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Precise PPP Molecular Orbital Calculations of Excitation Energies of Polycyclic Aromatic Hydrocarbons Part 3. Evaluation of the Spectrochemical Softness Based on the Model of Composite Molecules

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ABSTRACT

For Pariser–Parr–Pople molecular orbital (PPP MO) calculations of the p-*band of polycyclic aromatic hydrocarbons (PAHs), the values of spectrochemical softness parameter* k *of a novel two-centre electron repulsion integral, new-γ, were evaluated based on the model of composite molecules (MCM). The spectroactive portion (SP), namely the part which contributes mainly to the* p-*band, of a molecular framework was used as an index for the evaluation of the parameter* k *for* peri-*condensed PAHs together with* cata-*condensed PAHs. The calculated excitation energies of the* p-*band of PAHs using the new-γ included* k *values based on the SP reproduced accurately the observed ones. The precise MO calculations were performed.* © *1997 Elsevier Science Ltd*

INTRODUCTION

For many PAHs the *p*-band (nomenclature by Clar [2]: corresponds to Platt's ^1L_a band [3]) appears as the longest absorption band except for relatively small PAHs, so that it is responsible for the colour. The *p*-band is a π–π^*

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transition described by mainly HOMO→LUMO transition [2]. Thus, the *p*-band of a given PAH can be characterized by the character of HOMO (in an alternant hydrocarbon there is a mirror image relationship between HOMO and LUMO). For example, as shown later, in a given *peri*-condensed PAH series, the HOMOs of the first few members retain the HOMO character of the parent PAH, and their observed absorption maxima are almost the same as that of the parent PAH. When the acene-like portion in *peri*-condensed PAHs becomes sufficiently long, the character of the HOMO calculated by the PPP MO method changes to acene-like, and the observed absorption maxima of the *p*-band shift markedly towards longer wavelength as the length of the acene-like portion increases as the spectra of acene series show. This prompts the proposal that there is a spectroactive portion (SP) for the *p*-band of PAHs which is shown in the HOMO; the other part in PAHs works only as a perturbing portion (PP). It is suggested that the spectrochemical softness in a novel two-centre electron repulsion integral, new-γ [4], of PAHs can be estimated by the SP.

In this paper this proposal was examined and the excitation energies of the *p*-band of *peri*- and *cata*-condensed PAHs were calculated more accurately.

MODEL

In this study, the model of composite molecules (MCM) was used to evaluate the spectrochemical softness parameter, k, and to understand the characteristic feature of the *p*-band of given PAHs. The present model is to decompose the whole molecule into two parts; one SP and the other PP. The SP is represented by the aromatic sextet resonance system (ASRS) which is defined as the character of the π-conjugated system of acenes [5]. It is assumed that the spectrochemical softness of PAHs is determined by the SP. For example, when the SP is of an anthracene framework, the character of the *p*-band is related to the perturbed anthracene spectrum.

MO CALCULATIONS

PPP MO calculations were performed with computer software PPP-PC [6,7] in which variable β approximation [8] and the conventional parameters set [6,9,10] were used as reported previously [1,5]. For the two-centre electron repulsion integral, the following new-γ was used with 25 lower singly excited configurations in the CI calculations. For comparison with the calculated results, the conventional Nishimoto·Mataga γ (N·M-γ) function [11] was also used.

The new-γ is represented as [4]:

$$\gamma_{rs} = e^2/(R_{rs} + ka_{rs}) \qquad (1)$$

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

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

where e^2 is 14.397 eVÅ and $I_r[I_s]$ and $A_r[A_s]$ are the valence state ionization potential and the electron affinity, respectively. Essentially, k is a dimensionless parameter which indicates the relative magnitude of mobile π-electron polarization at the region between the r-th and s-th atoms, namely the spectrochemical softness of π-electrons. When the value of k is 1, the new-γ is equivalent to the N·M-γ. Large k values are suitable for chemically softer compounds such as acenes [5].

The observed excitation energies of the p-band of *cata*-condensed (**1**–**36**) and *peri*-condensed PAHs (**37**–**52**) (structural formulae are shown in Fig. 1) in inert solvent were extrapolated to the gas phase in order to minimize solvent effects [12–14].

RESULTS AND DISCUSSION

Regression expression for the evaluation of the spectrochemical softness parameter

The number of hexagons included in the SP as a parameter l, except for pyrene (**37**) and its some derivatives (**38**, **39** and **42**) (the reason for this is discissed below), were defined. The values of k° to regenerate the observed excitation energies of the p-band of 6 acenes (benzene to hexacene) were evaluated by trial and error PPP MO calculations using the new-γ (Table 1). The regression expression (eqn 3) to evaluate parameter k was derived from the values of l and k° shown in Table 1 using the least-squares method.

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

The values of k for each PAH were derived from the values of parameter l using eqn 3.

