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Precise PPP molecular orbital calculations of excitation energies of polycyclic aromatic hydrocarbons. Part 5☆ Spectroactive portion of fluoranthene derivatives

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Abstract

For Pariser–Parr–Pople molecular orbital (PPP MO) calculations of the *p*-band of fluoranthene derivatives, the values of the spectrochemical softness (SCS) parameter k in a novel two centre electron repulsion integral new-γ were evaluated based on the spectroactive portion (SP) of a molecular framework. The SP was determined by the character of MO calculated by the HMO method with reference to the structural analysis by ab initio MO calculations with 6-31G* level. The calculated excitation energies of the *p*-band of fluoranthene derivatives using the new-γ including k values based on the SP reproduced accurately the observed ones.

Keywords: PPP MO calculations; Fluoranthene derivatives; *p*-Band; New-γ; Spectrochemical softness parameter; Spectroactive portion

1. Introduction

In our previous papers dealing with PPP MO calculations of excitation energies of the *p*-band (nomenclature by Clar [2]: corresponds to Platt's ^1L_a band [3]) of alternate polycyclic aromatic hydrocarbons (PAHs) [4–6], the new-γ [7] was successfully applied. The calculated excitation energies were greatly improved for many alternate PAHs in comparison with the calculated ones using the conventional N·M-γ [8].

The SCS parameter k in the new-γ can be evaluated based on the absolute hardness η of a given molecule [4], spectroactive portion (SP) of the molecular framework [5,6], or Dewar-type resonance energies [1]. The SP contributes mainly to the electronic spectra of PAHs [5], and it is the most favorable index to evaluate the SCS parameter k in the above three indices [1].

In this paper, we extend the evaluating method of the SCS parameter k in the new-γ based on SP to non-alternate PAHs for precise calculation of the excitation energies of the longest absorption band (*p*-band). Formulae of non-alternate fluoranthene derivatives used for the calculation are shown in Fig. 1.

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2. MO calculations

PPP MO calculations were performed with a computer software revised PPP-PC [9], in which variable β approximation [10] and the conventional parameters set [9,11,12] were used as in our previous papers [1,4–6]. For two centre electron repulsion integral, the following new-γ was used. To compare with the calculated results, the conventional N·M-γ was also used. Twenty-five lower singly excited configurations were used in the CI calculations.

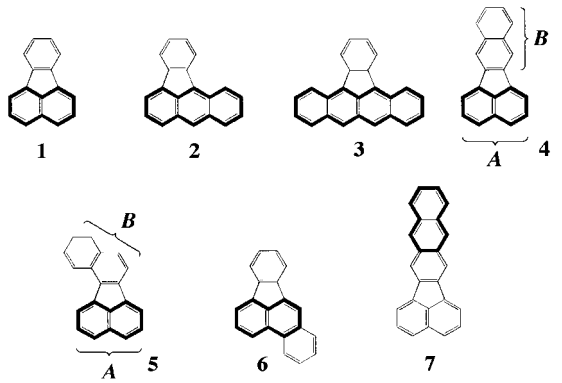

Fig. 1. Structural formulae of calculated non-alternate fluoranthene derivatives; SP is represented using bold lines.

Table 1
Values of SCS parameter k corresponding to SP

l[a]	2	3	4
k	1.14	1.47	1.80

[a] Number of six-membered rings contained in SP.

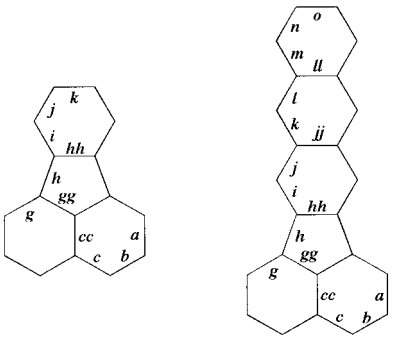

Fig. 2. Symboling scheme of compounds **1** and **7**.

