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ON THE ELECTRONIC SPECTRA OF SOME α,ω-DIARYLPOLY-YNES

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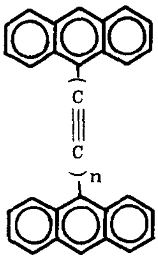
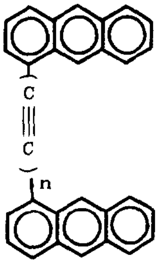
Two types of spectral reguralities have been recognized for the bathochromic shifts of the longest-wavelength absorption maxima, λ_{max}, of some linear conjugated systems, i.e., the square of the wavelength of λ_{max} varies linearly with the number of conjugated multiple bonds, n, in several series of polyenes (1) and poly-ynes (2), on the other hand, a linear relationship between λ_{max} and n is observed in some charge-resonance systems, such as cyanine dyes and poly-ene-Lewis acid complexes (1,3).

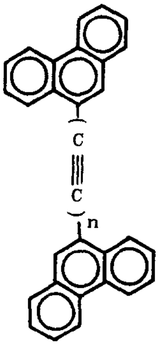
However, two of the present authors (S. A. and M. N.) have pointed out in the previous papers (4) that the variation of λ_{max} in the electronic spectra of 1,1'-dianthrylpoly-ynes (II_n) with the increasing number of the acetylenic bonds, n, is expressed by the linear relation:

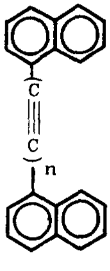
$$\lambda_{max} = an^2 + b$$

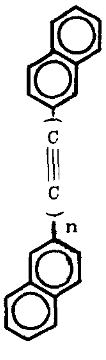
The interesting spectral behavior prompted the present authors to the synthesis of 9,9'-dianthryl-, 9,9'-diphenanthryl-, 1,1'-dinaphthyl- and 2,2'-dinaphthylpoly-ynes (I_n, III_n, IV_n and V_n, respectively) to get further information on the


(I_n)


(II_n)


(III_n)


(IV_n)


(V_n)

role of the terminal groups on the electronic spectra of these diarylpoly-ynes*.

Some physical properties of these diarylpoly-ynes (I_n-V_n) including the location of the longest-wavelength absorption maxima, λ_{max}, in tetrahydrofuran are listed in the following Tables I-III. (The asterisks in the Tables denote the decomposition points.).

TABLE I

Physical Properties of 9,9'-Dianthryl- and 1,1'-Dianthrylpoly-ynes (I_n and II_n)

n	I_n			II_n		
	colour	m.p. (°C)	λ_{max} (mμ)	colour	m.p. (°C)	λ_{max} (mμ)
1	orange	ca. 310*	shoulder	yellow	272-273*	425
2	orange	290-292*	470	bright yellow	289-291*	430
3	deep orange	ca. 295*	479	deep yellow	ca. 270*	440
4	orange red	ca. 265*	491	golden yellow	ca. 245*	456
5	red	ca. 250*	505	orange	ca. 220*	473
6	dark red	ca. 200*	523	red	ca. 210*	494

TABLE II

Physical Properties of 9,9'-Diphenanthrylpoly-ynes (III_n)

n	III_n		
	colour	m.p. (°C)	λ_{max} (mμ)
1	colourless	243-244	363
2	faint yellow	256-257	379
3	light yellow	285-286*	402
4	yellow	ca. 255*	425
5	orange yellow	ca. 200*	453
6	orange	ca. 130*	481

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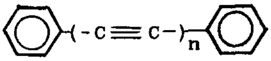
* All compounds described in this paper gave satisfactory elemental analytical and IR spectroscopic data.

TABLE III

Physical Properties of 1,1'-Dinaphthyl- and 2,2'-Dinaphthylpoly-ynes (IV_n and V_n)

n	IV_n			Vn		
	colour	m.p. (°C)	λ_{max} (mμ)	colour	m.p. (°C)	λ_{max} (mμ)
1	colourless	129	359	colourless	228-229	336
2	bright yellow	175-177	375	colourless	202-203	357
3	yellow	192-193	397	faint yellow	173-174	384
4	deep yellow	205-207	422	light yellow	ca. 172*	413
5	orange yellow	ca. 195*	452	yellow	ca. 180*	445
6	orange	ca. 175*	479	orange yellow	ca. 200*	473

The relation of λ_{max} to the number of acetylenic groups, n, of these diarylpoly-ynes (I_n-V_n) together with diphenylpoly-ynes (VI_n) (2) and di-t-butylpoly-ynes (VII_n) (5) are illustrated in Fig. 1.