Spectroactive portion of *cata*-condensed PAHs

The shift toward longer wavelength of the p-band (84 nm) along with the annellation from naphthalene to anthracene are interpreted qualitatively by the perturbation of *cis*-1,3-butadiene to naphthalene. Thus, at the divided

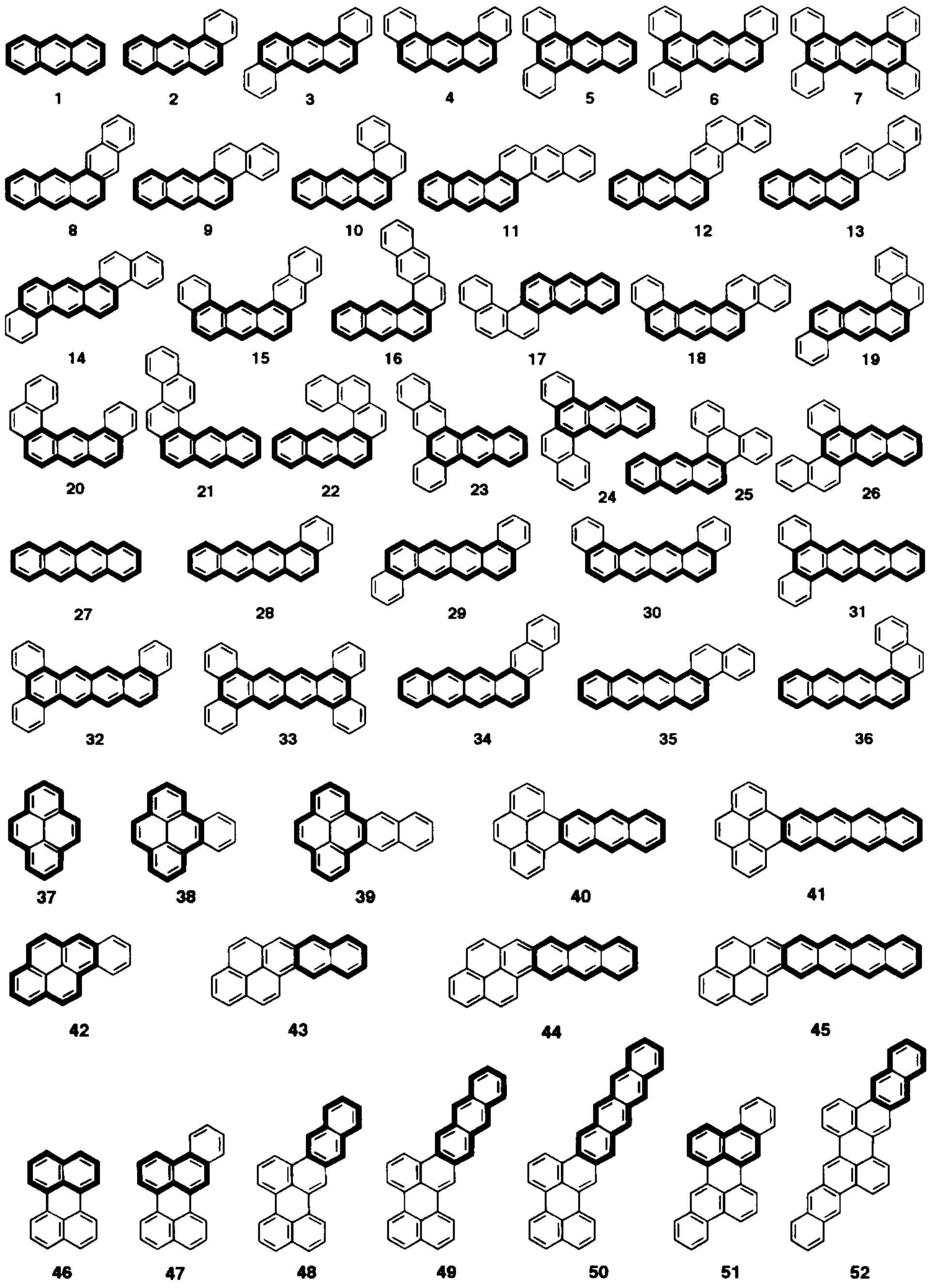


Fig. 1. Structural formulae of *cata*-condensed (**1**–**36**) and *peri*-condensed (**37**–**52**) PAHs; the spectroactive part is represented using bold lines.

positions of the anthracene molecule, the sign of the LCAO coefficients of HOMO (and LUMO) of *cis*-1,3-butadiene coincides with those of naphthalene (namely in-phase), so the difference of the energies between HOMO and LUMO of anthracene decreases by means of the orbital interaction (Fig. 2(a)). As noted by Clar [2], HOMO→LUMO transition is identified as the *p*-band in PAHs, so the *p*-band shifts toward longer wavelength.

TABLE 1
Values of k° and l of Six Acenes (Benzene to Hexacene)

Compound	*Benzene*	*Naphthalene*	*Anthracene*	*Naphthacene*	*Pentacene*	*Hexacene*
k°	0.85	1.25	1.29	1.71	2.14	2.52
l	1	2	3	4	5	6

