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Fluorescence Spectra Characteristics of α,ω-Di-1- and 9-Anthrylpoly-ynes

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ABSTRACT

*It has been found that the longest-wavelength of the absorption maxima (λ_L) in the electronic spectra of both the α,ω-diarylpoly-yne and polyene series varies linearly with the xth power of the number (n) of multiple bonds [$\lambda_L \propto n^x$, the value of x changes with both the structure of the terminal groups and the position of substitution of the unsaturated chain, e.g. $x = 2$ for α,ω-Di-1- and 9-anthrylpoly-ynes (**1**$_n$ and **2**$_n$, $n = 1$–6)]. The results are different from the formerly accepted regularity ($\lambda_L^2 \propto n$). The paper describes the fluorescence spectra characteristics of a series of **1**$_n$ and **2**$_n$. The results of this investigation shows that, as in the case of the absorption spectra, both the excitation maxima (λ_{ex}) and the emission maxima (λ_{em}) in the fluorescence spectra of **1**$_n$ and **2**$_n$ have a linear relationship with n^2 ($\lambda_{ex} \propto n^2$ and $\lambda_{em} \propto n^2$, respectively).*

INTRODUCTION

A linear relationship between the wavelength of absorption maxima (λ) and the number (n) of multiple bonds has been recognized for many years in a

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series of charge resonance systems, e.g. cyanine dyes.[1-5] Similarly, it has been considered that the square of the wavelength (λ_L^2) of the longest-wavelength absorption maxima of a series of linear polyenes[6-9] and linear poly-ynes[10,11] varies with n ($\lambda_L^2 \propto n$). However, we have found that the λ_L of 12 series of diarylpoly-ynes [Ar(C≡C)$_n$Ar, $n = 1$–6][12] and five series of diarylpolyenes [Ar(CH=CH)$_n$Ar, $n = 1$–6][13] bearing various types of aromatic terminal groups can be represented by the linear relationship:

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

The value of x varies from 0·5 to 2 ($0{\cdot}5 \leqq x \leqq 2$) depending on the nature of the terminal groups and on the position of linking of the unsaturated chain.

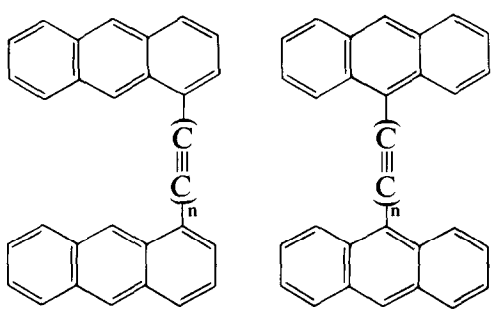
The linear relation in the diarylpoly-yne series could be explained satisfactorily on the basis of HMO calculation, assuming that the resonance integrals associated with the triple and single bonds of the poly-yne system should alter with n and be expressed by

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

and

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

respectively.[12] Similarly, the linear relation in a series of diarylpolyenes could be reproduced fairly well by the HMO method[13] based on a usual bond-alternation approximation.



1$_n$ **2**$_n$

In view of the interesting absorption spectral regularity found in the series of diarylpoly-ynes (**1**$_n$ and **2**$_n$), their fluorescence spectra behaviour is of considerable interest. However, until now almost no systematic fluorescence spectra data on a series of linear conjugated compounds have been reported. In this paper, the authors report fluorescence spectra data and the spectral behaviour of **1**$_n$ and **2**$_n$ (**n** = 1–6).

RESULTS AND DISCUSSION

As representatives of the series, the fluorescence spectra of $\mathbf{1}_2$ are shown in Fig. 1, in which the excitation spectra are similar to those of anthracene and the emission spectra consist of two clear bands. It was observed that the curves of both the excitation and emission spectra of $\mathbf{1}_n$ and $\mathbf{2}_n$ became progressively broader with increase in the length of the poly-yne chain ($n = \mathbf{n}$). The fluorescence spectra data (λ_{ex}, the longest-wavelength maxima; λ_{em}, the shortest-wavelength maxima corresponding to λ_{ex}) of $\mathbf{1}_n$ and $\mathbf{2}_n$ in tetrahydrofuran (THF) are shown, together with the longest-wavelength absorption maxima (λ_L) in Table 1. It is apparent from Table 1 that λ_{ex} is almost the same as the corresponding λ_L and the order of decrease of the relative fluorescence intensity (RFI) is

$$\mathbf{1}_2 > \mathbf{1}_1 \gg \mathbf{2}_3 \gg \mathbf{1}_3 > \mathbf{2}_1 > \mathbf{2}_2 \gg \mathbf{1}_4,\ \mathbf{2}_4 > \mathbf{2}_5 > \mathbf{1}_5 \gg \mathbf{2}_6 > \mathbf{1}_6$$

