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ELECTRONIC SPECTRA OF 1,1′-DIANTHRYLPOLY-YNES. A NOVEL LINEAR RELATION BETWEEN THE λ_{max} AND THE SQUARE OF THE NUMBER OF THE TRIPLE BONDS, n^2

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IN the course of the synthesis of macrocyclic tetra- and octa-acetylenes containing two anthracene nuclei[1], the present authors have synthesized 1,1′-dianthryldi-[2] and tetra-acetylenes[3] (V, n=2 and 4, respectively). It is now of interest to synthesize the corresponding tri-, penta- and hexa-acetylenes (V, n=3, 5 and 6) to compare their electronic spectra with those of the other poly-ynes and polyenes. The synthesis of V (n=3, 5 and 6) has been carried out according to the sequence of reactions outlined in the following chart.

The properties of 1,1′-dianthrylpoly-ynes (V) and the intermediate substances are summarized in Table 1.

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1 S. Akiyama, S. Misumi and M. Nakagawa, Bull. Chem. Soc. Japan, 33, 1293 (1960) ; 35, 1289 (1962).

2 S. Akiyama and M. Nakagawa, ibid. 33, 1291 (1960).

3 S. Akiyama, S. Misumi and M. Nakagawa, ibid. 35, 1826 (1962).

The analytical and infrared spectral data of the substances listed in Table 1 are in accord with the assigned structures.

The electronic spectral data of 1,1'-dianthrylpoly-ynes (V) are summarized in Table 2, and their absorption curves are illustrated in Fig. 1.

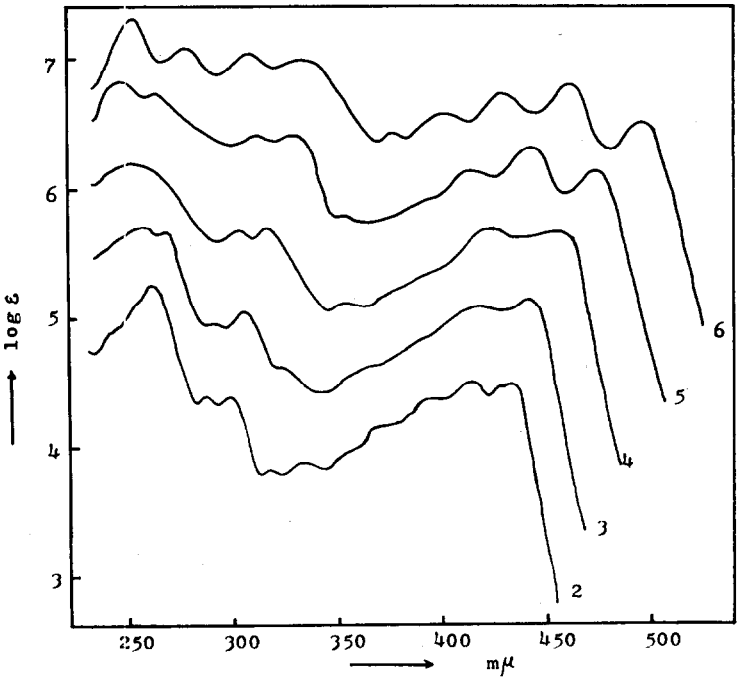
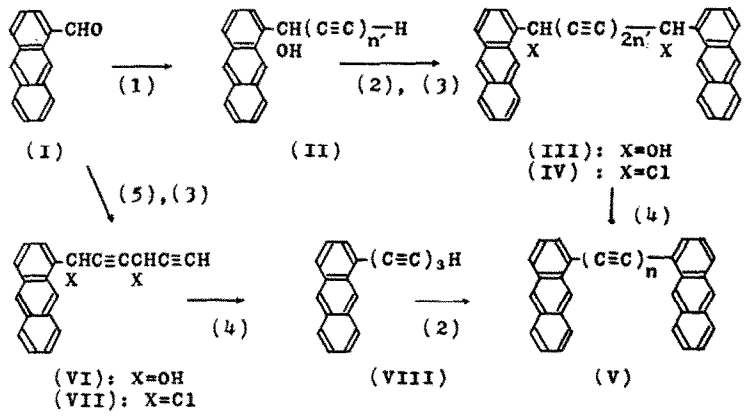