(VI_n)

$(CH_3)_3C(-C\equiv C-)_nC(CH_3)_3$

(VII_n)

As clearly seen from Fig. 1, all the poly-ynes bearing condensed aromatic nuclei as the terminal groups exhibit concave curves, whereas di-t-butylpoly-ynes (VII_n) shows a convex curve, and it seems to be noteworthy that diphenylpoly-ynes (VI_n) are the only one series which gives a fairly good straight line. These spectral behavior of the diarylpoly-ynes (I_n-V_n) indicate that the bathochromic shifts of λ_{max} in these series can not be expressed by the well-known linear relationships such as $\lambda^2_{max} \propto n$ or $\lambda_{max} \propto n$.

Good correlations between λ_{max} and n^x are observed as illustrated in Figs. 2-6. These linear relationships can be expressed by the following empirical formulae summarized in Table IV with excellent agreement with the observed values.

As mentioned above, the bathochromic shifts of λ_{max} of diphenylpoly-ynes (VI_n)

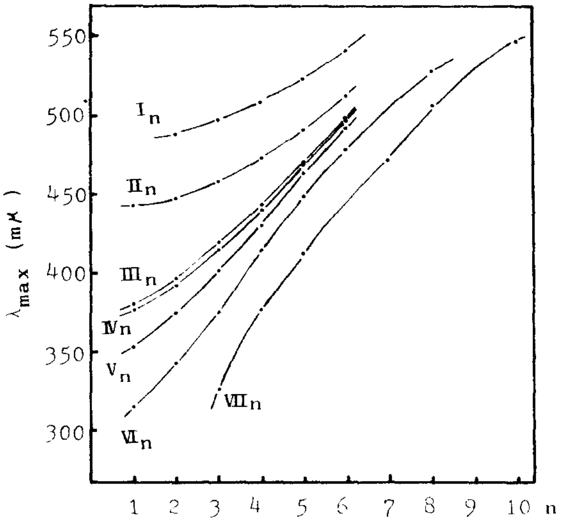


Fig. 1. The relation of λ_{max} to the number of acetylenic bond, n, in the poly-ynes (I_n-VII_n).

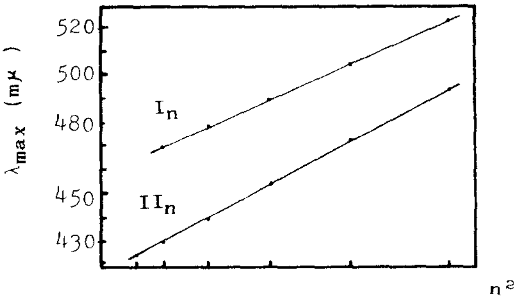


Fig. 2. Plot of λ_{max} versus n^2 for I_n and II_n.

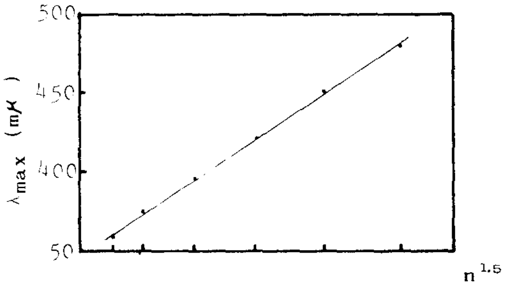


Fig. 3. Plot of λ_{max} versus $n^{1.5}$ for IV_n.

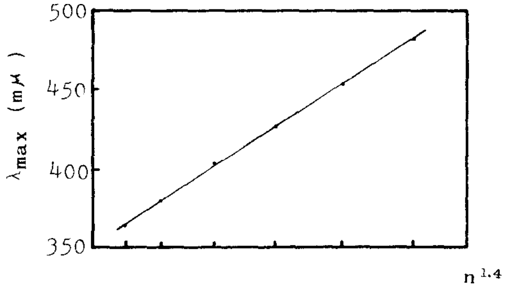


Fig. 4. Plot of λ_{max} versus $n^{1.4}$ for III_n.

