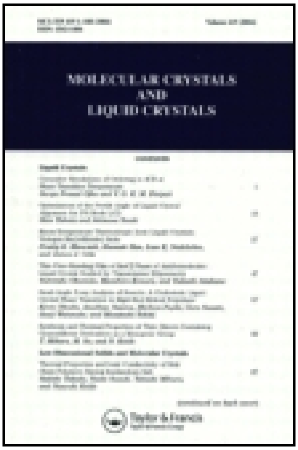

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Molecular Design of Polycyclic Aromatic Hydrocarbons Based on Computer Experiments

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MOLECULAR DESIGN OF POLYCYCLIC AROMATIC HYDROCARBONS BASED ON COMPUTER EXPERIMENTS

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Abstract The computer-assisted molecular design for PAHs which absorb in longer wavelength region was performed under PPP approximation. To predict the absorption wavelength accurately, the new-γ was used. The relationship between the annellation of PAHs and accompanying shift of the *p*-band was discussed.

INTRODUCTION

Langmuir-Blodgett (LB) films of organic dyes possessing long alkyl chains have attracted much attention as possible future materials for electronics and photonics.[1] The desired absorption wavelengths of dyes vary with the purpose to be used. The concept of 'molecular design' is effective to control the absorption wavelengths of dyes.[2] Nowadays, 'computer-assisted molecular design' is widely used, however, it is not satisfactory for the prediction of the absorption wavelengths of dyes, especially, in longer wavelength region.[3]

Polycyclic aromatic hydrocarbons (PAHs) are fundamental organic compounds possessing π-conjugated system which influences seriously on their color. Throughout our previous studies,[4,5] we proposed effective methods to predict the absorption wavelengths of the *p*-band of PAHs using Parisr-Parr-Pople (PPP) molecular orbital (MO) calculations containing a novel two-center electron repulsion integral new-γ [$\gamma_{rs} = e^2/(R_{rs}+ka_{rs})$].[6] The calculated results reproduced well the observed wavelengths, compared with the calculated ones using the conventional PPP MO method.

In this paper, we report a simple guideline to design PAHs which absorb in longer wavelength region. The absorption wavelengths of the *p*-bands of unknown PAHs were predicted by computer experiments.

RESULTS AND DISCUSSION

PPP MO calculations were performed with a computer software PPP-PC[2] as in our previous papers.[4,5] The concept of spectroactive portion (SP) was proved to be effective[5] for the prediction of the electronic spectra of the *p*-band of PAHs. As represented in Figure 1 using bold lines, the SPs of PAHs **1**-**9** are the acene-like branch portion of PAHs. We defined the number of hexagons included in the SP of PAHs as parameter *l*, and the regression expression (1) to evaluate the spectrochemical softness parameter *k* was derived by computer experiments.[5]

$$k = 0.33\, l + 0.48 \qquad (1)$$

The absorption wavelengths of the *p*-band of acenes (**1**, n = 0-9) were calculated using the new-γ which contains the k values evaluated from expression (1). The calculated absorption maxima ($\lambda_{\mathrm{calc.}}$) increase almost linearly with the number of six-membered rings n, as represented by regression expression (2) obtained by a least-squares method.

$$\lambda_{\mathrm{calc.}} = a \cdot n + b \qquad (2)$$

The values of statistical parameters a (slope), b (intercept), and r (correlation coefficient) are shown in Table 1. The observed absorption maxima ($\lambda_{\mathrm{obs.}}$) of **1** (n = 0-5) also increase linearly with the number of six-membered rings n.[7] The discrepancy between the value of a (92 nm) in the expression (2) and the value of average increment (89 nm) evaluated from $\lambda_{\mathrm{obs.}}$ was only 3 nm. These results indicate that the predicted wavelengths of **1** (n = 6-9), of which observed data have not been reported,[8] are reliable.