When the mobile π-electron polarization at the region between the r-th and the s-th atoms in a molecule is considered as follows,

$$R^+ - S^- \text{ and } R^- - S^+$$

the new-γ is represented as in Eq. (1):

$$\gamma_{rs} = e^2/\left[\left(R_{rs} + 2k_{rs}e^2\right)/(I_r - A_s + I_s - A_r)\right] \quad (1)$$

where R_{rs} is the interatomic distance (in Å) between the r-th and the s-th atoms, e^2 is 14.397 eV·Å, I_r [I_s] and A_r [A_s] are the valence state ionization potential and the valence state electron affinity, respectively [7]. Essentially, k_{rs} is the relative magnitude of the dynamical polarizability of mobile π-electrons at the region between the r-th

Table 2
The observed and calculated carbon–carbon bond lengths (in Å) in compounds **1** and **7**

Compound	Bond	Observed	Calculated ab intitio (6-31G*)	Calculated PPP (new-γ)
1	**a**	1.411	1.424	1.412
	b	1.368	1.366	1.383
	c	1.422	1.423	1.422
	cc	1.400	1.383	1.416
	g	1.367	1.360	1.390
	gg	1.411	1.413	1.426
	h	1.476	1.481	1.457
	hh	1.417	1.410	1.410
	i	1.384	1.380	1.404
	j	1.386	1.391	1.395
	k	1.379	1.387	1.400
7	**a**		1.422	1.410
	b		1.366	1.384
	c		1.422	1.421
	cc		1.387	1.416
	g		1.361	1.392
	gg		1.413	1.426
	h		1.479	1.452
	hh		1.458	1.433
	i		1.344	1.385
	j		1.440	1.427
	jj		1.430	1.428
	k		1.386	1.406
	l		1.393	1.407
	ll		1.422	1.426
	m		1.434	1.428
	n		1.349	1.377
	o		1.430	1.420

and the *s*-th atoms, namely, the 'spectrochemical softness' of π-electrons. When the value of k_{rs} is 1, the new-γ is equivalent to the N·M-γ. Large k_{rs} values are suitable for spectrochemically softer compounds such as polyacenes, except for benzene [4]. The *k* values shown in Table 1 were used for the calculation, corresponding to the number of six-membered rings in the SP [5].

The carbon–carbon bond lengths R_{c-c} calculated by PPP MO calculations can be evaluated from the Eq. (2) [10]

$$R_{c-c} = 1.517 - 0.180\rho \quad (2)$$

where ρ is the bond order.

Ab initio MO calculations with 6-31G* basis set were performed with a GAUSSIAN 94 program [13].

The observed excitation energies of given PAHs in an inert solvent were extrapolated to those in the gas phase in order to minimize solvent effects [2].

3. Results and discussion

3.1. *Fluoranthene* (**1**)

Fluoranthene **1** can be built up from a benzene unit (Fig. 2), a naphthalene unit and two bonds **h** and **n** which combine both units. The **h** and **n** bonds essentially belong to a π-conjugated system. However, they possess the nature of a single bond. The observed bond lengths obtained from X-ray crystallographic analysis [14] and the ab initio MO