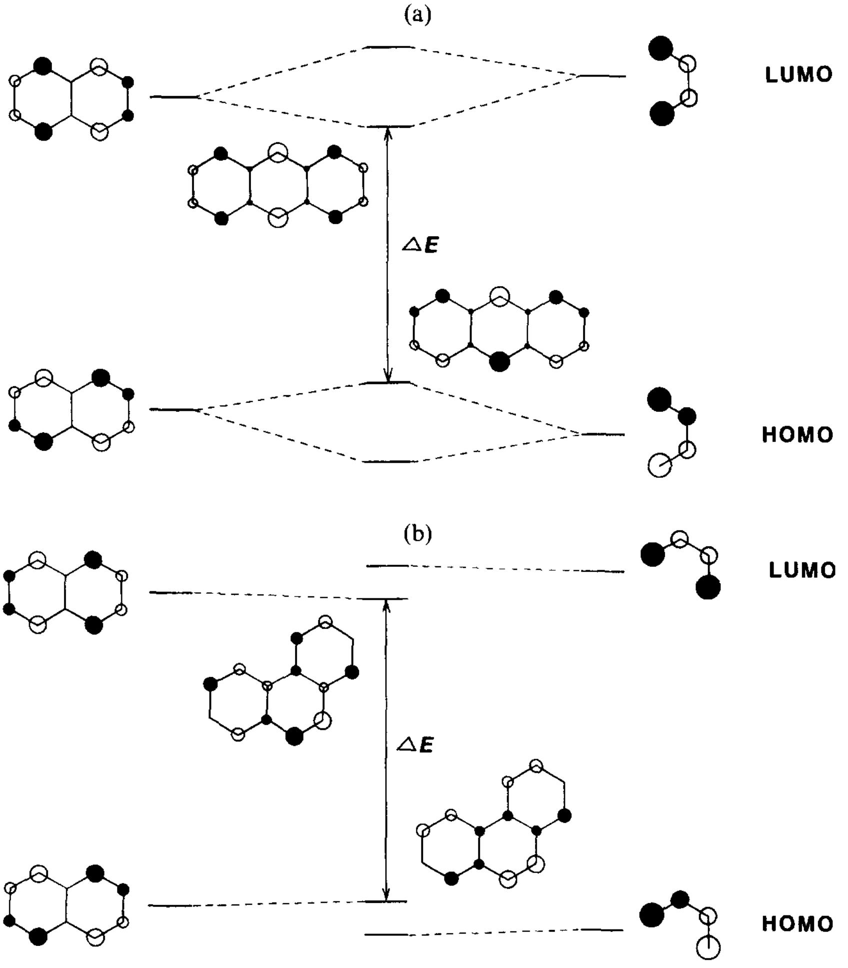


Fig. 2. Energy diagram of the orbital interaction of (a) anthracene and (b) phenanthrene.

For phenanthrene, the sign of the LCAO coefficient at C4 of HOMO (and LUMO) of *cis*-1,3-butadiene is opposite to that at the β-position of naphthalene (namely out-of-phase) as shown in Fig. 2(b). Therefore, the in-phase interaction at the α-position is largely cancelled out by the out-of-phase interaction at the β-position, so that the HOMO and LUMO energies of phenanthrene change only slightly from those of naphthalene. Figure 2(b) shows qualitatively the fact that a shift toward longer wavelength of only 10 nm is observed along with the annellation from naphthalene to phenanthrene. Thus, the *p*-band of phenanthrene is considered to be a perturbed naphthalene spectrum, and the naphthalene unit is the SP for phenanthrene (the residual benzene unit is the PP), whereas the anthracene unit, namely the whole molecular framework, is the SP for anthracene.

To predict the absorption wavelengths of the *p*-band of other types of PAHs, it is necessary to find the SP of a molecular framework. For the benzo-annellated anthracenes **2**–**7**, the character of the HOMO of anthracene (**1**) is maintained in the anthracene unit of these molecules (Fig. 3). The character of the LUMO of anthracene is, of course, maintained by the mirror image relationships for alternant hydrocarbons. Thus, the *p*-band of **2**–**7** can be considered to be a perturbed anthracene spectrum where the anthracene unit is the SP and the *cis*-1,3-butadiene units are the PPs. Analogously, the anthracene unit, namely the longest ASRS of a molecular framework, is the SP for PAHs **8**–**26** which consist of a five- or six-ring system (the SP is shown by bold lines in Fig. 1).

Here, the new-γ is defined with spectrochemical softness parameter, k, evaluated from the l value of the SP using eqn 3 as the new-γ^{SP}. For example,

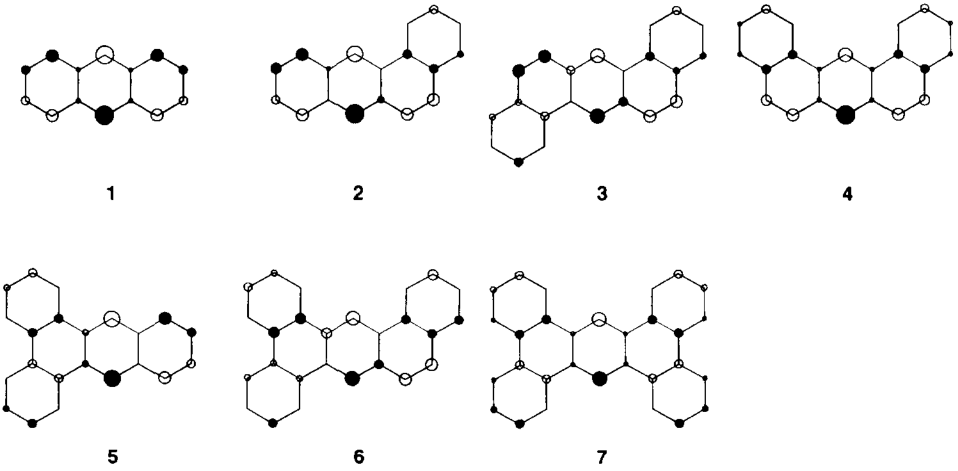


Fig. 3. The LCAO coefficients of the HOMO of anthracene (**1**) and benzo-annellated anthracenes **2**–**7**.

