MOLECULAR DESIGN OF POLYCYCLIC AROMATIC HYDROCARBONS BASED ON PRECISE PPP MOLECULAR ORBITAL CALCULATIONS

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Applying the procedure of precise Pariser-Parr-Pople molecular orbital (PPP MO) calculations, in which a novel two center electron repulsion integral new- γ was used and spectrochemical softness parameter in the new- γ was evaluated based on the spectroactive aromatic sextet resonance system (ASRS) of a molecule, the wavelengths of the *p*-band of acenes and their higher analogues were predicted. The relationship between the annellation and the shift of the wavelength of the *p*-band was revealed. The guideline to design PAHs which possess the long absorption wavelengths was proposed.

1. Introduction

The computer-assisted theoretical design of functional organic molecules has become possible along with the recent progress of computer science [1]. In various molecular orbital (MO) methods, non-empirical *ab initio* MO calculations is most sophisticated. However, *ab initio* MO calculations of electronic spectra of large organic molecules are expensive and impractical.

On the contrary, semi-empirical MO calculations, in particular Pariser-Parr-Pople (PPP) MO calculations, have been considered to be more practical for the prediction of absorption maxima of organic colorants [2-4]. Nishimoto proposed a novel two center electron repulsion integral new- γ , which takes the spectrochemical softness into account, for the PPP MO calculations [5]. The new- γ was successfully applied for the precise calculations of absorption wavelengths of the *p*-band, which especially affects the visual color, of polycyclic aromatic hydrocarbons (PAHs) [6-9]. The calculated results using new- γ were more accurate than the ones using the conventional Nishimoto-Mataga γ ($N \cdot M \cdot \gamma$) function [10].

In this paper, we would like to report the relationship between the annellation of acenes (1) and their higher analogues (2-4) (Fig. 1) and the shift of the wavelength of the *p*-band of them by means of the precise PPP MO calculations. We propose the guideline of the molecular design of PAHs which possess the long absorption wavelengths.

Fig. 1 Structural formulae; spectroactive ASRS is represented using bold lines

2. Method

PPP MO calculations were performed with a computer software PPP-PC [4,11] in which variable β approximation [12] and the conventional parameters set [4,13] were used. For two center electron repulsion integral, either the new- γ [5] or the N·M- γ [10] was used with 25 lower singly excited configurations in CI calculations.

New- γ is represented as

$$\gamma = e^2 / (R_{rs} + k a_{rs}) \quad (1)$$

where R_{rs} is the interatomic distance (in Å) between the r -th and s -th atoms in a molecule containing π -electrons; a_{rs} is given by

$$a_{rs} = 2e^2 / (I_r - A_s + I_s - A_r) \quad (2)$$

where e^2 is $14.397 \text{ eV} \cdot \text{\AA}$, I_r [I_s] and A_r [A_s] are the valence state ionization potential and the electron affinity, respectively. Thus, k is a dimensionless parameter which indicates the relative magnitude of mobile π -electron polarization at the region between r -th and s -th atoms, namely, the spectrochemical softness of π -electrons [5]. When the value of k is 1, new- γ is equivalent to the N·M- γ .

3. Results and Discussion

Acenes (1) are the most fundamental series in PAHs, and the absorption wavelengths of the p -band of them shift toward longer wavelengths along with the annellation [14,15]. We defined acenes as aromatic sextet resonance system (ASRS) based on the essential character of their mobile π -electrons [7]. On the contrary, the absorption wavelengths of the p -band of zig-zag phenes (phenanthrene, chrysene, picene, and so on) shift toward longer wavelengths more slightly compared with those of acenes, along with the annellation. We defined zig-zag phenes as aromatic sextet alternation system (ASAS), because their π -electrons trend to localize at the particular positions of the molecular framework [7].

The parameter k suitable for the calculations of the absorption wavelengths of the p -band of PAHs were evaluated based on the spectroactive ASRS of a molecule [9]. The spectroactive ASRS

Table 1 Calculated and observed absorption wavelengths of the *p*-band of PAHs 1-4

Compound	<i>n</i>	$\lambda_{obs.}^a$	$\lambda_{calc.}$		
			N·M- γ^b	new- γ^c	Clar ^d
1	0	208	201	211	205
	1	283	281	282	279
	2	367	356	373	364
	3	458	420	461	461
	4	556	481	556	569
	5	653	534	649	689
	6		581	756	820
	7		619	848	962
	8		651	939	1116
	9		678	1023	1281
2	0	283	281	282	
	1	417	407	413	
	2	524	501	513	
	3	611	579	596	
	4		642	663	
3	0	367	356	373	
	1	614	566	608	
	2		769	837	
	3		972	1056	
4	0	244	258	260	
	1	417	407	413	
	2	614	566	608	
	3		711	817	
	4		840	1010	

^a Extrapolated values to the gas phase (references 14 and 16). ^b Conventional Nishimoto·Mataga γ function. ^c New- γ based on the spectroactive ASRS. ^d Prediction using Clar's expression (reference 14).

is a portion which contributes mainly to the electronic spectra of PAHs. We defined the number of hexagons included in the spectroactive ASRS of PAHs as a parameter *l*. The regression expression (3) to evaluate the spectrochemical softness parameter *k* was shown as follows [9]:

$$k = 0.33 l + 0.48 \quad (3)$$

The spectroactive ASRSs of PAHs 1-4 are represented using bold lines in Fig. 1, and parameter *k* for them are evaluated using expression (3).