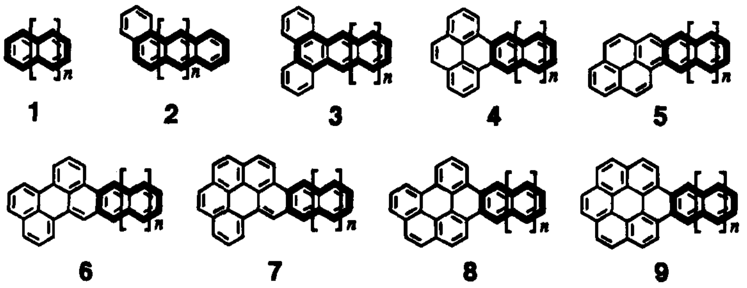


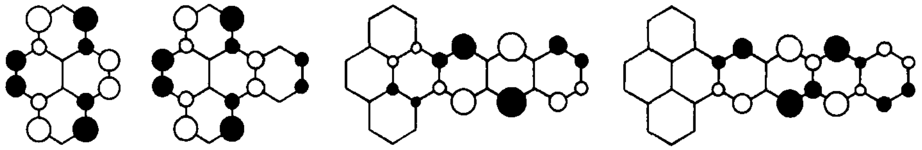
FIGURE 1 Structural formulae of PAHs.

TABLE 1 Relationship between the annellation and the shift of wavelength of the *p*-band of PAHs [$\lambda_{calc.} = a \cdot n + b$; where *a* is a slope, *b* is a intercept, and *r* is a correlation coefficient].

Compound	region of *n*	*a*	*b*	*r*
1	0 - 9	92	194	0.9995
2	1 - 8	93	254	0.9998
3	1 - 8	94	136	0.9983
4	1 - 7	88	234	0.9988
5	1 - 7	81	342	0.9992
6	2 - 6	82	294	0.9984
7	2 - 6	87	239	0.9996
8	2 - 6	83	303	0.9994
9	2 - 6	84	272	0.9990

Observed data for PAHs **2**-**9** of absorption wavelengths have been scarcely reported.[8] The absorption wavelengths of these PAHs were calculated using the new-γ, and statistical parameters *a*, *b*, and *r* for expression (2) were evaluated [Table 1] (by the reason described below, the evaluations were performed except for the compounds possessing small *n* values). As the values of correlation coefficient *r* are close to 1, expression (2) seems to be meaningful for the PAHs **2**-**9**. If we use expression (2) for each PAH of **2**-**9**, prediction of the absorption wavelengths of the *p*-band will be the most practical, because individual PPP MO calculations are not necessary.

When the values of *n* in PAHs **2**-**9** are very small ($n = 0, 1, 2, \cdots$), $\lambda_{calc.}$ do not increase linearly. With the increase of the values of *n* ($n = 2, 3, 4, \cdots$), however, $\lambda_{calc.}$ increase linearly, as is shown in the series of acenes (**1**, $n = 0, 1, 2, \cdots$). In other words, when the values of *n* are small, π-conjugated system of a molecule extends insufficiently in PAHs **2**-**9**. When the values of *n* increase, however, π-conjugated system in a molecule extends sufficiently, so that $\lambda_{calc.}$ increase linearly. These results are also supported from the consideration of LCAO coefficients of HOMO of **2**-**9**, since the *p*-band is assigned to a $\pi \rightarrow \pi^*$ transition described mainly as HOMO → LUMO transition.[8] For example, the character of HOMO in benzo[*e*]pyrene homologues (**4**) changes from the pyrene skeleton [Figure 2*a*] to the acene-like branch portion along with the increase of the value of *n* [Figure 2*c*, *d*].



a : pyrene ***b*** : **4** (*n* = 0) ***c*** : **4** (*n* = 2) ***d*** : **4** (*n* = 3)

FIGURE 2 The LCAO coefficients of HOMO of pyrene (*a*) and **4** (*b*-*d*).

In conclusion, the expression (2), namely, a simple guideline for the prediction of the absorption wavelengths of the *p*-band of PAHs **1-9**, was obtained by computer experiments. A guideline of molecular design of various PAHs will be accomplished utilizing similar procedure.

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