the value of k of new-γ^{SP} for **2**–**26** is evaluated as 1.47 (Table 2), which is identical with the k value in new-γ^{SP} for **1**. The excitation energies of the *p*-band of **1**–**26** were calculated using the new-γ^{SP}, in comparison with the calculated results using the N·M-γ or the new-γ^{η} (new-γ based on the absolute hardness of a molecule described in our previous paper [5]). The calculated results are shown in Table 2, together with the available observed data. The calculated and observed energies of the *p*-band of PAHs **27**–**36** which possess the naphthacene unit as the SP (Fig. 1) are also shown in Table 2. The calculated energies using the new-γ^{SP} were greatly improved compared with the ones using the N·M-γ, and were somewhat improved compared with the ones using the new-γ^{η} for several PAHs.

Spectroactive portion of *peri*-condensed PAHs

In this section, the benzo[*e*]pyrene derivatives **38**–**41**, benzo[*a*]pyrene derivatives **42**–**45** and benzo[*b*]perylene derivatives **47**–**52** are discussed as typical *peri*-condensed PAHs (the numbering scheme of pyrene (**37**) and perylene (**46**) is shown in Fig. 4).

*Benzo[*e*]pyrene derivatives*

Pyrene is a rather peculiar PAH because it is a $4n\pi$ system (n is an integer) but not a $(4n+2)\pi$ system. Therefore, it was assumed that the SP of pyrene (**37**) is the pyrene unit. When the excitation energy of **37** was calculated using new-γ, in which either $k=1.00$ (standard of spectrochemical softness [4,5]) or $k=0.81$ (evaluated for benzene using eqn 3), the results were almost the same (3.59 eV for $k=1.00$ and 3.61 eV for $k=0.81$; observed energy is 3.83 eV). The value $k=0.81$ was adopted for the SP of the pyrene unit. When the CI calculations with four singly excited configurations were carried out, results were 3.61 eV for $k=1.00$ and 3.65 eV for $k=0.81$.

The LCAO coefficients of the HOMO of **37**–**41** are shown in Fig. 5. It can be seen from this figure that the character of the HOMO changes from the pyrene skeleton to the branch portion along with the annellation. For benzo[*e*]pyrene (**38**) which possesses the benzene unit as the branch portion, the HOMO character of the pyrene unit maintains that of **37**. Thus, the SP of **38** is the pyrene unit.

For dibenzo[*de,qr*]naphthacene (**39**) the branch portion is the naphthalene unit. However, the character of the HOMO of the branch portion is different to that of naphthalene (Figs 2 and 5). On the other hand, the character of the HOMO of the pyrene unit maintains that of **37**. Thus, the SP of **39** is also the pyrene unit.

For dibenzo[*de,uv*]pentacene (**40**) and dibenzo[*de,yz*]hexacene (**41**), the characters of the HOMO of the branch portion maintain those of anthracene

TABLE 2

Calculated and Observed Excitation Energies of the *p*-band of PAHs **1–52**.