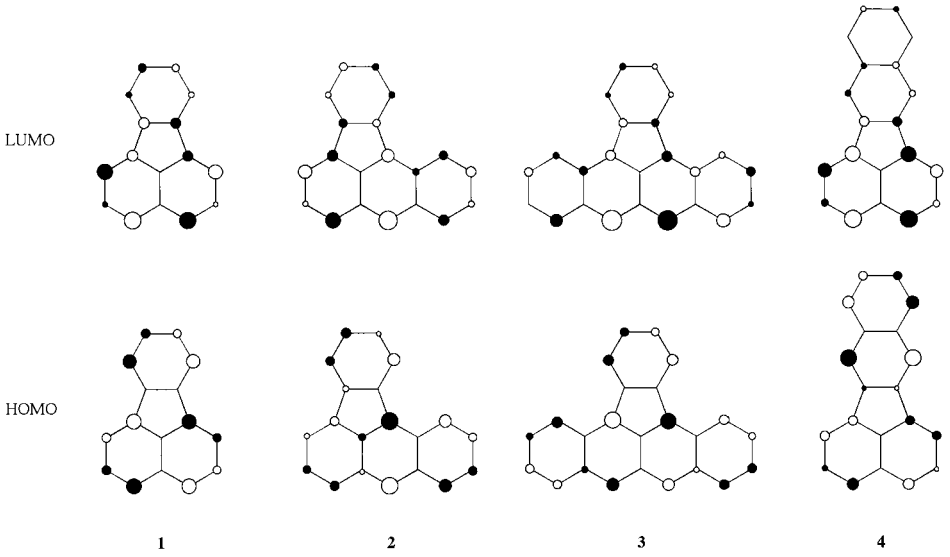

Fig. 3. The LCAO coefficients of HOMO and LUMO of compounds **1**, **2**, **3** and **4**.

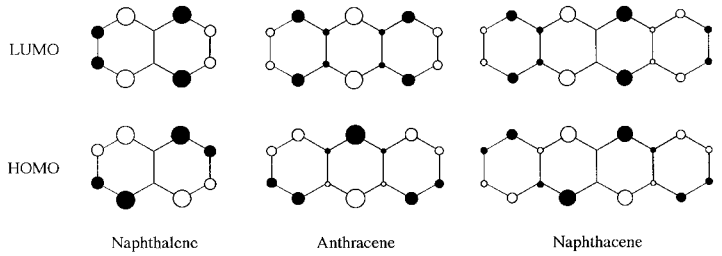

Fig. 4. The LCAO coefficients of HOMO and LUMO of polyacenes.

Table 3
The observed and calculated excitation energies (in eV) of the *p*-band of compounds **1**–**7**

Compound	$E_{obs.}$(gas phase)	$E_{calc.}$ [N·M-γ](f)	$E_{calc.}$ [new-γ](f)	Transition [N·M-γ] (coefficient)
1	3.57	3.61 (0.456)	3.56 (0.459) [$k = 1.14$]	H→L (0.954)
2	2.77[a]	2.88 (0.319)	2.72 (0.323) [$k = 1.47$]	H→L (0.875)
3	2.32	2.54 (0.522)	2.28 (0.469) [$k = 1.80$]	H→L (0.983)
4	3.21	3.26 (0.496)	3.20 (0.490) [$k = 1.14$]	H→L (0.919)
5	3.35	3.38 (0.409)	3.32 (0.406) [$k = 1.14$]	H-1→L (0.881)
6	3.47	3.47 (0.114) 3.53 (0.092) 3.59 (0.546) {3.56[b]}	3.41 (0.113) 3.47 (0.088) 3.54 (0.577) (3.51[b]} [$k = 1.14$]	H-2→L (0.769) H-1→L (0.889) H→L (0.831)
7	2.95	3.06 (0.641)	2.83 (0.573) [$k = 1.47$] 2.98 (0.616) [$k = 1.14$]	H→L (0.911)

[a] Shoulder.
[b] Weighted mean.

calculations with 6-31G* level [15] support the nature of the bonds (Table 2).

The character of the naphthalene HOMO is maintained in the naphthalene unit for the HOMO of **1** from the LCAO coefficients of the HOMO using HMO calculations (Figs. 3 and 4). Similarly, the character of the naphthalene LUMO is maintained in the naphthalene unit for the LUMO of **1** (Figs. 3 and 4). The longest absorption band (the *p*-band) is considered to be $\pi \rightarrow \pi^*$ transition of HOMO→LUMO by PPP MO calculations with the M·M-γ. Therefore, the SP of **1** is the naphthalene unit as shown in Fig. 1. The excitation energy of the *p*-band of **1** calculated by PPP MO calculations using the new-γ ($k = 1.14$: See Table 1) reproduced the observed value better than that by using the N·M-γ (Table 3). The calculated bond lengths also reproduced the observed ones, rather than those calculated by the ab initio method with 6-31G* level (Table 2).