FIG. 1

The Absorption Curves of 1,1'-Dianthrylpoly-ynes (V)

The curves, with the exception of the diacetylene at the bottom, have been displaced upward on the ordinate axis by 0.5·log ε unit increments from the curve immediately below.

It is well known that the square of the wavelength of the absorption maxima (λ_{max}) varies linearly with the number of the conjugated multiple bonds (n) in some series of poly-



(1) $LiC{\equiv}CH$ ($n'=1$) and $Li(C{\equiv}C)_2H$ ($n'=2$); (2) $Cu(OCOCH_3)_2$ in pyridine; (3) $SOCl_2$ in tetrahydrofuran and pyridine; (4) $NaNH_2$ in liq. NH_3; (5) $BrMgC{\equiv}CCH(OMgBr)C{\equiv}CH$

III ($n'=2$), IV ($n'=2$) and VIII (yellow needles, extremely unstable) were used without purification.

TABLE 1

Properties of 1,1'-Dianthrylpoly-ynes (V)

and the Related Compounds

	m.p. (°C)	colour and crystal form
II, $n'=1$	120	pale yellow tiny cubes
III, $n'=1$	135-140	pale yellow tiny cubes
IV, $n'=1$	165-170 (dec.)	yellow fine needles
II, $n'=2$	106-109 (dec.)	pale yellow fine needles
VI	166	pale yellow fine leaflets
V, $n=3$	ca. 270 (dec.)	yellow leaflets
V, $n=5$	ca. 220 (dec.)	orange fine needles
V, $n=6$	ca. 210 (dec.)	red fine needles

TABLE 2

The Spectral Data of 1,1′-Dianthrylpoly-ynes (V)

n	λ_{max} in mμ and log ε (in parentheses) in tetrahydrofuran										
2	260 (5.27)		285 (4.39)	297 (4.42)	317 (3.80)	332 (3.89)	349* (3.90)	367 (4.14)	391 (4.36)	410 (4.50)	430 (4.46)
3	256 (5.20)	263 (5.17)	287 (4.45)	304 (4.55)	320* (4.10)	380* (4.24)	406* (4.50)	420 (4.53)	440 (4.62)		
4	250 (5.20)		299 (4.67)	315 (4.71)	352 (4.09)	370* (4.12)	390* (4.34)	422 (4.62)	456 (4.61)		
5	252 (5.30)	265 (5.16)	312 (4.86)	328 (4.88)	354 (4.26)	380* (4.30)	410 (4.60)	440 (4.79)	473 (5.61)		
6	254 (5.29)	273 (5.05)	307 (5.00)	325 (4.96)	373 (4.38)	397 (4.53)	425 (4.75)	457 (4.81)	494 (4.50)		

Asterisk indicates the shoulder.

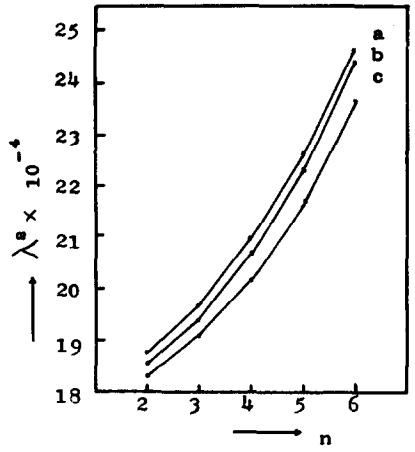


FIG. 2

Plot of λ^s_{max} versus n for 1,1′-Dianthrylpoly-ynes (V)