The calculated wavelengths in the gas phase of the *p*-band of acenes (1) using the new- γ or the N·M- γ are shown in Table 1. Clar proposed the empirical expression (4) to predict wavelengths of 1 as follows [14]:

Table 2 The statistical parameters for the linear relationship between the number of π -electrons and the absorption wavelengths of the p -band of PAHs 1-4

($\lambda = a \cdot PE + b$; r is a correlation coefficient)

Compound	n	a	b	r
1	0~9	23.1	55.2	0.9995
2	0~4	9.5	209.9	0.9916
3	0~3	16.3	149.0	0.9999
4	0~4	23.8	-44.8	0.9987

$$\lambda_p = D^2/16R \quad (4)$$

where D is the number of reciprocal nuclear charges, and R is the Rydberg constant. The calculated wavelengths using expression (4) for pentacene and hexacene (1, $n=4$ and 5) are longer than the observed ones (Table 1), so the predicted values for long acenes may be overestimated. On the other hand, the calculated wavelengths using the N·M- γ are shorter than the observed ones. The calculated wavelength using new- γ may be more reasonable than other predicted ones, judging from the curve depicted in Fig. 2.

The wavelengths of annellated acenes derived formally by connecting all the *peri*-positions of acenes are calculated. The first member of them is "rylene" [14] series (2) which are annellated analogues of naphthalene (1, $n=1$). The spectroactive ASRS of perylene (2, $n=1$) is naphthalene unit, so the spectroactive ASRSs of other member of rylene series may be also naphthalene unit ($l=2$, $k=1.14$). In fact, the calculated wavelengths of the p -band of 2 ($n=0-3$) using new- γ in which the parameter k is evaluated as 1.14 reproduce well the observed ones (Table 1). Similarly, the spectroactive ASRSs of "anthene" [14] series (3) are regarded as anthracene unit ($l=3$, $k=1.47$). The calculated wavelengths of the p -band of 3 ($n=0-3$) are shown in Table 1. The wavelengths of the p -band of 4 ($n=0-4$), which are regarded as higher analogues of biphenyl and contains perylene (2, $n=1$) and bisanthene (3, $n=1$), are calculated (Table 1) to compare with those of 2 and 3.

The relationships between the annellation and the shift of the p -band of 1-4 are shown in Fig. 3. To evaluate them quantitatively, the statistical parameters for the linear relationship between the calculated wavelengths and the number of π -electrons (PE) of 1-4 are used (Table 2): $\lambda_p = a \cdot PE + b$, where a is a slope, b is a intercept, and r is a correlation coefficient of this regression expression, respectively. For 2 and 3, the values of a are lower than that of 1. Thus, the extension of π -conjugated system in 2 or 3 poorly contributes to the shift toward longer wavelength of the p -band, compared with that of 1. In other words, the annellation from 1 to 2 or 3 poorly contributes to the extension of π -conjugated system. It is supported that the calculated bond order in the ground state of the bonds which connected two naphthalene units of perylene (2, $n=1$) using PPP MO calculations is 0.33, which is lower than that of other bond (Fig. 4). Thus, the character of the bonds which connected two naphthalene units is close to that of single bond.

Fig. 2 The number n of acenes (1) vs. the observed and calculated wavelengths of the p -band

Fig. 3 The number of π electrons PE of 1-4 vs. the calculated wavelengths of the p -band

On the other hand, the extension of π -conjugated system in **4** contributes to the shift toward longer wavelength of the p -band likewise that in **1**. The value of a of **4** is not two times of that of **1**, but almost identical with that of **1**. Thus, the annellation manner in **1** seems to be most effective to obtain PAHs which possess the long absorption wavelengths.

Large PAHs are in general not easily accessible because of their high reactivity and poor solubility in common organic solvents. Koch *et.al.* [17] synthesized the four *tert*-butyl substituted derivative in the β -position of **2** ($n=4$) which is sufficiently soluble in organic solvent to investigate their photophysical properties. Utilizing this method, some novel molecular frameworks described in this paper may be synthesized.

Fig. 4 Bond order in the ground state

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