ELSEVIER

Dyes and Pigments, Vol. 31, No. 4, pp. 309–322, 1996

PII: S0143-7208(96)00006-X 0143-7208/96 $15.00+0.00

Precise PPP Molecular Orbital Calculations of the Excitation Energies of Polycyclic Aromatic Hydrocarbons. Part 2: Evaluation of the Spectrochemical Softness Parameter based on the Spectroactive Partial Structure of a Molecule

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(Received 5 December 1995; accepted 3 January 1996)

ABSTRACT

*For precise Pariser-Parr-Pople molecular orbital (PPP MO) calculations, the values of the spectrochemical softness parameter (*k*) of a new two centre electron repulsion integral (new-*γ*) were evaluated based on an appropriate partial structure of* cata-*condensed polycyclic aromatic hydrocarbons (PAHs). The spectroactive aromatic sextet resonance system [ASRS] was defined as a spectroactive partial structure of a molecule. The calculated excitation energies of the* p-*band of the* cata-*condensed PAHs accurately reproduced the observed values. In particular, the calculated energies of branched PAHs were improved compared with those obtained using our previous method. Copyright © 1996 Elsevier Science Ltd*

INTRODUCTION

The semi-empirical PPP MO method has proved to be a useful tool for the prediction of the electronic spectra of organic colourants.[2–5] In order to perform precise PPP MO calculations of the excitation energies of the *p*-band

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(nomenclature by Clar[6]: corresponds to Platt's ^1L_a band[7]) of non-branched *cata*-condensed PAHs, a new two centre electron repulsion integral (new-γ[8]) has been successfully applied.[1]

New-γ is represented as

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

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

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

where e^2 is 14.397 eV·Å, $I_r[I_s]$ 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 between the r-th and s-th atoms, namely, the 'spectrochemical softness'† of π-electrons. When the value of k is 1.0, new-γ is equivalent to the conventional Nishimoto·Mataga γ (N·M-γ) function.[9]

We adopted[1] the absolute hardness η[10] of a molecule as an index to evaluate the values of k of new-γ suitable for non-branched *cata*-condensed PAHs **1–38** (Fig. 1). However, this index may be often insufficient for other kinds of PAHs, e.g., branched *cata*-condensed PAHs, because the value of η was calculated for a whole molecular framework. From a consideration in our previous paper,[1] we assume that absorption spectra of PAHs are greatly affected by the shape of a molecule. We define here the partial structure of a molecule which affects the absorption spectra of PAHs as a 'spectroactive partial structure'. The spectroactive partial structure of a molecule should be correlated with the spectrochemical softness.

In this study, we calculate the excitation energies of the p-band of branched *cata*-condensed PAHs **39–54**, together with non-branched *cata*-condensed PAHs **1–38** (Fig. 1). We propose a new method to evaluate the values of the spectrochemical softness parameter k suitable for such PAHs, based on the spectroactive partial structure of a molecule.

MO CALCULATIONS

PPP MO calculations were performed with a computer software PPP-PC,[5,11] in which variable β approximation[12] and the conventional parameters set[5,13]

†To avoid ambiguity between the term used as indices of spectroscopic properties[1] and the one used as indices of reactivities,[10] the term 'chemical softness' used in our previous paper[1] was substituted by 'spectrochemical softness' in this paper.