Compound		*ΔEp/eV*			
		Observed[a]	*Calculated*		
			N·M-γ[b]	*New-γ*	
No.	*Name*			*SP* (k)[c]	*Hardness* (k)[d]
1	Anthracene	3.38	3.48	3.32 (1.47)	3.35 (1.38)
2	Benz[*a*]anthracene	3.53	3.63	3.49 (1.47)	3.54 (1.31)
3	Dibenz[*a*,*h*]anthracene	3.57	3.65	3.52 (1.47)	3.58 (1.28)
4	Dibenz[*a*,*j*]anthracene	3.60	3.73	3.63 (1.47)	3.69 (1.25)
5	Benzo[*b*]triphenylene	3.56	3.75	3.66 (1.47)	3.71 (1.24)
6	Naphtho[1,2-*b*]triphenylene	3.68	3.77	3.67 (1.47)	3.73 (1.21)
7	Tetrabenz[*a*,*c*,*h*,*j*]anthracene	3.71	3.81	3.76 (1.47)	3.80 (1.15)
8	Pentaphene	3.55	3.55	3.43 (1.47)	3.47 (1.33)
9	Benzo[*b*]chrysene	3.27	3.39	3.24 (1.47)	3.26 (1.40)
10	Dibenzo[*b*,*g*]phenanthrene	3.44	3.44	3.30 (1.47)	3.33 (1.37)
11	Dibenzo[*b*,*k*]chrysene	3.02	3.16	2.98 (1.47)	2.96 (1.53)
12	Benzo[*c*]pentaphene	3.42	3.49	3.38 (1.47)	3.34 (1.47)
13	Benzo[*b*]picene	3.34	3.41	3.26 (1.47)	3.29 (1.38)
14	Naphtho[1,2-*b*]chrysene	3.39	3.47	3.31 (1.47)	3.35 (1.35)
15	Benzo[*a*]pentaphene		3.57	3.45 (1.47)	3.49 (1.32)
16	Benzo[*b*]naphtho[2,3-*g*]phenanthrene		3.22	3.02 (1.47)	3.01 (1.50)
17	Dibenzo[*b*,*n*]chrysene		3.45	3.31 (1.47)	3.34 (1.37)
18	Benzo[*a*]naphtho[1,2-*j*]anthracene		3.52	3.37 (1.47)	3.42 (1.33)
19	Benzo[*a*]naphtho[1,2-*h*]anthracene		3.56	3.42 (1.47)	3.47 (1.31)
20	Benzo[*g*]naphtho[2,1-*b*]phenanthrene		3.54	3.40 (1.47)	3.45 (1.31)
21	Naphtho[2,3-*c*]chrysene		3.50	3.37 (1.47)	3.41 (1.34)
22	Phenanthro[3,4-*a*]anthracene		3.41	3.25 (1.47)	3.28 (1.37)
23	Benzo[*h*]pentaphene	3.63	3.72	3.63 (1.47)	3.69 (1.23)
24	Naphtho[2,3-*g*]chrysene	3.27	3.52	3.37 (1.47)	3.41 (1.32)
25	Dibenzo[*b*,*g*]chrysene		3.31	3.16 (1.47)	3.18 (1.41)
26	Dibenzo[*b*,*p*]chrysene		3.51	3.36 (1.47)	3.41 (1.32)
27	Naphthacene	2.71	2.95	2.69 (1.80)	2.71 (1.70)
28	Benzo[*a*]naphthacene	2.83	3.09	2.84 (1.80)	2.89 (1.59)
29	Dibenzo[*a*,*j*]naphthacene	2.95	3.24	2.97 (1.80)	3.06 (1.50)
30	Dibenzo[*a*,*l*]naphthacene	2.95	3.27	2.99 (1.80)	3.08 (1.49)
31	Dibenzo[*a*,*c*]naphthacene	2.92	3.21	2.98 (1.80)	3.06 (1.51)
32	Tribenzo[*a*,*c*,*j*]naphthacene	3.03	3.37	3.11 (1.80)	3.23 (1.41)
33	Tetrabenzo[*a*,*c*,*j*,*l*]naphthacene	3.08	3.48	3.24 (1.80)	3.37 (1.36)
34	Hexaphene	2.94	3.15	2.89 (1.80)	2.96 (1.56)
35	Naphtho[2,1-*a*]naphthacene	2.72	2.97	2.71 (1.80)	2.75 (1.67)
36	Naphtho[1,2-*a*]naphthacene		2.98	2.71 (1.80)	2.76 (1.65)
37	Pyrene	3.83	3.59	3.61 (0.81)	3.50 (1.32)
38	Benzo[*e*]pyrene	3.85	3.72	3.73 (0.81)	3.67 (1.24)
39	Dibenzo[*de*,*qr*]naphthacene	3.74	3.67	3.67 (0.81)	3.64 (1.23)
40	Dibenzo[*de*,*uv*]pentacene	2.95	3.23	3.08 (1.47)	3.08 (1.50)
41	Dibenzo[*de*,*yz*]hexacene	2.47	2.81	2.54 (1.80)	2.54 (1.83)
42	Benzo[*a*]pyrene	3.34	3.21	3.27 (0.81)	3.07 (1.46)
43	Naphtho[8,1,2-*arq*]naphthacene	2.86	2.92	2.86 (1.14)	2.68 (1.67)
44	Naphtho[8,1,2-*avu*]pentacene	2.44	2.67	2.48 (1.47)	2.34 (1.94)
45	Naphtho[8,1,2-*azy*]hexacene	2.11	2.45	2.15 (1.80)	2.03 (2.28)

TABLE 2—*contd.*

Compound		ΔEp/eV			
		Observed[a]	Calculated		
			N·M-γ[b]	New-γ	
No.	Name			SP (k)[c]	Hardness (k)[d]
46	Perylene	2.97	3.05	3.00 (1.14)	2.86 (1.53)
47	Benzo[*b*]perylene	2.96	3.05	2.99 (1.14)	2.86 (1.52)
48	Dibenzo[*de*,*st*]pentacene	2.93	2.97	2.91 (1.14)	2.77 (1.59)
49	Dibenzo[*fg*,*yz*]hexacene		2.83	2.65 (1.47)	2.56 (1.77)
50	Dibenzo[*no*,*uv*]heptacene		2.62	2.33 (1.80)	2.26 (2.06)
51	Dibenzo[*fg*,*qr*]pentacene	3.01	3.06	3.00 (1.14)	2.87 (1.51)
52	Dibenzo[*jk*,*yz*]heptacene	2.94	2.93	2.87 (1.14)	2.70 (1.64)

[a] See refs 12–14.
[b] Conventional Nishimoto·Mataga-γ function.
[c] New-γ^{SP} based on the spectroactive part and the values of k were derived using regression eqn 3.
[d] New-γ^{η} based on the absolute hardness ([5]; $k = 0.33/\eta + 0.58$).

