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NOVEL LINEAR RELATION IN THE ELECTRONIC SPECTRA OF α,ω-DIARYLPOLY-YNES[1]

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Abstract—Twelve series of diarylpoly-ynes [$Ar(C{\equiv}C)_nAr$. $n = 1 \sim 6$] bearing various kinds of aromatic terminal groups have been synthesized. It was found that the shifts of the longest-wavelength absorption maxima (λ_L) with the increase in the number of triple bonds (n) can be excellently expressed by the linear relationship:

$$\lambda_L = An^x + B$$

The value of x varies from 1 to 2 [$1 \leqslant x \leqslant 2$] depending on the nature of the terminal groups and on the position of linking of the poly-yne chain, being $x = 1$ in the case of diphenylpoly-yne and $x = 2$ for 1.1'- and 9.9'-dianthrylpoly-ynes. The linear relation could be explained satisfactorily on the basis of HMO calculation assuming that the resonance integrals associated with triple and single bonds of the polyacetylene system should alter with n and be expressed by $\beta_{c\equiv c} = [1 + 1/(n + 4)]\beta$ and $\beta_{c-c} = [1 - 1/(n + 4)]\beta$, respectively. It was also shown that the wavenumbers of the longest-wavelength absorption maxima are in good correlation with the reactivity indices of the terminal aromatic hydrocarbon (Z_r) proposed by Brown.

INTRODUCTION

IT HAS been well-known that the square of wavelength (λ^2) of the longest-wavelength absorption maxima of a series of linear polynes[2] or linear poly-ynes[3] varies with the number (n) of multiple bonds ($\lambda^2 \propto n$). Also, a linear relation between λ and n has been recognized for many years in a series of charge-resonance systems, such as cyanine dyes and polyene–Lewis acid complexes ($\lambda \propto n$).[4]

In the course of the studies on the syntheses of dianthra-tetradehydro[18]-[5] and dianthra-octadehydro[26]annulenes,[6] we have prepared a series of 1,1'-dianthrylpoly-ynes (I_n)[7] as a model of dehydroannulenes containing anthracene nuclei. It was anticipated that the plot λ_L^2 of the dianthrylpoly-ynes against the number of acetylenic bond, n, should give a straight line in analogy with other poly-ynes. However, the plot of λ_L^2 *vs* n gave a concave curve and, unexpectedly, the plot of λ_L against the square of the number of triple bond, n^2, gave an excellent straight line ($\lambda \propto n^2$). This fact clearly indicates the prominent influence of the aromatic terminal groups on the electronic excitation of polyacetylenic chromophore, and prompted the present authors to the syntheses and the measurements of electronic spectra of poly-ynes bearing various kinds of aromatic terminal groups to get further informations on the role of the terminal groups.

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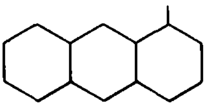
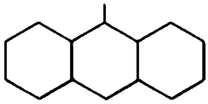
I. *Syntheses*

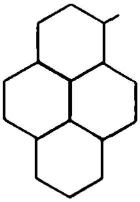
A series of twelve diarylpoly-ynes bearing aromatic terminal groups indicated below [$\mathrm{I}_n \sim \mathrm{XII}_n$, $n = 1 \sim 6$] have been synthesized.



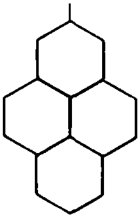
I_n[7]



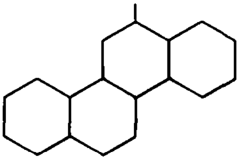
II_n[8]



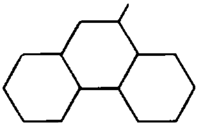
III_n[9]



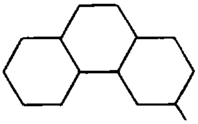
IV_n[9]



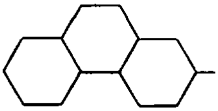
V_n[9]



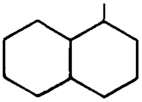
VI_n[10]



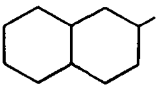
VII_n[10]



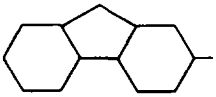
VIII_n[10]



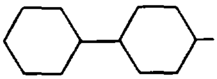
IX_n[11]



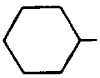
X_n[11]



XI_n[9]



XII_n[9]



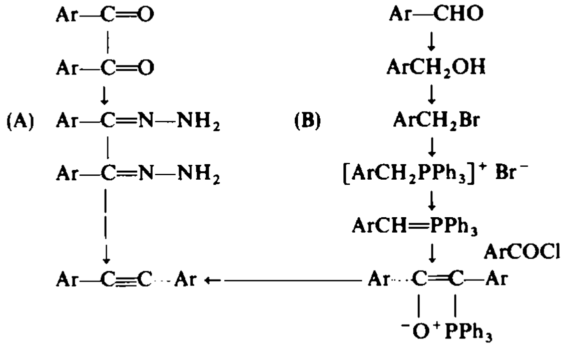
XIII_n[12]

(CH$_3$)$_3$C—

XIV_n[12]

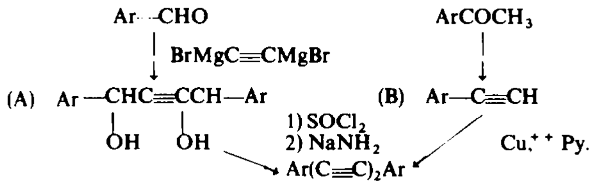
The reaction sequence of the syntheses of monoacetylenes are shown in Scheme 1. Compounds IX_1 and X_1 were obtained according to the classical Curtius reaction (route A), and I_1, II_1, III_1, IV_1, V_1, VI_1, VII_1, VIII_1 and IX_1 were synthesized by the intramolecular Wittig reaction (route B).[13] XI_1 was also synthesized by route B.[9]

Scheme 1. Syntheses of monoacetylenes



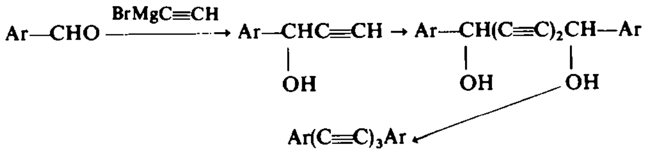
The formyl and the acetyl derivatives of terminal aromatic compounds were used as common precursors for the syntheses of diarylpoly-ynes. Scheme 2 indicates the syntheses of diaryldiacetylenes. Route A was applied for the preparation of II_2, VI_2, IX_2 and XI_2, and I_2, III_2, IV_2, V_2, VI_2, VII_2, $VIII_2$, IX_2 and XII_2 were synthesized according to route B.