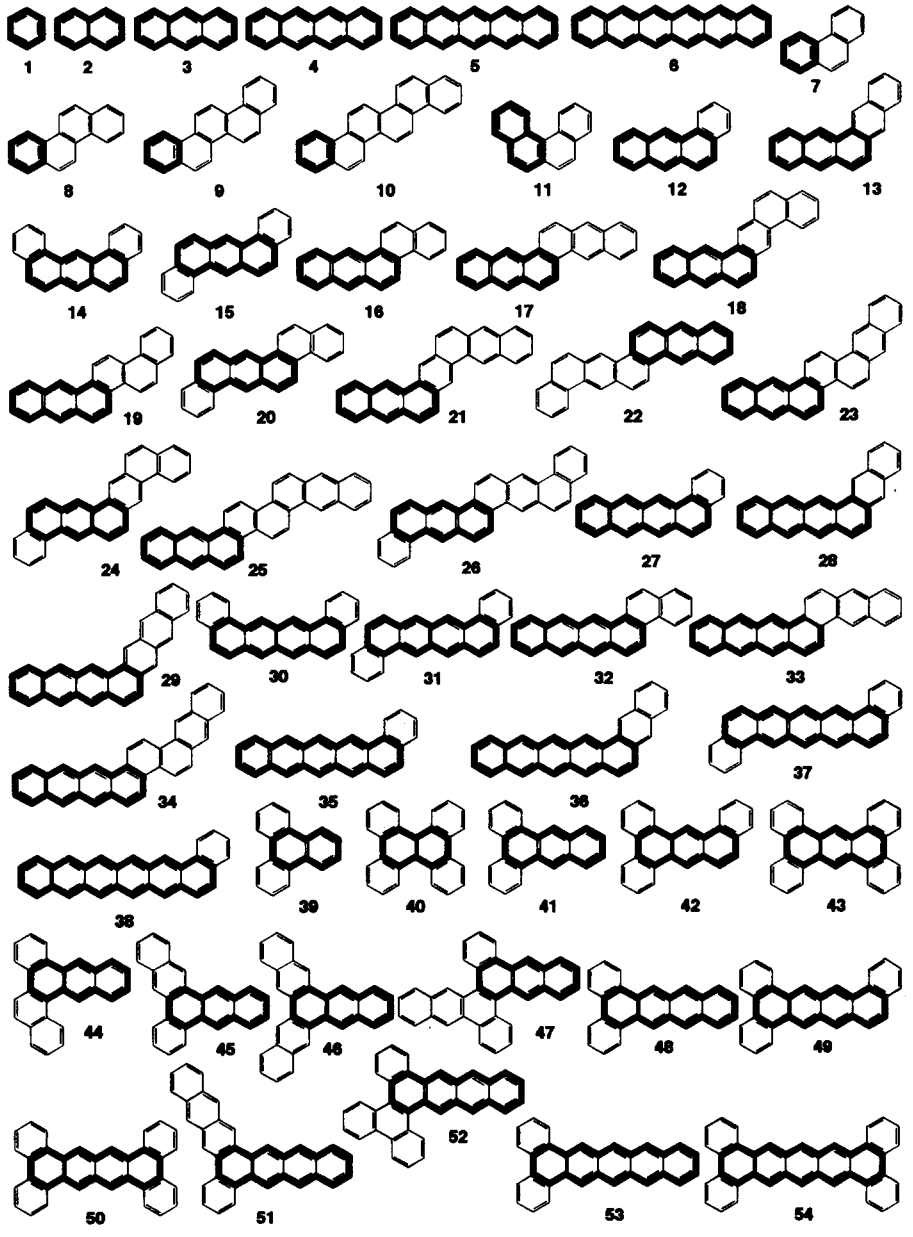

Fig. 1. Structural formulae of non-branched (**1–38**) and branched (**39–54**) *cata*-condensed PAHs; spectroactive ASRS is represented using bold lines.

were used as in our previous paper.[1] For two centre electron repulsion integral, either the conventional N·M-γ[9] or the new-γ[8] was used with 25 singly excited configurations in the CI calculations.

The observed excitation energies of the *p*-band of PAHs in inert solvent were extrapolated to the gas phase, in order to minimize solvent effects.[14]

RESULTS AND DISCUSSION

The relationship between the spectrochemical softness and the spectroactive partial structure of a molecule

We have defined the π-conjugated system of acenes as an 'aromatic sextet resonance system' [ASRS], and that of zig-zag phenes as an 'aromatic sextet alternation system' [ASAS] (Fig. 2).[1] The ASRS is a spectrochemically soft system, and the ASAS is a spectrochemically hard one. To predict precisely the excitation energies of the *p*-band of PAHs, large *k* values should be used for spectrochemically soft compounds.

The absorption maxima of the *p*-band of acenes **1–6** (ASRS) shift toward longer wavelength with annellation (Fig. 3). For acenes, a whole molecular framework, namely ASRS, is exactly identical with the spectroactive partial structure, so that spectroactive partial structure can be substituted by 'spectroactive ASRS'. For generalized *cata*-condensed PAHs, spectroactive ASRS is defined as follows.

According to the definition of ASAS, the aromatic sextet is localized in only a single benzene unit in zig-zag phenes **7–10**. Thus, the spectroactive ASRSs of **7–10** are identical, as are shown in Fig. 1 using bold lines; this is supported by the fact that the absorption maxima of the *p*-band of zig-zag phenes shift only slightly towards longer wavelength with annellation (Fig. 3).