*3.2. Benz[*a*]aceanthrylene* (**2**)*, Dibenzo[*a,d*]aceanthrylene* (**3**) *and Benzo[*k*]fluoranthene* (**4**)

From the LCAO coefficients of HOMO using HMO calculations, the character of the anthracene HOMO and LUMO are maintained in the anthracene unit for the HOMO and the LUMO of **2** (Figs. 3 and 4). Therefore, the SP of **2** is the anthracene unit (Fig. 1).

Similarly, the SP of **3** is determined to be the naphthacene unit (Figs. 1, 3 and 4). The excitation energies of the *p*-band of **2** and **3** calculated by PPP MO calculations using the new-γ (k = 1.47 and 1.80: see Table 1) reproduced the observed values in comparison with that by using the N·M-γ (Table 3).

For the HOMO of **4**, the character of the naphthalene HOMO is maintained in both **A** and **B** naphthalene units (Fig. 3). The character of the naphthalene LUMO is only maintained in the **A**

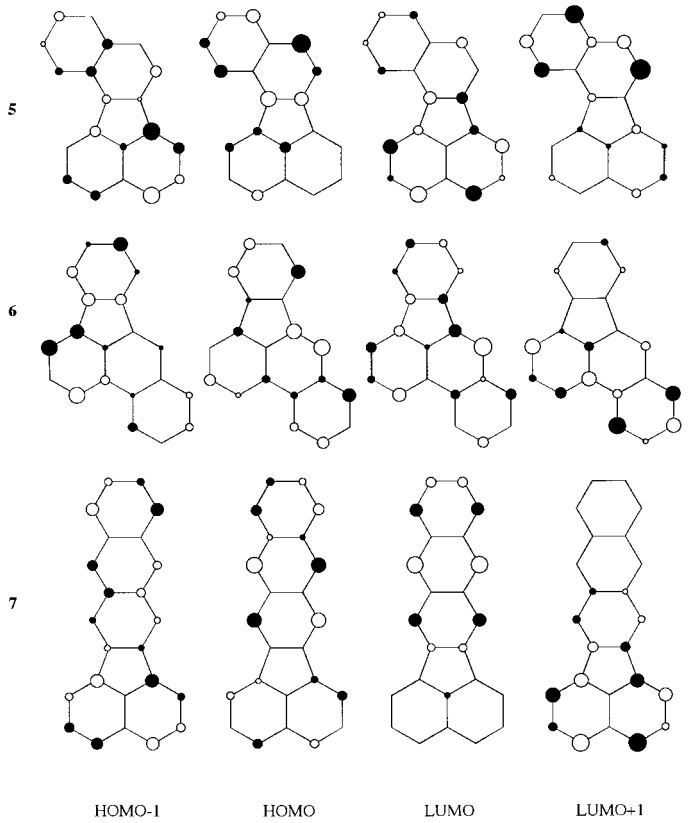

Fig. 5. The LCAO coefficients of HOMO-1, HOMO, LUMO and LUMO + 1 of compounds **5**, **6** and **7**.

naphthalene unit for the LUMO of **4** (Fig. 3). Therefore, the SP of **4** is determined to be the **A** naphthalene unit (Fig. 1). The excitation energy of the *p*-band of **4** calculated by PPP MO calculations using the new-γ ($k = 1.14$: see Table 1) reproduced better the observed value in comparison with that using the N·M-γ (Table 3).