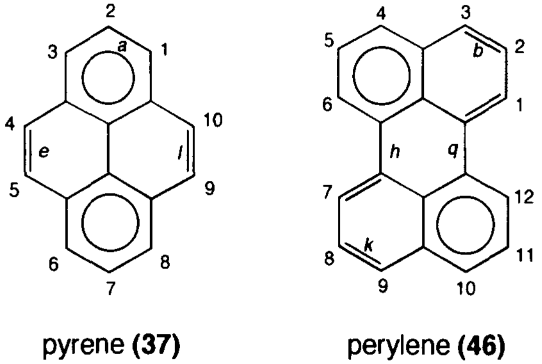
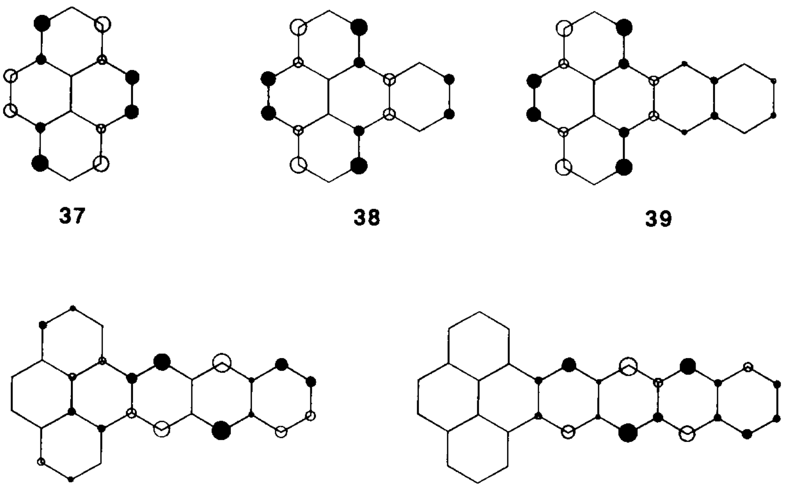


Fig. 4. Numbering scheme and Clar's aromatic sextet description of pyrene (**37**) and perylene (**46**).

and naphthacene, respectively, so the SPs of **40** and **41** are the branch portions.

The SPs of **37**–**41** are shown in Fig. 1 using bold lines, where parameter l for **37**–**39** corresponds to 1, but for **40** and **41** is the same value as the number of hexagons included in the SPs. Using the k values based on such SPs, the absorption wavelengths of the p-band of **37**–**41** were calculated using the new-γ^{SP}. The calculated results are shown in Fig. 6(a), together with the calculated ones using the N·M-γ or the new-γ^{η}, and the observed data. For **37**–**39** the calculated results using the new-γ^{SP} were improved in comparison with those using the new-γ^{η}, and for **40** and **41** were improved compared with the results using the N·M-γ.



37 38 39

40 41

Fig. 5. The LCAO coefficients of the HOMO of pyrene (**37**) and benzo[*e*]pyrene derivatives **38**–**41**.

Benzo[a]pyrene derivatives

For benzo[*a*]pyrene (**42**) the character of the HOMO of the pyrene unit maintains that of **37** (Fig. 7). Thus, the SP of **42** is the pyrene unit. On the other hand, in the HOMO of naphtho[8,1,2-*arq*]naphthacene (**43**), the pyrene character disappears (Fig. 7), so the SP of **43** is the branch portion. Similarly, the SPs of **44** and **45** are the branch portions (Fig. 1)

The calculated wavelengths of the *p*-band of **42**–**45** using the k values based on such SPs are shown in Fig. 6(b). In this case, the calculated wavelengths using the new-γ^{SP} correlate well with the observed ones. However, the calculated wavelengths using the N·M-γ for **44** and **45** were shorter than the observed ones, and the calculated values using the new-γ^{n} for **42**–**45** were longer than the observed ones (the values of k were overestimated).

Benzo[b]perylene derivatives

As shown in Fig. 4 using Clar's aromatic sextet representation [15], perylene (**46**) can be buillt up from two naphthalene units connected by [*h*] and [*q*] single bonds, so the SP of **46** should be the naphthalene unit. This is supported by the fact that the calculated excitation energy of the *p*-band of **46** using the new-γ^{SP} ($l=2$, $k=1.14$) is close to the observed one (Table 2). For benzo[*b*]perylene derivatives **47**–**50**, the SP is determined by comparing the size of the branch portion with that of the naphthalene unit (the SP of perylene skeleton) as the larger portion (Fig. 1). The calculated and observed wavelengths of the *p*-band of **46**–**50** are shown in Fig. 6(c) (the observed data