From the shape of a molecular framework, benzo[*c*]phenanthrene **(11)** may be classified as a zig-zag phene; however, it possesses both the naphthalene **(2)** and the phenanthrene **(7)** unit in its molecular framework. Clar noted that HOMO→LUMO excitation is identified as the *p*-band in PAHs.[6] LCAO coefficients of HOMO (Fig. 4) and LUMO (the absolute value of coefficients of LUMO are identical with that of HOMO, though the sign of some coefficients are not identical with the change of orbital symmetry) of **11**, the resulting PPP MO calculations indicate that the naphthalene unit is more appropriate for HOMO→LUMO excitation than the phenanthrene unit. Thus, the naphthalene unit is the spectroactive ASRS for **11**. Similarly, LCAO coefficients of HOMO indicate that the anthracene **(3)** unit is the spectroactive ASRS for PAHs **12, 14**, or **15** (Fig. 5).

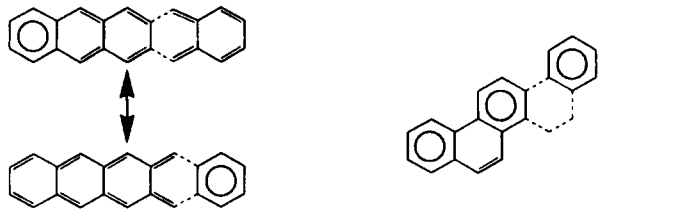

Fig. 2. π-Conjugated system of acenes and zig-zag phenes.

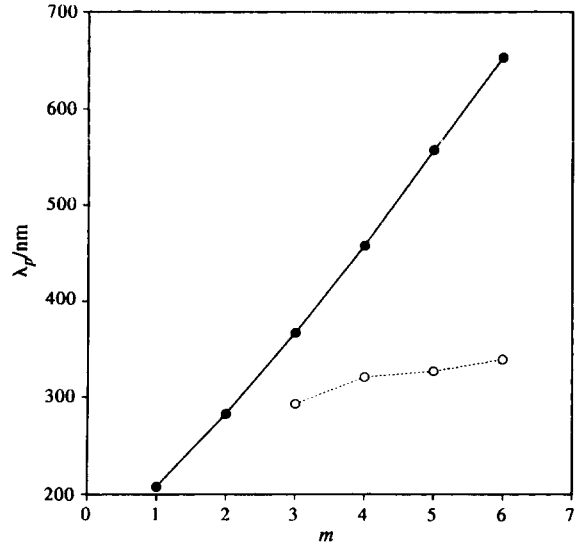

Fig. 3. The number of rings m vs the observed wavelengths of the p-band of acenes (●) and zig-zag phenes (○).

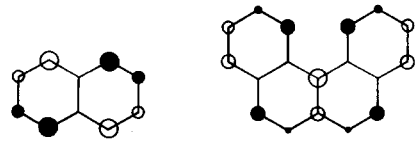

Fig. 4. The LCAO coefficients of HOMO of naphthalene (**2**) and benzo[*c*]phenanthrene (**11**).