Scheme 2. Syntheses of diaryldiacetylenes

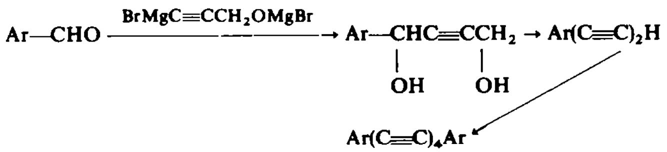


The preparation of diaryltriacetylenes were performed according to the sequence indicated in Scheme 3. Similarly, diaryltetraacetylenes were synthesized starting from the formyl derivatives as illustrated in Scheme 4.

Scheme 3. Syntheses of diaryltriacetylenes

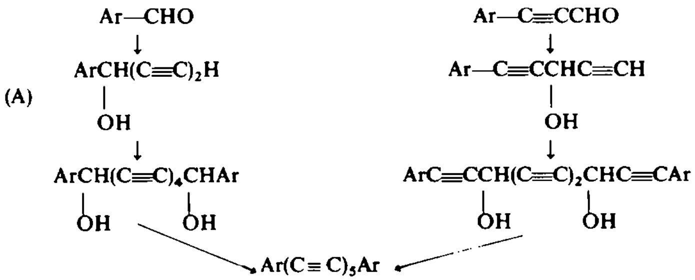


Scheme 4. Syntheses of diaryltetraacetylenes



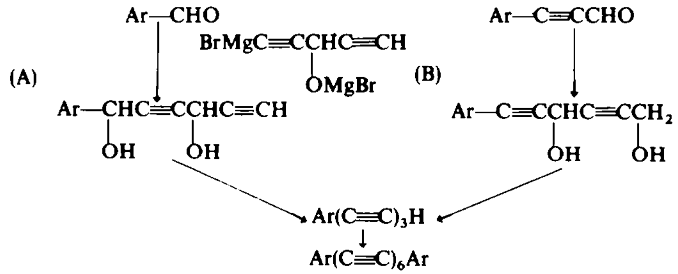
The syntheses of diarylpentaacetylenes were accomplished by two different routes indicated in Scheme 5. I_5, II_5 and VI_5 were obtained according to route A, whereas route B gave satisfactory results in the case of III_5, IV_5, V_5, VII_5, $VIII_5$, IX_5 and X_5. Unfortunately, 2,2′-difluorenylpentaacetylene (XI_5) could not be prepared yet, because neither route A nor B gave fruitful results.

Scheme 5. Syntheses of diarylpentaacetylenes



The syntheses of I_6, II_6, III_6, V_6, VI_6, VII_6, $VIII_6$ and XI_6 were achieved according to route A in Scheme 6. On the other hand, IV_6, IX_6, X_6 and XII_6 were successfully prepared by route B. 2,2′-Dipyrenylhexaacetylene (IV_6) was found to be an unstable compound and satisfactory elemental analysis could not be obtained.

Scheme 6. Syntheses of diarylhexaacetylenes



II. *Physical properties of diarylpoly-ynes*

The physical properties of a representative series of five diarylpoly-ynes (I_n, III_n, V_n, VI_n and IX_n) are summarized in Tables 1, 2, 3, 4 and 5.

Throughout all the series, the color of crystals becomes progressively deeper as the length of the acetylenic chain is increased. The lower members of diarylpoly-ynes showed definite mps, however, the higher members changed to infusible black material without change of crystal form at elevated temperature.

The IR absorption due to stretching vibration of acetylenic linkage ($\nu_{C\equiv C}$) appeared at *ca* 2000 ~ 2200 cm^{-1}. The highest wavenumber of $\nu_{C\equiv C}$ was observed in the case of $n = 4$, and this wavenumber became lower with the increase of n. The correlation of $\nu_{C\equiv C}$ with the spacing of vibrational fine structure of the electronic spectra ($\Delta\nu$) will be discussed in the following part of this paper.

Table 1. The physical properties of 1,1′-dianthrylpoly-ynes (I_n)

n	Color of crystals	Mp* (°C)	λ_{max}(nm)**	Log ε
1	yellow	272–273	425	4·36
2	bright yellow	289–291	430	4·46
3	deep yellow	(*ca* 270)	440	4·62
4	golden yellow	(*ca* 245)	456	4·61
5	orange	(*ca* 220)	473	4·61
6	red	(*ca* 210)	494	4·51

* The figures in parentheses indicate decomposition point.
** Measured in tetrahydrofuran.

Table 2. The physical properties of 1,1′-dipyrenylpoly-ynes (III_n)

n	Color of crystals	Mp* (°C)	λ_{max} (nm)**	Log ε
1	yellow	266	434	4·68
2	yellow	297–298	442	4·76
3	yellow	(*ca* 300)	454	4·79
4	orange yellow	(*ca* 260)	470	4·83
5	orange	(*ca* 215)	487	4·72
6	red	(*ca* 200)	507	4·73

* The figures in parentheses indicate decomposition point.
** Measured in toluene.

Table 3. The physical properties of 6,6′-dichrysenylpoly-ynes (V_n)

n	Color of crystals	Mp* (°C)	λ_{max}(nm)**	Log ε
1	pale yellow	>330	400	4·45
2	yellow	>330	411	4·67
3	yellow	(*ca* 295)	428	4·76
4	yellow	(*ca* 250)	449	4·70
5	light orange	(*ca* 230)	471	4·63
6	orange red	(*ca* 150)	495	4·53

* The figures in parentheses indicate decomposition point.
** Measured in toluene.