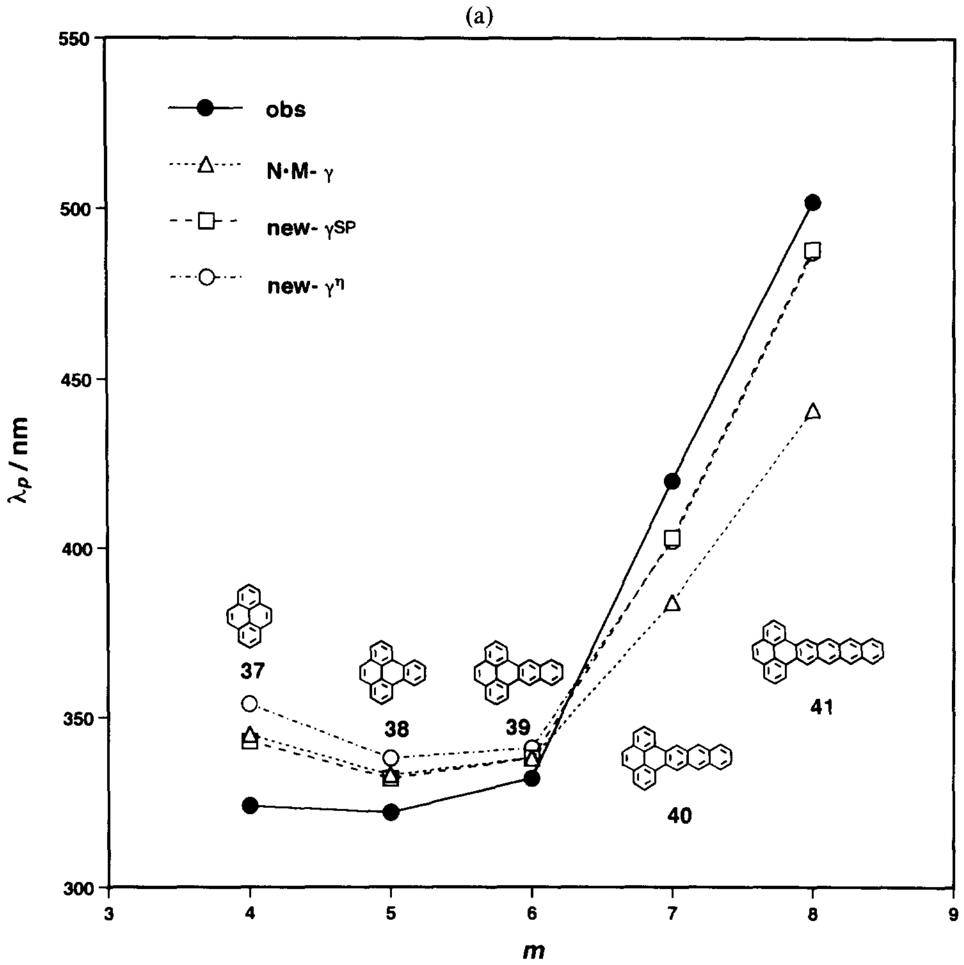


Fig. 6. The number of rings, m, vs the observed and calculated wavelengths of the p-band using the N·M-γ, new-γ^{SP} and new-γ^{η} of (a) aceno[*e*]pyrenes, (b) aceno[*a*]pyrenes and (c) aceno[*b*]perylenes.

of **49** and **50** is presumably absent). For **46–48** the calculated wavelengths using the new-γ^{η} were longer than the observed ones or the calculated ones using the new-γ^{SP}. Therefore, the values of k in the new-γ^{η} are most certainly overestimated for **49** and **50**. Similar overestimation of k values were evident for the interpretation of benzo[*a*]pyrene derivatives. From these examples it is evident that the values of k in the new-γ^{η} tend to be often overestimated in the calculations of the p-band of *peri*-condensed PAHs, whereas the new-γ^{SP} is certainly suitable for such calculations.

The calculated excitation energies of analogues **51** and **52** using the new-γ^{SP} ($l=2$, $k=1.14$) correlated well with the observed ones, ulike those calculated using new-γ^{η} (Table 2).