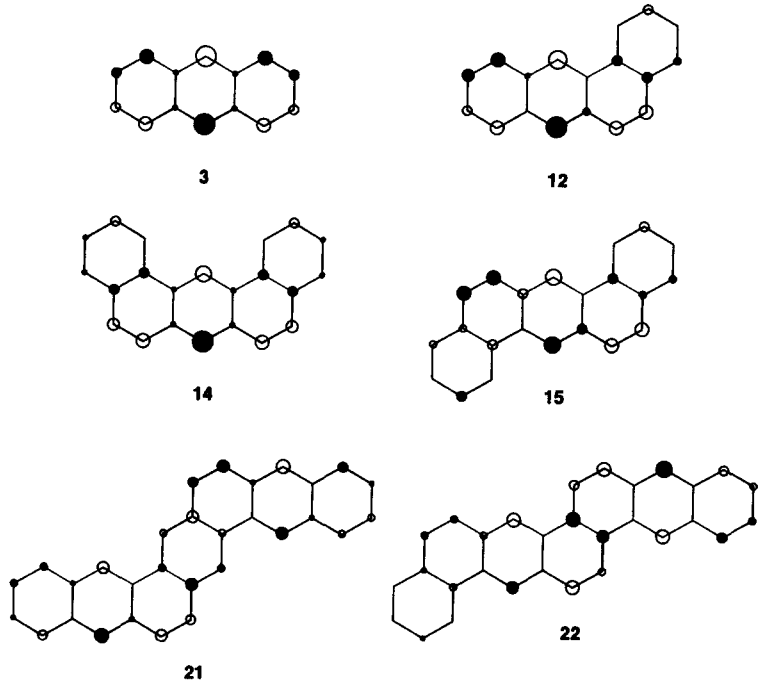

Fig. 5. The LCAO coefficients of HOMO of PAHs **3**, **12**, **14**, **15**, **21** and **22**.

Naphtho[2,3-*c*]pentaphene **(21)** possesses three anthracene units, which are classified into two spectroactive partial structures. Benzo[*b*]naphtho[1,2-*k*]-chrysene **(22)** also possesses two anthracene units. Their LCAO coefficients of HOMO (Fig. 5) indicate that the anthracene unit (shown by bold lines in Fig. 1) is the spectroactive ASRS of them.

The spectroactive ASRSs for PAHs **1–54** are shown by bold lines in Fig. 1.

Calculations of excitation energies

We defined the number of benzene rings included in the spectroactive ASRS as a parameter l. The values of k° to regenerate the observed excitation energies of the *p*-band of 6 acenes **1–6** were evaluated by trial-and-error PPP MO calculations using new-γ (Table 1). The regression expression (3) to evaluate the values of k was derived from the values of l and k° shown in Table 1, using the least-squares method.

$$k = 0.33l + 0.48 \tag{3}$$

The values of spectrochemical softness parameter k for 38 non-branched *cata*-condensed PAHs **1–38** and 16 branched *cata*-condensed PAHs **39–54**

TABLE 1
Values of l, $k°$ and k of acenes **1–6**

Compound	**1**	**2**	**3**	**4**	**5**	**6**
l	1	2	3	4	5	6
$k°$	0.85	1.25	1.29	1.71	2.14	2.52
k	0.81	1.14	1.47	1.80	2.13	2.46

were derived from the values of the spectroactive ASRS parameter l, using Eqn (3).

The excitation energies of the p-band of PAHs were calculated using new-γ^{ASRS} including these k values (Table 2). Calculated results using the N·M-γ or new-γ^{η} (new-γ in our previous paper[1]) are also shown in Table 2. To compare the calculated results quantitatively, the statistical parameters[1,15] for the linear relationship between the calculated and the observed energies were used; $E_{calc.} = a \cdot E_{obs.} + b$, where a is a slope, b is an intercept and r is a correlation coefficient of this regression expression; and s is a standard deviation of the discrepancies between the calculated and observed energies (Table 3). In the ideal case, the values of a and r approach 1, and the values of b and s approach 0.

In the case of non-branched *cata*-condensed PAHs **1–38**, the calculated energies using new-γ^{ASRS} were greatly improved compared with the ones using the N·M-γ, and were slightly improved compared with those using the new-γ^{η} (Table 2 and 3).

The calculated energies of branched *cata*-condensed PAHs **39–54** using new-γ^{ASRS} were greatly improved compared with those using the N·M-γ, and were somewhat improved compared with the ones using new-γ^{η} (Table 2 and Table 3). Thus, for calculations of excitation energies of the p-band of branched *cata*-condensed PAHs, evaluation of the values of the spectrochemical softness parameter k based on the spectroactive ASRS seems to be more suitable than that based on the absolute hardness of a molecule.

The plots of calculated energies vs. observed energies of 54 PAHs are shown in Fig. 6 (a: using N·M-γ; b: using new-γ^{ASRS}). From these figures, it is apparent that the calculated energies using new-γ^{ASRS} are greatly improved compared with those using N·M-γ. Values of the statistical parameters shown in Table 3 show that the calculated energies using new-γ^{ASRS} are somewhat improved compared with the ones using new-γ^{η}: the values of b, r and s using new-γ^{ASRS} were even accurate more than the ones using new-γ^{η}, although the value of a was similar in both cases. For *cata*-condensed PAHs, the usefulness of the spectroactive ASRS as an index to

TABLE 2
Calculated and observed excitation energies of the *p*-band of *cata*-condensed PAHs **1–54**