Table 4. The physical properties of 9,9′-diphenanthrylpoly-ynes (VI_n)

n	Color of crystals	Mp* (°C)	λ_{max} (nm)**	Log ε
1	colorless	243–244	363	4·51
2	faint yellow	256–257	379	4·67
3	pale yellow	285–286	402	4·81
4	yellow	(*ca* 255)	425	4·59
5	orange yellow	(*ca* 200)	453	4·53
6	orange	(*ca* 130)	481	4·35

* The figures in parentheses indicate decomposition point.
** Measured in tetrahydrofuran.

TABLE 5. THE PHYSICAL PROPERTIES OF 1,1'-DINAPHTHYLPOLY-YNES (IX_n)

n	Color of crystals	Mp* (°C)	λ_{max} (nm)**	Log ε
1	colorless	129	359	4·36
2	bright yellow	175–177	375	4·54
3	yellow	192–193	397	4·60
4	deep yellow	205–207	422	4·49
5	orange yellow	(*ca* 195)	452	4·42
6	orange	(*ca* 175)	479	4·27

* The figures in parentheses indicate decomposition point.

** Measured in tetrahydrofuran.

III. *Electronic spectra of diarylpoly-ynes*

The absorption curves of I_n, III_n, V_n, VI_n and IX_n are recorded in Figs 1, 2, 3, 4 and 5 as representative examples.

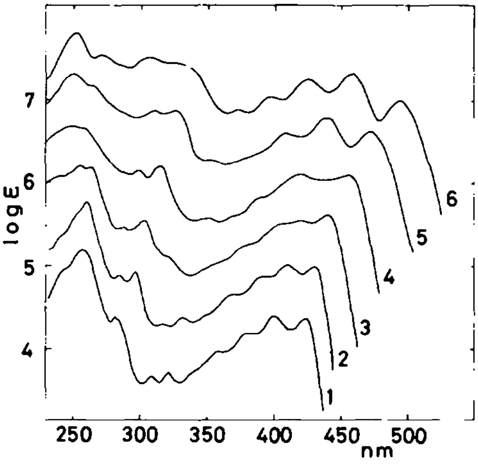


FIG 1. The absorption curves of 1,1'-dianthrylpoly-ynes (I_n) in tetrahydrofuran. The curves, with the exception of I_1 at the botton, have been displaced upward on the ordinate axis by 0·5 log ε unit increments from the curve immediately below.

The characteristic feature of the electronic spectra of diarylpoly-ynes is the regular bathochromic shifts of absorption maxima and the enhancement of the vibrational fine structure according to the increase in the number of acetylenic bond (*n*).

Among the illustrated absorption curves, the spectra of VI_n and IX_n higher than tetraacetylene ($n > 4$) exhibit the most characteristic poly-yne absorption (Figs 4 and 5).

The spacing of vibrational fine structure in the electronic spectra of diarylpoly-ynes ($\Delta\nu$) can be pertinently ascribed to the stretching vibration of acetylenic linkage in the excited state. On the other hand, the IR absorption at *ca* 2000 ~ 2200 cm^{-1} ($\nu_{c\equiv c}$) can be attributed to the stretching vibration in the ground state. Consequently,

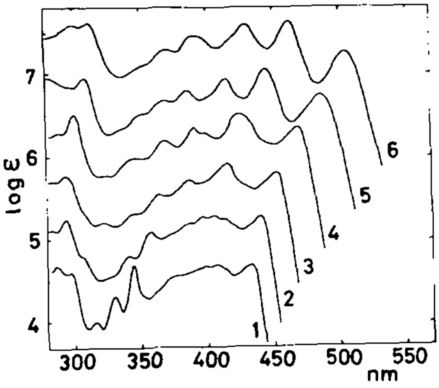


FIG 2. The absorption curves of 1,1′-dipyrenylpoly-ynes (III_n) in toluene. The curves, with the exception of III_1 at the bottom, have been displaced upward on the ordinate axis by 0·5 log ε unit increments from the curve immediately below.

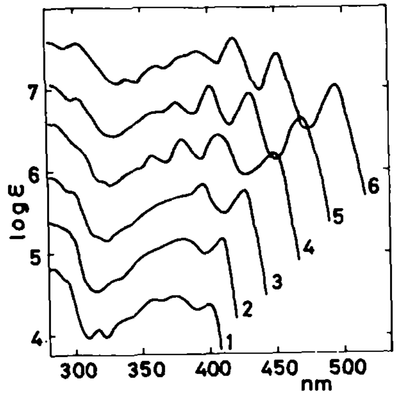


FIG 3. The absorption curves of 2,2′-dichrysenylpoly-ynes (V_n) in toluene. The curves, with the exception of V_1 at the bottom, have been displaced upward on the ordinate axis by 0·5 log ε unit increments from the curve immediately below.

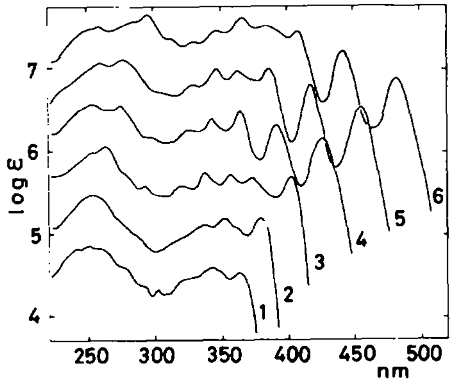


Fig 4. The absorption curves of 9,9'-diphenanthrylpoly-ynes (VI_n) in tetrahydrofuran. The curves, with the exception of VI_1 at the bottom, have been displaced upward on the ordinate axis by 0·5 log ε unit increments from the curve immediately below.