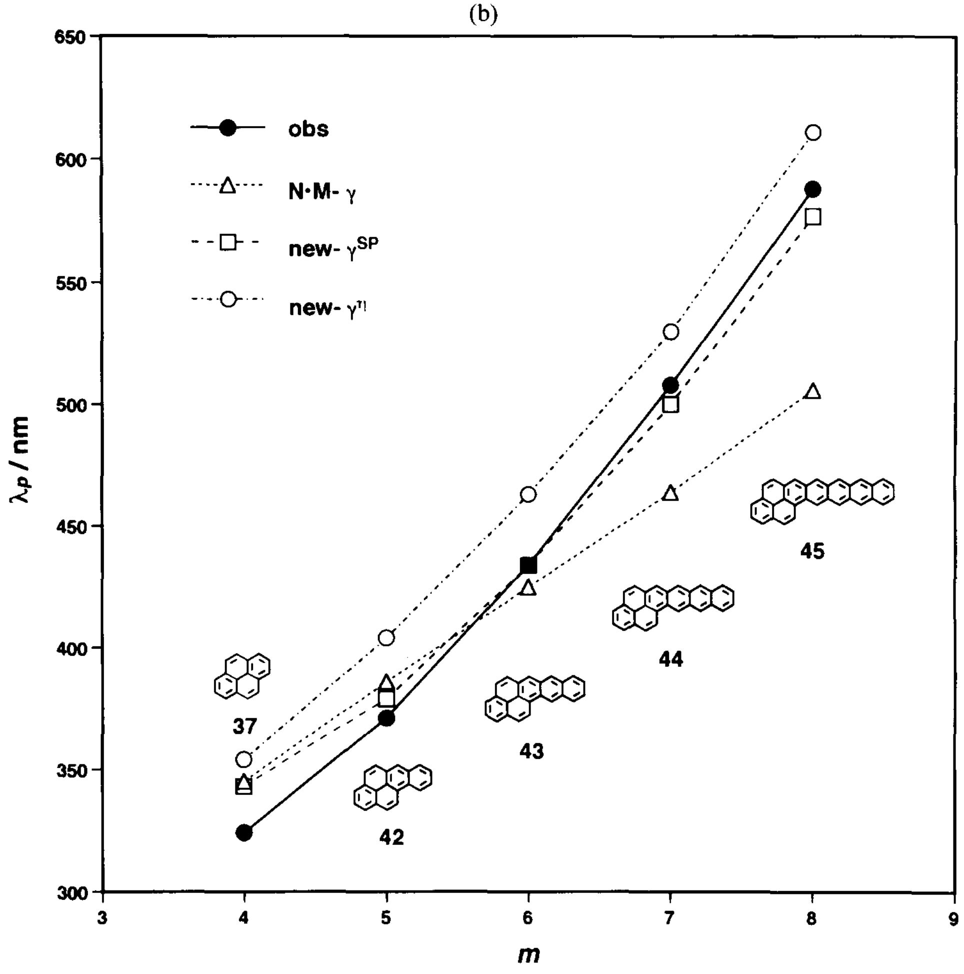


Fig. 6.—*contd.*

CONCLUSION

The usefulness of using the new-γ^{SP} based on the MCM to calculate the excitation energies of the *p*-band of PAHs seems to be generally established. The calculated results using the new-γ^{SP} are greatly improved compared with those using the N·M-γ; that is, in this case, precise MO calculations are performed.

For *cata*-condensed PAHs, the longest ASRS, namely the longest acene-like portion of a molecular framework, is the SP and the residual portions are the PPs. On the other hand, for *peri*-condensed PAHs the SP migrates from the parent molecular framework to the longest acene-like portion in the branch with annellation. The SP of PAHs is clearly recognized by the character of the HOMO.

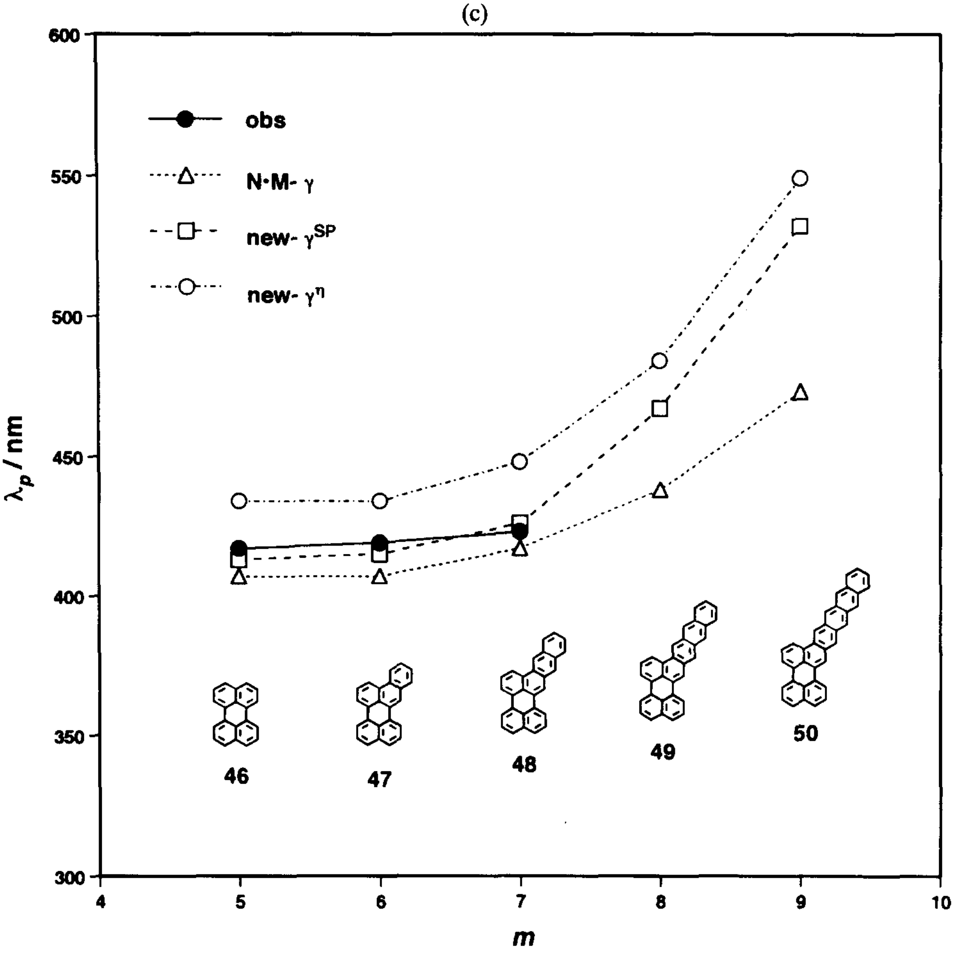


Fig. 6.—*contd.*

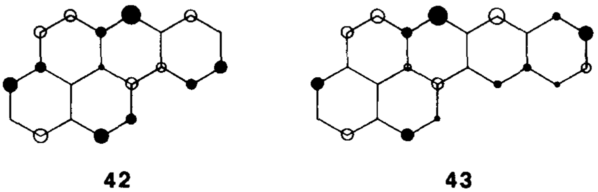


Fig. 7. The LCAO coefficients of the HOMO of benzo[*def*]chrysene (**42**) and naphtho-[8,1,2-*arq*]naphthacene (**43**).

For PAHs, the annellation, namely the extension of the π-conjugated system, does not always contribute to the shift toward longer wavelength of the *p*-band. This rather peculiar property is easily explained by MCM.

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