Compound			$\Delta E_p/eV$ *Calc.*		
				New-γ	
No.	*Name*	*Obs.*[a]	*N·M-γ*[b]	*Hardness*(k)[c]	*ASRS*(k)[d]
1	Benzene	5.96	6.18	6.06(0.91)	5.89(0.81)
2	Naphthalene	4.38	4.42	4.41(1.11)	4.40(1.14)
3	Anthracene	3.38	3.48	3.35(1.38)	3.32(1.47)
4	Naphthacene	2.71	2.95	2.71(1.70)	2.69(1.80)
5	Pentacene	2.23	2.58	2.24(2.08)	2.23(2.13)
6	Hexacene	1.90	2.32	1.90(2.53)	1.91(2.46)
7	Phenanthrene	4.23	4.18	4.17(1.13)	4.14(1.14)
8	Chrysene	3.87	3.80	3.75(1.21)	3.82(1.14)
9	Picene	3.80	3.69	3.63(1.24)	3.72(1.14)
10	Benzo[*c*]picene	3.66	3.56	3.47(1.28)	3.61(1.14)
11	Benzo[*c*]phenanthrene	3.84	3.93	3.91(1.16)	3.92(1.14)
12	Benz[*a*]anthracene	3.53	3.63	3.54(1.31)	3.49(1.47)
13	Pentaphene	3.55	3.55	3.47(1.33)	3.43(1.47)
14	Dibenz[*a,j*]anthracene	3.60	3.73	3.69(1.25)	3.63(1.47)
15	Dibenz[*a,h*]anthracene	3.57	3.65	3.58(1.28)	3.52(1.47)
16	Benzo[*b*]chrysene	3.27	3.39	3.26(1.40)	3.24(1.47)
17	Dibenzo[*b,k*]chrysene	3.02	3.16	2.96(1.53)	2.98(1.47)
18	Benzo[*c*]pentaphene	3.42	3.49	3.38(1.35)	3.34(1.47)
19	Benzo[*b*]picene	3.34	3.41	3.29(1.38)	3.26(1.47)
20	Naphtho[1,2-*b*]chrysene	3.39	3.47	3.35(1.35)	3.31(1.47)
21	Naphtho[2,3-*c*]pentaphene	3.28	3.38	3.22(1.42)	3.20(1.47)
22	Benzo[*b*]naphtho[1,2-*k*]chrysene	3.10	3.23	3.05(1.48)	3.05(1.47)
23	Dibenzo[*b,n*]picene	3.37	3.34	3.21(1.41)	3.19(1.47)
24	Dibenzo[*c,m*]pentaphene	3.43	3.47	3.35(1.34)	3.31(1.47)
25	Benzo[*b*]naphtho[2,3-*m*]picene	3.09	3.25	3.07(1.48)	3.07(1.47)
26	Dinaphtho[1,2-*b*:1′,2′-*k*]chrysene	3.18	3.29	3.12(1.44)	3.10(1.47)
27	Benzo[*a*]naphthacene	2.83	3.09	2.89(1.59)	2.84(1.80)
28	Hexaphene	2.94	3.15	2.96(1.56)	2.89(1.80)
29	Heptaphene	2.97	3.14	2.94(1.59)	2.87(1.80)
30	Dibenzo[*a,l*]naphthacene	2.95	3.27	3.08(1.49)	2.99(1.80)
31	Dibenzo[*a,j*]naphthacene	2.95	3.24	3.06(1.50)	2.97(1.80)
32	Naphtho[2,1-*a*]naphthacene	2.72	2.97	2.75(1.67)	2.71(1.80)
33	Benzo[*b*]naphtho[2,3-*k*]chrysene	2.65	2.88	2.60(1.76)	2.59(1.80)
34	Benzo[*b*]naphtho[2,3-*n*]picene	2.75	3.05	2.81(1.64)	2.77(1.80)
35	Benzo[*a*]pentacene	2.37	2.70	2.40(1.93)	2.35(2.13)
36	Benzo[*b*]hexaphene	2.39	2.75	2.45(1.89)	2.40(2.13)
37	Dibenzo[*a,l*]pentacene	2.47	2.85	2.56(1.81)	2.48(2.13)
38	Benzo[*a*]hexacene	2.00	2.42	2.02(2.34)	2.00(2.46)
39	Triphenylene	4.36	4.15	4.15(1.06)	4.15(1.14)
40	Dibenzo[*g,p*]chrysene	3.43	3.63	3.58(1.23)	3.60(1.14)
41	Benzo[*b*]triphenylene	3.56	3.75	3.71(1.24)	3.66(1.47)
42	Naphtho[1,2-*b*]triphenylene	3.68	3.77	3.73(1.21)	3.67(1.47)
43	Tetrabenz[*a,c,h,j*]anthracene	3.71	3.81	3.80(1.15)	3.76(1.47)