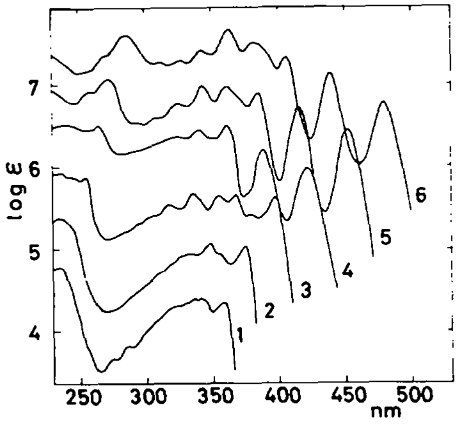


Fig 5. The absorption curves of 1,1'-dinaphthylpoly-ynes (IX_n) in tetrahydrofuran. The curves, with the exception of IX_1 at the bottom, have been displaced upward on the ordinate axis by 0·5 log ε unit increments from the curve immediately below.

the comparison of wavenumber of $\Delta\nu$ and $\nu_{c\equiv c}$ seems of interest with regard to the bond strength of acetylenic linkage in the excited and the ground states. The values of $\nu_{c\equiv c}$ and $\Delta\nu$ are summarized in Table 6. The plots of $\Delta\nu$ and $\nu_{c\equiv c}$ *vs* n are recorded in Fig 6. The data of spacing ($\Delta\nu$) of diarylpoly-ynes bearing large terminal groups, *i.e.*, dianthryl- ($\mathrm{I_n}$ and $\mathrm{II_n}$), dipyrenyl- ($\mathrm{III_n}$ and $\mathrm{IV_n}$) and dichrysenylpoly-ynes ($\mathrm{V_n}$) are omitted because the observed vibrational fine structure of these poly-ynes seems to be a superposition of the fine structure arising from the stretching vibration of poly-yne chain with that of inherent in the terminal groups. Throughout all the series, the IR absorption ($\nu_{c\equiv c}$) appears at higher wavenumber than the spacing of the electronic spectrum ($\Delta\nu$). The variation of the terminal groups exerts relatively minor effect on the wavenumber of $\nu_{c\equiv c}$. However, appreciable scattering of wavenumber of $\Delta\nu$ with the variation of the terminal groups is observed. The highest wavenumbers of $\nu_{c\equiv c}$ and $\Delta\nu$ were observed in the case of tri- or tetraacetylenes ($n = 3$ or 4). The solid lines in Fig 6 indicate the average values of $\Delta\nu$ and $\nu_{c\equiv c}$. It has been reported that $\nu_{c\equiv c}$ of dimethylpoly-ynes also shows the highest value in the tetraacetylene.[14] This fact indicates that this phenomenon is not associated with the electronic structure of terminal groups, but seems to be related solely with the length of polyacetylene chain.

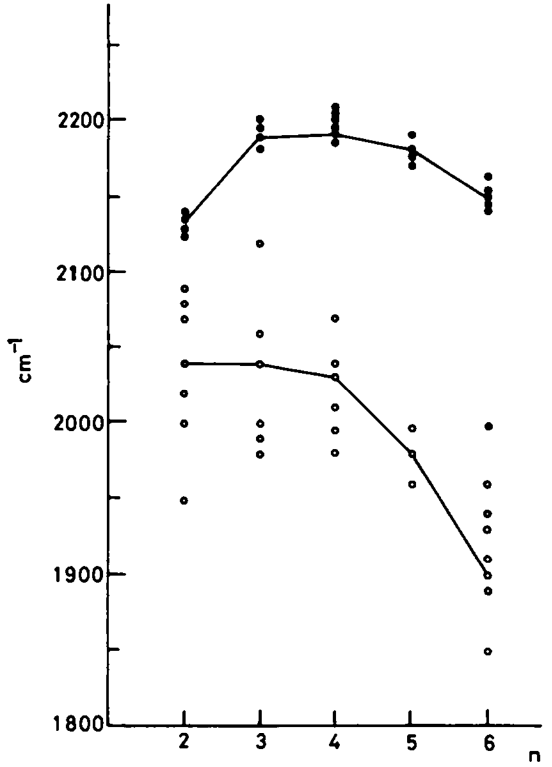


FIG 6. The plots of $\nu_{c\equiv c}$ (●) and $\Delta\nu$ (○) *vs* n. ●—●: averaged $\nu_{c\equiv c}$; ○—○: averaged $\Delta\nu$.

TABLE 6. COMPARISON OF $\nu_{c\equiv c}$ and $\Delta\nu$

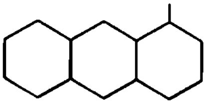
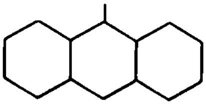
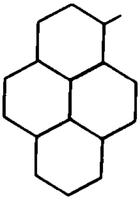
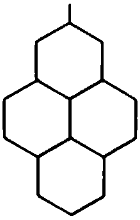
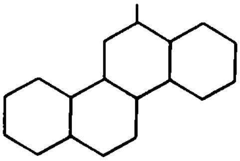
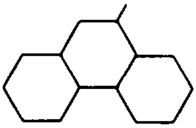
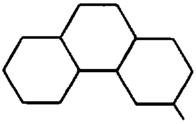
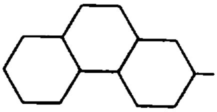
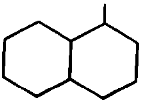
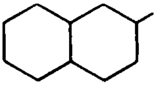
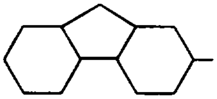
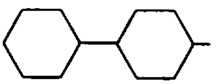
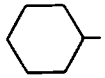
	Ar	$n =$	2	3	4	5	6
I_n		$\nu_{c\equiv c}$	2140	2220	2190	2180	2160
		$\Delta\nu$	1130	1080	1770	1590	1640
II_n		$\nu_{c\equiv c}$	2115	2185	2200	2150	2120
		$\Delta\nu$	1920	1690	1800	1660	1630
III_n		$\nu_{c\equiv c}$	2125	2185	2190	2175	2145
		$\Delta\nu$	1590	1950	2140	1890	1790
IV_n		$\nu_{c\equiv c}$	—	2190	2195	2185	*
		$\Delta\nu$	1390	2030	2080	1990	1960
V_n		$\nu_{c\equiv c}$	—	2185	2190	2170	2150
		$\Delta\nu$	2050	1890	2300	1970	1870
VI_n		$\nu_{c\equiv c}$	2135	2195	2195	2175	2150
		$\Delta\nu$	2020	2000	1980	1960	1940
VII_n		$\nu_{c\equiv c}$	2125	2190	2190	2180	2140
		$\Delta\nu$	2000	1980	2070	1980	1910
VIII_n		$\nu_{c\equiv c}$	—	2200	2195	2175	2145
		$\Delta\nu$	2090	2040	1995	1960	1930
IX_n		$\nu_{c\equiv c}$	2130	2190	2205	2180	2155
		$\Delta\nu$	2070	2060	2010	1980	1850