Figure 2 shows the correlation between the excitation and emission maxima

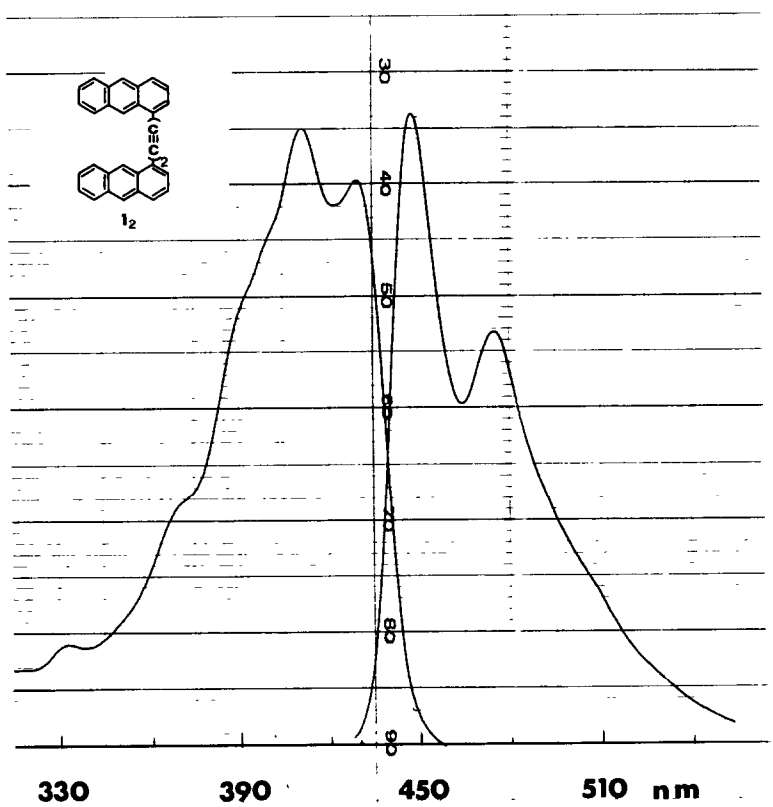


Fig. 1. Fluorescence spectra of $\mathbf{1}_2$ in THF.

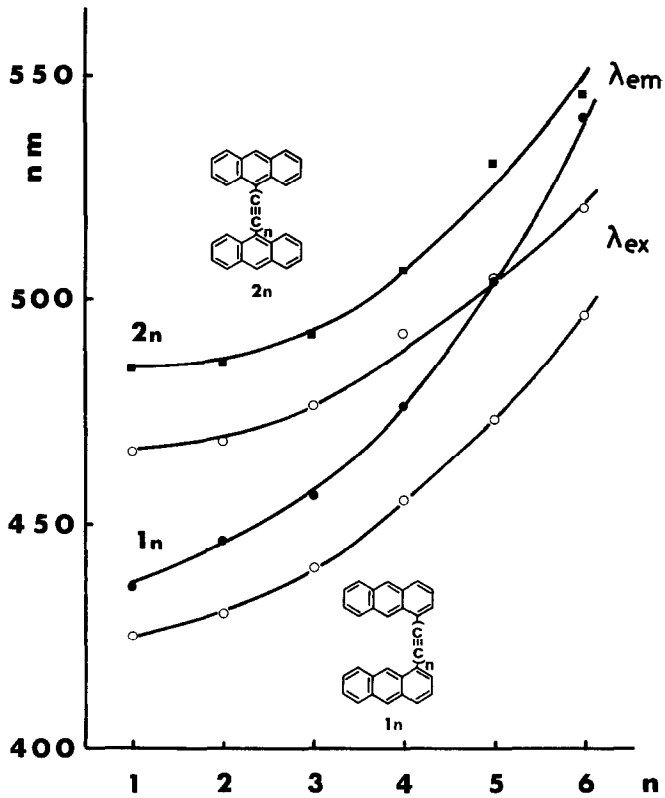


Fig. 2. Plots of λ_{ex} and λ_{em} versus n.