TABLE 2 — *Continued*

Compound			$\Delta E_p/eV$ *Calc.*		
				New-γ	
No.	*Name*	*Obs.*[a]	*N·M-γ*[b]	*Hardness(k)*[c]	*ASRS(k)*[d]
44	Naphtho[2,3-*g*]chrysene	3.27	3.52	3.41(1.32)	3.37(1.47)
45	Benzo[*h*]pentaphene	3.63	3.72	3.69(1.23)	3.63(1.47)
46	Naphtho[2,3-*h*]pentaphene	3.62	3.71	3.69(1.22)	3.66(1.47)
47	Tetrabenzo[*b,g,k,p*]chrysene	2.97	3.24	3.06(1.45)	3.05(1.47)
48	Dibenzo[*a,c*]naphthacene	2.92	3.21	3.06(1.51)	2.98(1.80)
49	Tribenzo[*a,c,j*]naphthacene	3.03	3.37	3.23(1.41)	3.11(1.80)
50	Tetrabenzo[*a,c,j,l*]naphthacene	3.08	3.48	3.37(1.36)	3.24(1.80)
51	Benzo[*j*]heptaphene	2.93	3.25	3.10(1.50)	3.03(1.80)
52	Dibenzo[*g,p*]naphtho[2,3-*b*]chrysene	2.73	3.06	2.83(1.60)	2.77(1.80)
53	Dibenzo[*a,c*]pentacene	2.42	2.79	2.52(1.84)	2.46(2.13)
54	Tetrabenzo[*a,c,l,n*]pentacene	2.57	3.05	2.81(1.64)	2.69(2.13)

[a]Reference 14.
[b]Conventional Nishimoto·Mataga γ function.
[c]New-γ^{η} based on the absolute hardness (ref. 1; $k = 0.33/\eta + 0.58$).
[d]New-γ^{ASRS} based on the spectroactive ASRS, and values of k were calculated using regressive expression (3).

TABLE 3

Statistical parameters [slope (a), intercept (b) and correlation coefficient (r)] of regressive expressions [$E_{calc.} = a \cdot E_{obs.} + b$], and standard deviation (s) between the observed and calculated excitation energies

Class	Number of compounds		N·M-γ[a]	New-γ	
				Hardness[b]	ASRS[c]
Non-branched	38	*a*	0.872	0.986	0.979
cata-condensed PAHs		*b*	0.568	0.035	0.030
(**1–38**)		*r*	0.985	0.995	0.998
		s	0.142	0.075	0.053
Branched *cata*-condensed	16	*a*	0.691	0.856	0.899
PAHs (**39–54**)		*b*	1.227	0.583	0.384
		r	0.986	0.983	0.988
		s	0.162	0.105	0.084
All (**1–54**)	54	*a*	0.843	0.966	0.967
		b	0.681	0.135	0.096
		r	0.981	0.988	0.993
		s	0.151	0.103	0.078

[a]Conventional Nishimoto·Mataga γ function.
[b]New-γ^{η} based on the absolute hardness (ref. 1).
[c]New-γ^{ASRS} based on the spectroactive ASRS.