TABLE 6- *Cont.*

	Ar	n =	2	3	4	5	6
X_n		$\nu_{c\equiv c}$	——	2190	2185	2170	2140
		$\Delta\nu$	2020	2040	2010	1980	1900
XI_n		$\nu_{c\equiv c}$	——	2190	2180	*	2140
		$\Delta\nu$	2080	1990	2010	*	1890
XII_n		$\nu_{c\equiv c}$	2140	2185	2200	2180	2145
		$\Delta\nu$	1950	2120	2030	1980	1940
$XIII_n$		$\nu_{c\equiv c}$	2141	2193	2208	2193	2166
		$\Delta\nu$	2120	2100	2130	1990	1840
XIV_n	*t*—Bu—	$\nu_{c\equiv c}$	2210	2220	2236	2220	2206
		$\Delta\nu$	——	——	2110	2100	2040

* Not measured.

If we assume that the skeletal effect can be eliminated by taking the difference between $\nu_{c\equiv c}$ and $\Delta\nu$ [$\delta\nu = \nu_{c\equiv c} - \Delta\nu$], the difference ($\delta\nu$) seems to reflect the change of bond strength of acetylenic linkage in the ground and the excited states. The $\delta\nu$-values between the averaged $\nu_{c\equiv c}$ and that of $\Delta\nu$ are summarized in Table 7. The fact that the $\delta\nu$ increases monotonously with the increase in the number of n may probably be ascribed to a progressive decrease of triple bond character in the excited state with the increase in the length of polyacetylene chain. In other words, the contribution of cumulenic structure in the excited state seems to increase with the increase in the number of n.

It seems reasonable to assume that the long-wavelength absorption band in the electronic spectrum of diarylpoly-yne should result from the interaction of ^1L_a band of aromatic nucleus with the absorption of polyacetylenic chromophore. The spectra of the lower members of diarylpoly-ynes show rather close resemblance to that of parent terminal hydrocarbons indicating the predominant role of the terminal groups.

TABLE 7. THE DIFFERENCES ($\delta\nu$) BETWEEN AVERAGED $\nu_{c\equiv c}$ AND $\Delta\nu$

n	2	3	4	5	6
averaged $\nu_{c\equiv c}$	2130	2190	2190	2180	2150
averaged $\Delta\nu$	2040	2040	2030	1980	1900
$\delta\nu$	90	150	160	200	250

Consequently, the location of the longest-wavelength absorption peak (λ_L) varies markedly with the change of the terminal groups or with the change of the position of substitution in the terminal nuclei. Particularly, in the case of dianthryl- (I_n and II_n) and the dipyrenyl-series (III_n and IV_n), the difference in the position of substitution exerts prominent shift of λ_L. However, the separation of location of λ_L between the corresponding member of various series of diarylpoly-ynes gradually diminishes according to an increase in the length of poly-yne chromophore. This fact suggests that the contribution of polyacetylenic chromophore progressively increases with an increase in the length of poly-yne chain accompanying the relative decrease of the effect of the terminal groups. The above-stated situation is illustrated in Fig. 7.

$\mathrm{Ar(C \equiv C)_nAr}$

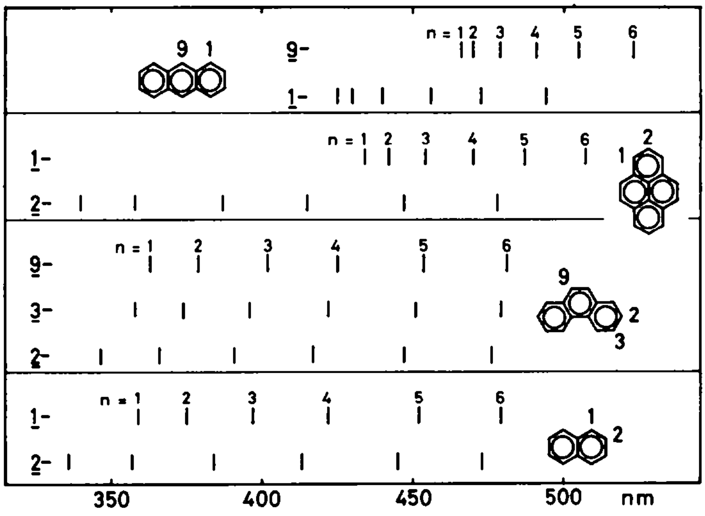


FIG 7. Effect of the terminal groups and the position of substitution on the location of λ_L.

The gradual change of the spectral behaviour of diarylpoly-ynes which is caused by the structural change of the terminal groups is well demonstrated by the plot of λ_L *vs* n. The data of the representative five series (II_n, III_n, V_n, VI_n and X_n) are shown in Fig 8 together with those of XIII_n and XIV_n. Di-t-butylpoly-ynes (XIV_n) gave a convex curve, and diphenylpoly-ynes (XIII_n) showed a straight line. However, all the other diarylpoly-ynes bearing terminal groups larger than phenyl group gave concave curves. These spectral trends clearly indicate that the shifts of λ_L of poly-yne compounds with an increase in the length of acetylenic chain can not be expressed simply by the widely accepted relationship, $\lambda^2 \propto n$.

IV. *Spectral regularities*

It has been pointed out that the plot of λ_L against n^2 gave an excellent straight line in the case of 1,1'-dianthrylpoly-ynes (I_n).[7] According to this finding, we have assumed that the shifts of λ_L of various kinds of diarylpoly-ynes might be proportional to n^x.