a: benzene ; b: tetrahydrofuran ; c: cyclohexane

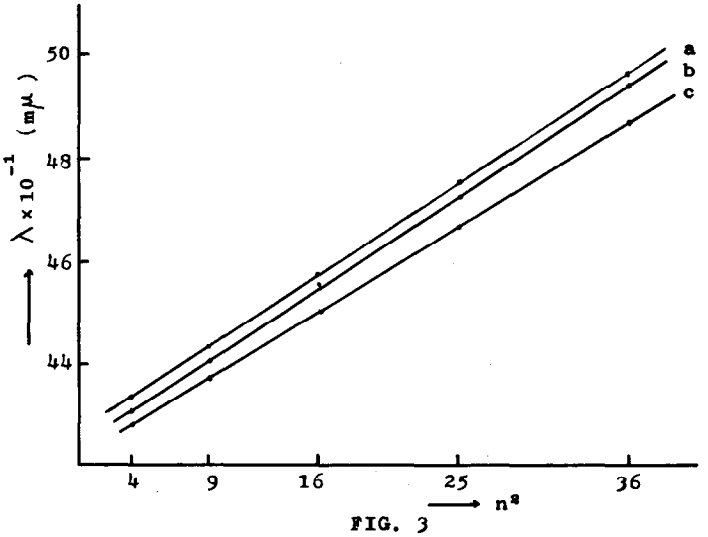


FIG. 3

Plot of λ_{max} versus n^2 for 1,1′-Dianthrylpoly-ynes (V)

a: benzene ; b: tetrahydrofuran ; c: cyclohexane

enes[4] and poly-ynes[5] ($\lambda^{2}_{max} \propto n$). On the other hand, a linear relation between the λ_{max} and the n ($\lambda_{max} \propto n$) in some charge-resonance systems such as cyanine dyes and polyene - Lewis acid complexes was also well recognized[5].

It was anticipated that the plots of λ^{2}_{max} of the polyynes (V) versus n might give a straight line as in the case of other series of poly-yne compounds. But in fact, the linear relationship did not hold in these polyacetylenes as illustrated in Fig. 2. Unexpectedly, a linear relation was obtained by plotting the λ_{max} of the longest wavelength peaks against n^2 (Fig. 3). This linear relationship could be expressed by the following empirical formulae with excellent agreement with the observed values. The observed and calculated values of these peaks are given in Table 3.

$\lambda_{max} = 2.0n^2 + 425$ mμ (benzene)

$\lambda_{max} = 2.0n^2 + 422$ mμ (tetrahydrofuran)

$\lambda_{max} = 1.85n^2 + 420.5$ mμ (cyclohexane)

The novel relationship ($\lambda_{max} \propto n^2$) seems to indicate the pronounced contribution of the 1-anthryl end-groups to the electronic excitation of the polyacetylenic chromophore. The further studies on the synthesis and the spectral proper-

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4 L. N. Ferguson, Chem. Revs., 43, 408 (1948) and references cited therein.

5 H. H. Schlubach and V. Franzen, Ann., 573, 110 (1951) ; J. B. Armitage, N. Entwistle, E. R. H. Jones and M. C. Whiting, J. Chem. Soc., 1954, 147 ; C. L. Cook, E. R. H. Jones and M. C. Whiting, ibid. 1952, 2883.

TABLE 3

The Wavelength of the Longest Absorption Maxima

n	λ_{max} (mμ) benzene obs.	calc.	tetrahydrofuran obs.	calc.	cyclohexane obs.	calc.
2	433	433	430	430	428	428
3	443	443	440	440	437	437
4	457	457	456	454	450	450
5	475	475	473	472	466	467
6	496	497	494	494	487	487

ties of 2,2′- and 9,9′-dianthrylpoly-ynes are now in progress in order to get further information on the role of the end-groups in the electronic excitation of poly-yne system.

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The details and the theoretical part of this research will be published elsewhere.