379	399	420	440	458	474
		BA	351	375	398	418	437	453
		MBA	351	379	410	441	472	501
2-Fluorenyl-	VII	Obsd	382	404	424	442	461	476.5
		BA	329	359	386	410	430	447
		MBA	329	368	409	449	487	524

Obsd =Observed values.
BA=Calculated values by bond-alternation approximation (Eq. (3)).
MBA=Calculated values by modified bond-alternation approximation (Eq. (4)).

(4)) analogous to Eq. (2) are given in Table 2.

$$\beta_{C=C} = [1+0.5/(n+4)]\beta;\ \beta_{C-C} = [1-0.5/(n+4)]\beta;\ \beta_{C\doteq C} = \beta \qquad (4)$$

($C\doteq C$ denotes aromatic double bond.)

The plots of calculated wavelength against corresponding n^x yielded no straight lines. This can be regarded as a further support for the pertinence of assumption of increasing contribution of cumulenic structure (VIII) in diarylpoly-ynes along with the increase in the number of n.

It is accepted that the square of wavelength of the longest wavelength absorption maxima (λ^2) of various kinds of linear polyenes varies linearly with the number of ethylenic bond (n) [*i.e.*, $\lambda = An^{0.5}+B$]. However, the present study demonstrates that the validity of $\lambda = An^{0.5}+B$ relationship is restricted to polyenes (I) and presumably to α,ω-dialkylpolyenes, the power of $n(x)$ varying from 0.5 to 0.8 [$0.5 \leq x \leq 0.8$] depending on the nature of terminal groups and the position of linking of polyene chain to terminal aromatic system.