As shown in Fig 9, fine linear relationships between the observed λ_L and n^x are obtained. In the case of I_n, II_n, III_n, IV_n, V_n, VI_n, VII_n, VIII_n, IX_n, X_n and XIII_n, the

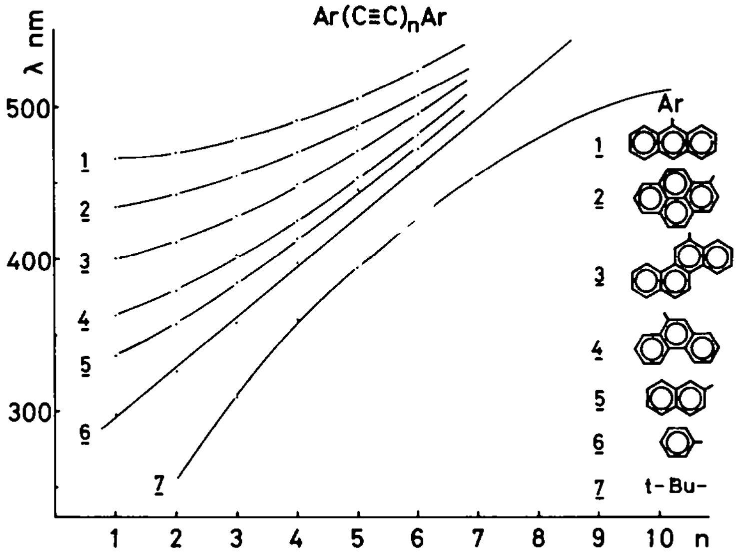


FIG 8. The plots of λ_L vs n.

results of a theoretical calculations which will be described in the following section of this paper are also indicated in the figure. As clearly shown in Fig 9. excellent linear relation between λ_L and n^x is held in the spectra of various diarylpoly-ynes ($I_n \sim XIII_n$). The value of x was found to be dependent on the structure of the terminal groups and on the position of substitution of acetylenic chain.

Regarding the gradual change of the value of x with the variation of the terminal groups. it seems to be pertinent to conclude that the spectral shifts of diphenylpoly-ynes ($XIII_n$) are expressed by $\lambda_L \propto n^{1{\cdot}0}$ instead of the widely accepted relation. $\lambda_L^2 \propto n$.

The above-mentioned spectral regularities are well expressed by the following empirical formulae:*

	Ar	$\lambda_L = A \times n^x + B$ (nm)
II_n	9-anthryl-	$1.65 \times n^{2{\cdot}0} + 465$
I_n	1-anthryl-	$2{\cdot}0 \times n^{2{\cdot}0} + 422$
III_n	1-pyrenyl-	$3{\cdot}8 \times n^{1{\cdot}7} + 426$
V_n	6-chrysenyl-	$5{\cdot}8 \times n^{1{\cdot}6} + 394$
IX_n	1-naphthyl-	$9{\cdot}0 \times n^{1{\cdot}5} + 350$
XI_n	2-flyorenyl-	$9{\cdot}0 \times n^{1{\cdot}5} + 350$
VI_n	9-phenanthryl-	$10{\cdot}5 \times n^{1{\cdot}4} + 352$
VII_n	3-phenanthryl-	$10{\cdot}8 \times n^{1{\cdot}4} + 347$
IV_n	2-pyrenyl-	$12{\cdot}6 \times n^{1{\cdot}4} + 327$
$VIII_n$	2-phenanthryl-	$13{\cdot}9 \times n^{1{\cdot}3} + 333$
X_n	2-naphthyl-	$15{\cdot}5 \times n^{1{\cdot}3} + 319$
XII_n	4-biphenylyl-	$24{\cdot}0 \times n^{1{\cdot}1} + 304$
$XIII_n$	phenyl-	$33{\cdot}0 \times n^{1{\cdot}0} + 263$

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* The spectral data in tetrahydrofuran were used except for V_n and $XIII_n$. The data of V_n in toluene and that of $XIII_n$ in ethanol were employed.