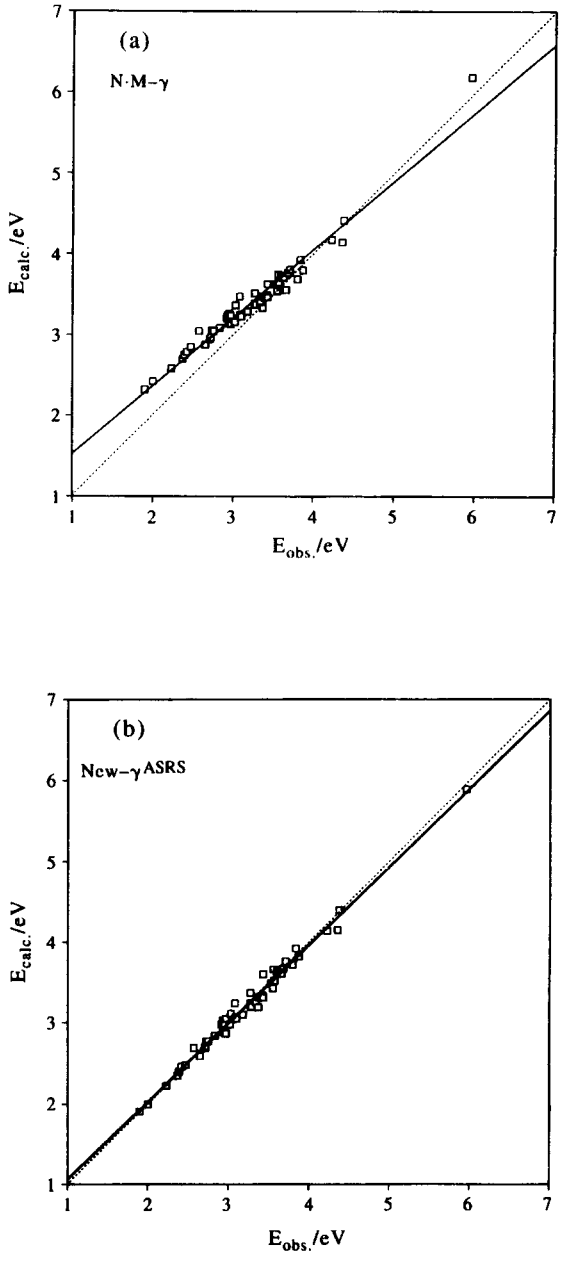

Fig. 6. The observed excitation energies vs the calculated ones using (a) N·M-γ and (b) new-γ^{ASRS}.

evaluate the values of the spectrochemical softness parameter k of new-γ seems to be generally established.

Clar described how the *p*-band of PAHs is correlated to a localization of two π-electrons in the para position.[16] On the other hand, spectroactive ASRS of *cata*-condensed PAHs, except zig-zag phenes, is identical with the longest acene-like portion of a molecule, and Balaban and co-workers[17] reported that the longest acene-like portion of PAHs is highly correlated to the Diels-Alder reactivity of the para position of a molecule. Thus, it is not surprising that the longest acene-like portion of a molecule is well correlated to the excitation energies of the *p*-band.

Absorption wavelengths of benzo-annellated polyacenes

Benzo-annellated polyacenes (structural formulae are shown in Fig. 7a–c) are among the chemically best studied PAHs. For example, Gutman and Petrović have recently reported the cyclic conjugation of these compounds.[18]

In the series of anthracene derivatives **(3, 12, 41, 42** and **43)** (with spectroactive ASRS parameter $l = 3$), the plots of the number of rings (m) vs the observed and calculated wavelengths of the *p*-band, using the N·M-γ, new-γ^{η} or new-γ^{ASRS}, are shown in Fig. 7a. In this series, the observed wavelengths were satisfactorily reproduced by all three methods.

On the other hand, in the series of naphthacene derivatives **(4, 27, 48, 49** and **50)** (with $l = 4$), the observed wavelengths were not reproduced by the calculations using N·M-γ (Fig. 7b). The calculated wavelengths using new-γ^{η} were slightly improved; however, the discrepancies between the observed and calculated wavelengths increase with the annellation. Using new-γ^{ASRS}, the calculated wavelengths were more improved compared with the ones using new-γ^{η}.

In the series of pentacene derivatives **(5, 35, 53** and **54)** (with $l = 5$), the tendency of discrepancies between the calculated and observed wavelengths shown in the series of naphthacene derivatives was emphasized significantly (Fig. 7c).

From these examples, it is evident that the calculations of absorption wavelengths of the *p*-band of *cata*-condensed PAHs using new-γ^{ASRS} are more accurate compared with the calculations using new-γ^{η}.