TABLE 1
Absorption and Fluorescence Spectra Data of $\mathbf{1}_n$ and $\mathbf{2}_n$ in THF

Poly-yne	λ_{max} (*nm*)	λ_{ex} (*nm*)	λ_{em} (*nm*)	*RFI*
$\mathbf{1}_1$	425	425	436	100
$\mathbf{1}_2$	430	430	446	130
$\mathbf{1}_3$	440	440	456	15
$\mathbf{1}_4$	456	455	476	0·9
$\mathbf{1}_5$	456	473	503	0·1
$\mathbf{1}_6$	473	496	540	0·04
$\mathbf{2}_1$	457	466	485	8
$\mathbf{2}_2$	470	468	486	3
$\mathbf{2}_3$	479	476	492	52
$\mathbf{2}_4$	491	492	506	0·9
$\mathbf{2}_5$	505	504	530	0·3
$\mathbf{2}_6$	523	520	545	0·07

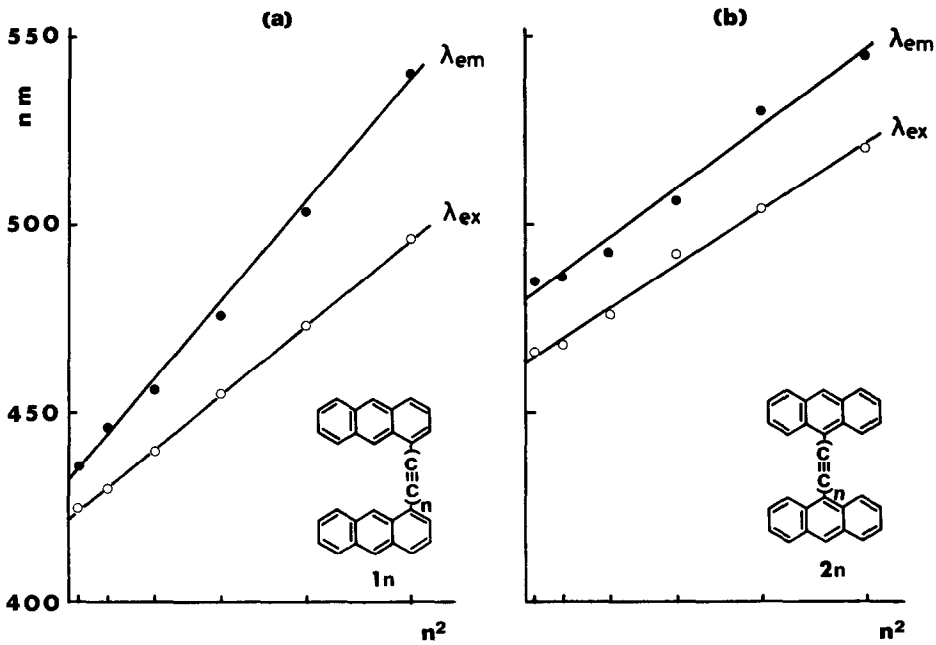


Fig. 3. Linear relationships between fluorescence maxima (λ_{ex} and λ_{em}) and n^2.

of $\mathbf{1}_n$ and $\mathbf{2}_n$ with n (= **n**), and it is characteristic that the emission maximum of $\mathbf{1}_6$ is near that of $\mathbf{2}_6$.

It has been pointed out that a plot of λ_L against n^2 gives a straight line in each case of the poly-yne series ($\mathbf{1}_n$ and $\mathbf{2}_n$).[1,2] The concave curves shown in Fig. 2 seem to suggest that the shifts of λ_{ex} and λ_{em} of the two types of poly-ynes might be proportional to n^2. As shown in Fig. 3 (a) and (b), fairly good linearities between the observed fluorescence maxima (λ_{ex} and λ_{em}) and n^2 are obtained. The equations obtained by linear regression analysis are shown in Table 2 together with those of absorption maxima.

TABLE 2
Linear Regressions

Poly-yne	$\lambda = A \times n^2 + B$ (*nm*)	*CC*[a]
$\mathbf{1}_n$	$\lambda_L = 2{\cdot}0 \times n^2 + 423$	0·999 5
	$\lambda_{ex} = 2{\cdot}0 \times n^2 + 422$	0·999 8
	$\lambda_{em} = 2{\cdot}9 \times n^2 + 432$	0·998 0
$\mathbf{2}_n$	$\lambda_L = 1{\cdot}65 \times n^2 + 464$	0·999 7
	$\lambda_{ex} = 1{\cdot}6 \times n^2 + 463$	0·999 8
	$\lambda_{em} = 1{\cdot}85 \times n^2 + 479$	0·990 4

[a] Correlation coefficient.

CONCLUSION

It was found that, in two dianthrylpoly-yne series ($\mathbf{1}_n$ and $\mathbf{2}_n$), excellent linear relationships (as in the case of λ_L) exist between λ_{ex} and λ_{em} respectively and the square of *n*.

EXPERIMENTAL

The synthesis of the dianthrylpoly-ynes ($\mathbf{1}_n$ and $\mathbf{2}_n$) has been reported previously.[12] Fluorescence spectra were recorded on a Hitachi 650-10S fluorescence spectrophotometer using matched 10 mm × 10 mm quartz cells. THF was purchased from Wako Pure Chemicals Co. Ltd, Japan, and distilled before use. The concentrations of the sample solutions used for measurements of fluorescence spectra were $5{\cdot}5 \times 10^{-7}$ M.

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