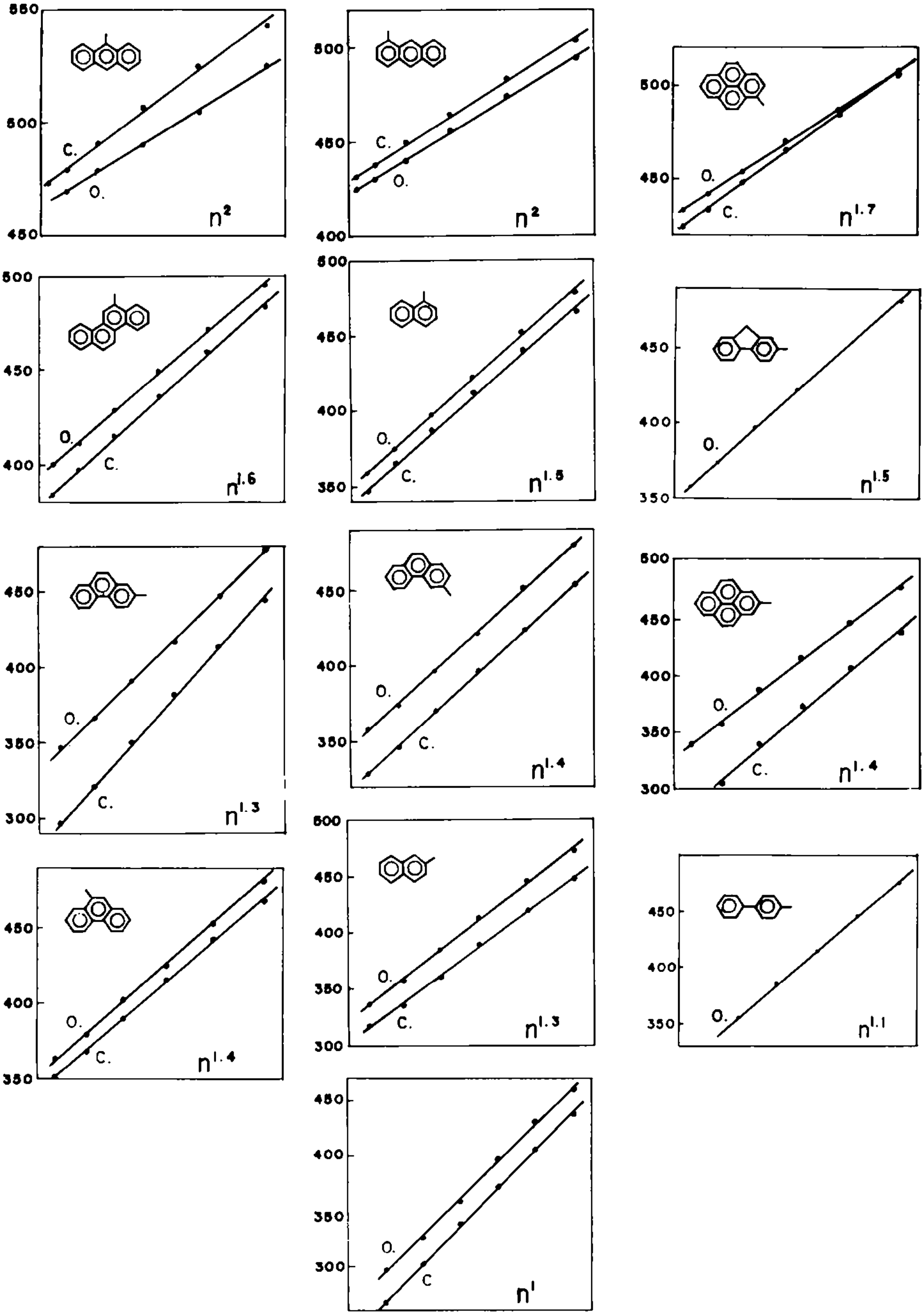

FIG 9. Linear relationship between λ_L and n^x. O. : Observed; C. : Calculated.

The value of ***B*** increases with the augmentation of conjugate system in the terminal group. thus. indicating the close correlation of the ***B***-value with the excitation energy of L_a band of the terminal aromatic system. Formally. the value ***B*** should correspond to the absorption maximum of respective biaryl in a planar conformation. It was revealed that the value ***A*** decreases with the increase of ***B***, *i.e.*, the magnitude of the bathochromic shift of λ_L with an increase in the number of ***n*** in the series of large ***B***-value is smaller than that of in the series of small ***B***-value. This fact suggests, in the case of small number of ***n***, the effect of conjugation of the acetylenic chain on the electronic structure of the terminal group having a large conjugate system is smaller than that of the terminal group having a small conjugate system. However, the magnitude of bathochromic shift of λ_L tends to increase with the chain length. because the small ***A***-value series has a large ***x***.

V. *MO calculation of electronic spectra*

In order to calculate the electronic spectra of a molecule, we must usually consider electronic repulsion explicitly. However. as shown in the previous paper[15]. for an alternant hydrocarbon. there is a good correlation between the absorption wavelength. $\lambda(^1L_a)$. associated with the ^1L_a band and the Hückel MO (HMO) energy difference between the highest occupied and the lowest vacant orbitals. **Δm** (in unit of β). The correlation is expressed by the Eq (1).

$$\lambda(^1L_a) = 474(\Delta\mathbf{m})^{-1/2} - 145\,\mathrm{nm} \tag{1}$$

The longest-wavelength absorptions of diarylpoly-ynes can be regarded as ^1L_a species. So that. in the present study. the longest-wavelength absorptions of diarylpoly-ynes (λ_L) are calculated by HMO method using Eq (1). In the calculation of the electronic spectra of 1.1′-dianthrylpoly-ynes (I_n).[16] we found that only a modified bond alternation approximation can satisfactorily explained the electronic spectral shifts. This approximation is based on an idea that a diarylpoly-yne is a resonance hybrid of a conventional covalent structure (**i**) and cumulene type ionic structures (**ii** and **iii**). In this approximation. we have. furthermore. assumed that the contribution of the ionic

$$\underset{\mathbf{i}}{\mathrm{Ar{-}(C{\equiv}C)_n{\cdots}Ar}} \leftrightarrow \underset{\mathbf{ii}}{\mathrm{{}^+Ar{=}(C{=}C)_n{=}Ar^-}} \leftrightarrow \underset{\mathbf{iii}}{\mathrm{{}^-Ar{=}(C{=}C)_n{=}Ar^+}}$$

structures (**ii** and **iii**) increases with an increase in the length of polyacetylene chain. This assumption may be justified by the following argument. The structures **ii** and **iii** can be realized by the electron transfer through the cumulene chain. The lowest vacant orbital (LVO) of the cumulene chain might be responsible for the charge resonance between **ii** and **iii**. Therefore, lowering of the energy of LVO will enhance the contribution of the charge resonance structures (**ii** and **iii**). The energy of LVO. $\mathbf{E}_L$. is given by Eq (2).

$$\mathbf{E}_L = \alpha - 2\beta \sin\,[\pi/(4\boldsymbol{n} + 2)] \tag{2}$$

Or. when $\pi/(4\boldsymbol{n} + 2) \ll 1$. Eq. (2) can be rewritten as (2′).

$$\mathbf{E}_L = \alpha - \pi\beta/(2n + 1) \tag{2′}$$

Consequently. an increase in the number of ***n*** brings about the lowering of LVO. leading to the increase of contribution of the charge resonance structures (**ii** and **iii**) to the resonance hybrid. This argument is consistent with our indication in Section III based on the analysis of vibrational fine structure of the electronic spectra. Therefore, the resonance integral was assumed to be expressed as follows:*

$$\beta_{C\equiv C} = [1 + 1/(n + 4)]\,\beta$$
$$\beta_{C-C} = [1 - 1/(n + 4)]\,\beta$$
$$\beta_{C\overset{\cdots}{-}C} = \beta$$

The calculated results are shown in Fig 9. The agreement between the experimental data and the calculated results is quite satisfactory. The present MO calculation explains the experimental n^x relationship with λ_L, except only the constant term, B's. This fact suggests that in order to improve the theory, it is necessary to examine the crude expression for resonance integral, β and to take into account the effect of interactions between the excited configurations.