CONCLUSION

Using the spectroactive ASRS of a molecule as an index, the values of spectrochemical softness parameter k of new-γ^{ASRS} could be evaluated. PPP calculations of the excitation energies of the *p*-band of *cata*-condensed PAHs using this parameter were more effective compared with calculations using

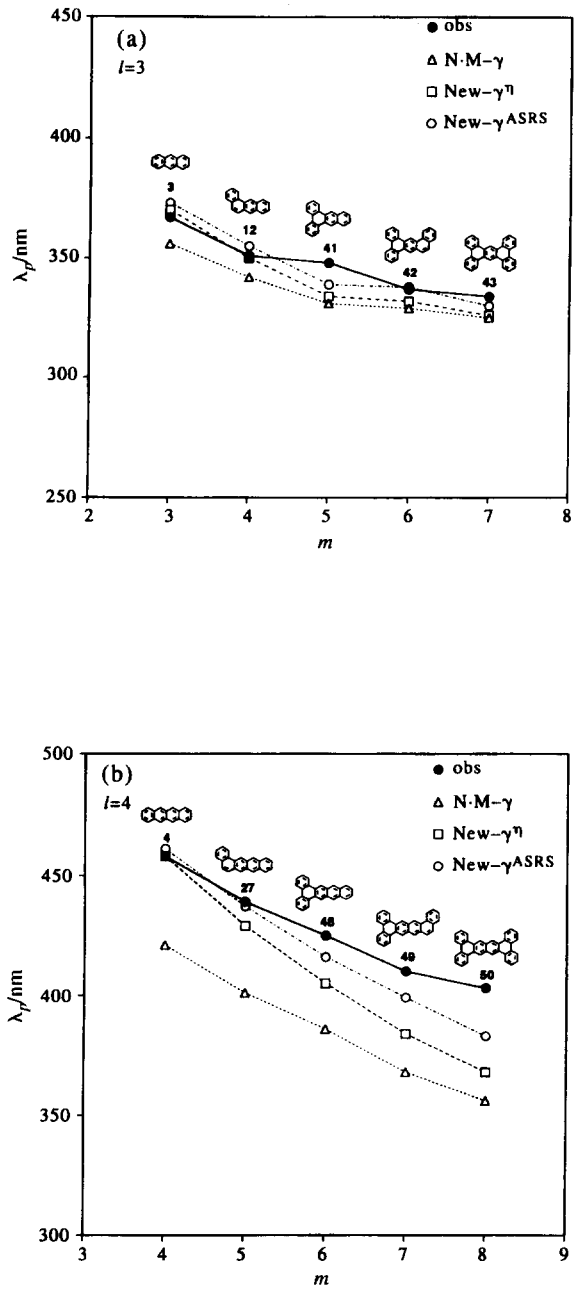

Fig. 7. The number of rings m vs the observed and calculated wavelengths of the p-band of (a) benzo-annellated anthracenes, (b) benzo-annellated naphthacenes and (c) benzo-annellated pentacenes.

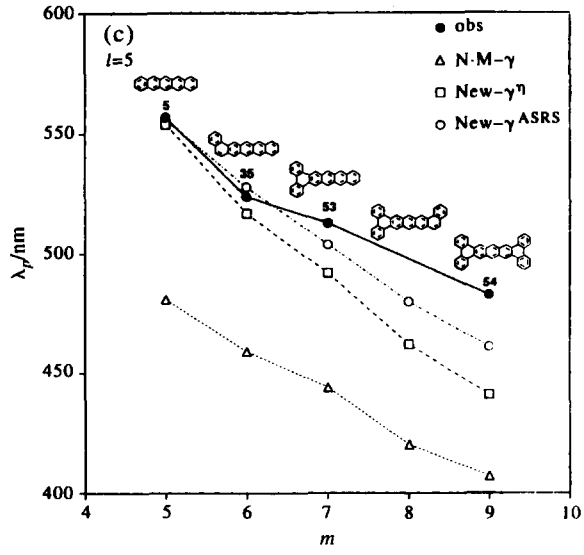

Fig. 7. — *Continued*

the N·M-γ or new-γ^{η} described in our previous paper.[1] It is apparent that the spectrochemical softness correlates very well with the spectroactive ASRS of a molecule.

In spite of the success in the calculations for *cata*-condensed PAHs, a detailed consideration for the spectroactive ASRS is concluded to be necessary with calculations for *peri*-condensed PAHs, because of the complexity of their annellation manner. Investigations of the precise PPP MO calculations of *peri*-condensed PAHs are currently in progress, as are investigations of calculations of substituted PAHs, in which functional groups are regarded as the spectroactive partial structure.

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