3.3. *Benzo[j]fluoranthene* (**5**)

The first absorption band (*p*-band) of **5** is considered to be a $\pi \rightarrow \pi^*$ transition of HOMO-1→LUMO by PPP MO calculations using the N·M-γ. For the HOMO-1 of **5**, the character of the naphthalene HOMO is maintained in the **A** naphthalene unit (Fig. 5). The character of the naphthalene LUMO is maintained in the **A** naphthalene unit for the LUMO of **5** (Fig. 5). Therefore, the sp of **5** is determined to be the **A** naphthalene unit (Fig. 1). The excitation energies of the *p*-band of **5** calculated by PPP MO calculations using the new-γ ($k = 1.14$: see Table 1) reproduced well the observed value, as well as that using the N·M-γ (Table 3).

3.4. *Benzo[a]phenanthrylene* (**6**)

The SP of phenanthrene is a naphthalene unit which is the longest acene-like portion in the molecular framework, as described in our previous papers [5,6]. However, the character of the HOMO or the LUMO of naphthalene cannot be seen in the HOMO-1, the HOMO, the LUMO and the LUMO + 1 of **6** (Fig. 5).

From the PPP MO calculations using the N·M-γ, the first absorption band of **6** is considered to be a $\pi \rightarrow \pi^*$ transition of HOMO-2→LUMO, the second absorption band is considered to be a $\pi \rightarrow \pi^*$ transition of HOMO-1→LUMO, and the third absorption band is considered to be a $\pi \rightarrow \pi^*$ transition of HOMO→LUMO. The excitation

energies of the first, the second and the third absorption band are very close (Table 1). Thus, the observed excitation energy of the *p*-band may be the combination of the above three absorption bands.

We assumed that the SP of **6** is the naphthalene unit in the phenanthrene unit (Fig. 1) as is the case of phenanthrene, and calculated the excitation energies of **6** using the new-γ ($k = 1.14$: see Table 1). The weighted mean value of the calculated excitation energies of the first, the second and the third absorption bands reproduced the observed excitation energy of the *p*-band, in comparison with the calculated value using the N·M-γ (Table 3).

3.5. *Naphtho[2,3-k]phenanthrylene* (**7**)

The longest acene-like portion in the molecular framework of **7** is the anthracene unit. For the HOMO and the LUMO of **7**, the character of the anthracene HOMO and LUMO are maintained in the anthracene unit (Fig. 5). So we considered that the SP of **7** is the anthracene unit (Fig. 1). The excitation energy of the *p*-band was calculated by the PPP MO method using new-γ ($k = 1.47$: see Table 1). However, the calculated energy value was lower than the observed one (Table 3).

The bond length of the **hh** bond of **7** (1.458 Å) calculated by the ab initio method with 6-31G* level, whose reliability is proved by the calculation of the bond lengths of **1**, is longer than the bond length of the same position of anthracene (observed value:1.418 Å [16], calculated value by ab initio method with 6-31G* level: 1.433 Å). The **hh** bond possesses the nature of single bond, though it is essentially contained in the π-conjugated system (Table 2). This character of **7** is different from that of **1** (See Table 2). Thus, the nature of anthracene seems to be weakened in the anthracene unit of **7**. Therefore, we concluded the residual naphthalene unit in the anthracene unit to be SP (Fig. 1). The excitation energy of the *p*-band of **7** was calculated using the new-γ ($k = 1.14$: see Table 1), and the result reproduced well the observed value (Table 3).

The bond lengths calculated by the PPP MO method using the new-γ are closer to the those calculated by the ab initio method with 6-31G* level. However, its reliability could not be ascertained because of the absence of experimental values, to the best of our knowledge.

4. Conclusion

The SP was decided by the character of HOMO-1, HOMO, LUMO and LUMO + 1, and was calculated by the HMO method for non-alternate PAHS **1**–**6** as alternate PAHs, and was decided referring the structural analysis using the ab initio calculation with 6-31G* level for **7**. The calculated excitation energies of the *p*-band using the PPP MO method with the new-γ containing the SCS parameter *k* evaluated based on the SP reproduced the observed ones well, in comparison with data using the conventional N·M-γ.

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