VI. *Correlation of the wavenumber of absorption maximum with Brown's reactivity index*

As stated above, the gradual change of the spectral behavior of diarylpoly-ynes along with the variation of the nature of terminal groups and of the position of substitution was satisfactorily explained in terms of a modified bond alternation approximation. This fact seems to suggest the presence of correlation between the location of absorption maximum and some other parameter of the respective position of the terminal aromatic hydrocarbon.

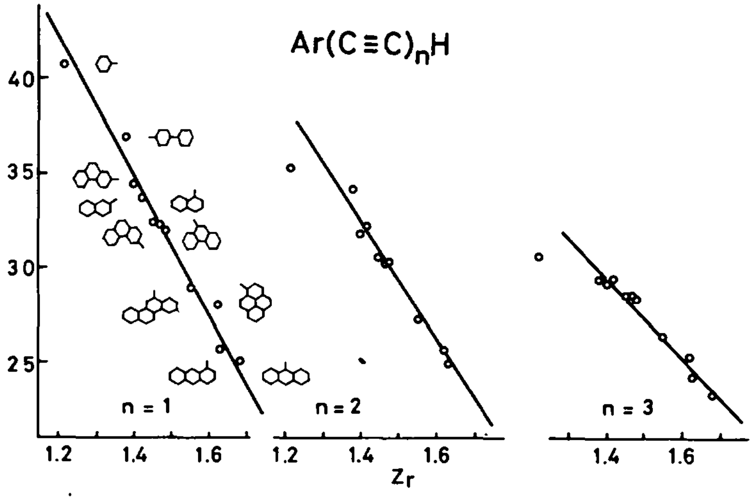

FIG 10. Linear relationship between $\bar{\nu}$ and Z_r in arylpoly-ynes. Oridinate: $\bar{\nu}$ (cm^{-1}) × 10^{-3}; Abscissa: Z_r.

An excellent linear correlation was found between the wavenumbers of absorption maxima ($\bar{\nu}$) and Brown's reactivity indices (Z_r).[17] Fig 10 shows the plots of Z_r-values of the respective position of the terminal hydrocarbon *vs* the $\bar{\nu}$-values of intermediate compounds, arylpoly-ynes [$Ar(C\equiv C)_nH$, n = 1, 2 and 3]. The plots of Z_r against $\bar{\nu}$

* $C\overset{\cdots}{-}C$ denotes aromatic double bond.

of diarylpoly-ynes (n = 1, 2, 3, 4, 5 and 6) are shown in Fig 11. It should be noted that the $\bar{\nu}$-values corresponding to the B-values in the empirical formulae, *i.e.*, $\bar{\nu}$ of the hypothetical coplanar biaryls (n = 0), also hold the straight line relationship. The slope of the lines tends less steeper along with an increase in the number of n.

The reactivity index (Z_r) was derived by application of perturbation theory to a model of transition state in which charge transfer from the highest occupied or the frontier orbital of the respective position of aromatic nucleus to the attacking electrophilic reagent. As described above, charge transfer from a terminal group to another one to form a cumulene type ionic structure seems to have an important role in the photoexcitation of diarylpoly-ynes. Therefore, the existence of correlation between

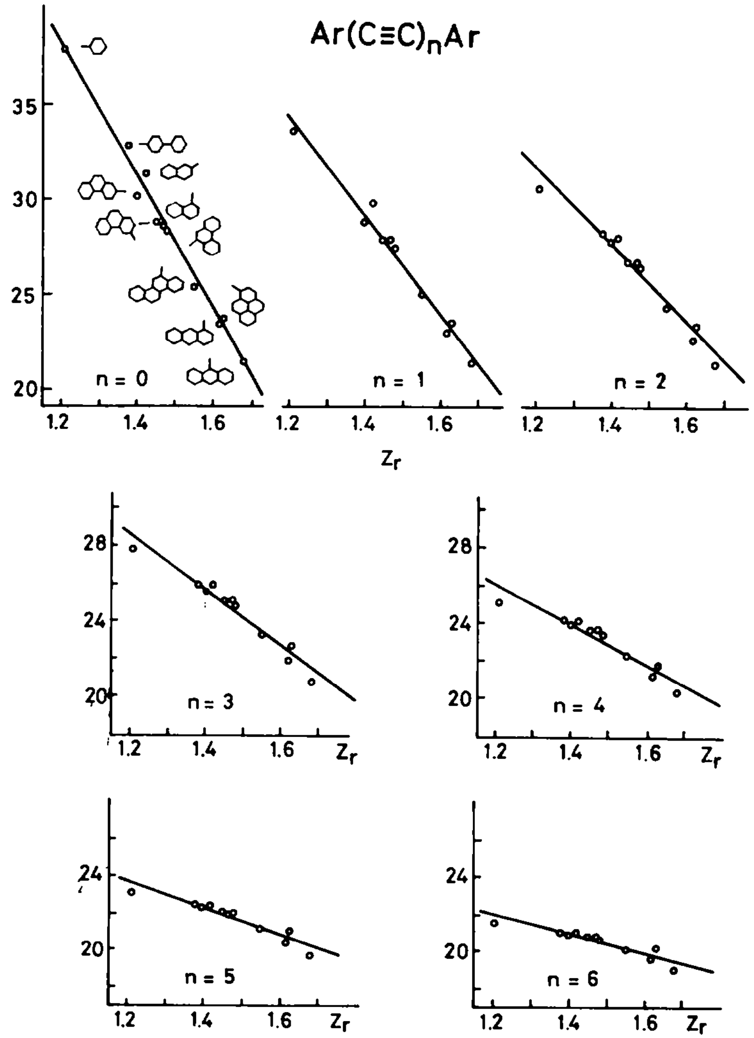

Fig 11. Linear relationship between $\bar{\nu}$ and Z_r in diarylpoly-ynes. Ordinate: $\bar{\nu}$ (cm^{-1}) × 10^{-3}; Abscissa: Z_r.

Z_r and $\tilde{\nu}$ seems to be rather reasonable. The other parameters which are in linear correlation with Z_r, such as Dewar's reactivity number, N_r,[18] or Fukui's superdelocalizability, S_r,[19] show, of course, linear relationship with $\tilde{\nu}$.

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