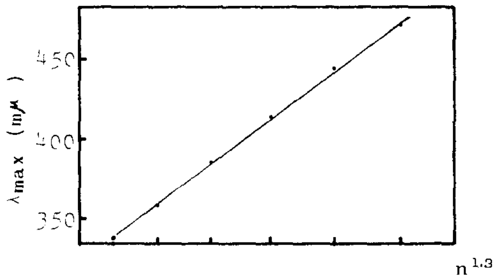


Fig. 5. Plot of $_{max}$ versus $n^{1.3}$ for V_n.

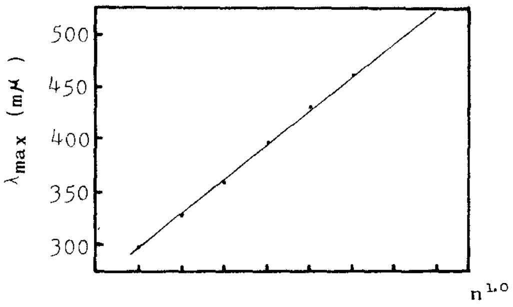


Fig. 6. Plot of λ_{max} versus $n^{1.0}$ for VI_n.

TABLE IV

The Empirical Formulae of the Linear Relationships

	terminal group	$\lambda = a\ n^x + b$
VI_n	phenyl-	$\lambda = 33.0\ n^1 + 263$ (in ethanol)
V_n	2-naphthyl-	$\lambda = 15.5\ n^{1.3} + 319$
III_n	9-phenanthryl-	$\lambda = 10.45\ n^{1.4} + 352$
IV_n	1-naphthyl-	$\lambda = 9.0\ n^{1.5} + 350$
II_n	1-anthryl-	$\lambda = 2.0\ n^2 + 422$
I_n	9-anthryl-	$\lambda = 1.65\ n^2 + 465$

solvent: tetrahydrofuran

has been considered to be expressed by the linear relationship, $\lambda^2_{max} \propto n$, as in the cases of poly-enes (2). However, as illustrated in Fig. 6, the plot of λ_{max} against n gave an excellent straight line. In view of the gradual change of the exponent, x, for n according to the varying nature of the terminal groups, it seems to be conceivable to conclude that the linear relationship of $\lambda_{max} \propto n$ is held in the series of diphenylpoly-ynes (VI_n).

The above-mentioned linear relationships for diarylpoly-ynes are only approximate, but when n is small the approximation is very good. An inspection of Fig. 1 reveals that the bathochromic shifts of λ_{max} of various poly-ynes bearing condensed aromatic terminal groups as compared with the λ_{max} of the corresponding member of diphenylpoly-ynes (VI_n) are dependent on the nature of the terminal groups and the position of substitution. Also, the magnitude of the shifts are large when n is small, but the shifts rapidly diminish with the increasing number of n.

The absorption bands at longer-wavelength region of the diarylpoly-ynes (I_n-VI_n) are reasonably attributed to the interaction of the ^1L_a-state of the terminal aromatic nucleus with the polyacetylenic chromophore. Therefore, the above-mentioned facts seem to indicate that the magnitude of the bathochromic shift is closely related to the energy level of the ^1L_a-state and the position of substitution of the terminal group. As the result of the interaction, the electronic state of the polyacetylenic chain may change gradually with the increasing number of n resulting in the bathochromic shift according to the linear relationship, $\lambda_{max} \propto n^x$. However, at the large number of n, the gradual change of the electronic state of the poly-yne chromophore seems to approach to the inherent one of the chromophore. Consequently, it might be anticipated that the linear relationship, $\lambda_{max} \propto n^x$, at the rather small number of n may shift to that of dialkylpoly-ynes, $\lambda_{max}^2 \propto n$, at the more larger number of n.

The details of this study will be published elswhere in near future, and the further studies along this line are now in progress.

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