Precise PPP molecular orbital calculations of excitation energies of polycyclic aromatic hydrocarbons. Part 1. On the correlation between the chemical softness and the absolute hardness

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By considering the character of π-conjugated systems of polycyclic aromatic hydrocarbons (PAHs), it has become apparent that a new two centre electron repulsion integral, new-γ, which takes the chemical softness of a π-conjugated system into account is useful for the Pariser–Parr–Pople molecular orbital (PPP MO) calculations of the excitation energy of the *p*-band of PAHs. Employing the correlation between the chemical softness and the absolute hardness, the method to evaluate the chemical softness parameter *k* was established. The calculated excitation energies for 38 PAHs were greatly improved compared with the calculated ones using the conventional Nishimoto•Mataga γ (N•M-γ) function, and were well correlated with the observed ones. This is the first example of precise PPP MO calculations of excitation energies of various PAHs using new-γ.

The recent progress of computer science has brought organic chemists very convenient tools, molecular orbital calculations, which predict various properties of organic molecules. Especially, semiempirical PPP MO calculations are often useful to predict the colour of organic molecules.[1–3] PPP MO calculations have been considered to be more practical than sophisticated non-empirical *ab initio* MO calculations, however, they have a serious defect.[4] Thus, when molecules possessing a large π-conjugated system are treated, the wavelengths of the absorption maxima are often calculated to be shorter than the observed ones, and the discrepancies between them increase with the extension of the π-conjugated system.

To remove this defect, Nishimoto, one of the authors, proposed a novel two centre electron repulsion integral, new-γ, which takes a new concept of 'chemical softness' for a π-conjugated system into account.[4] New-γ brought good agreement between the calculated and the observed absorption wavelengths for linear polyenes [$H\text{-}(CH{=}CH)_n\text{-}H$ (n = 1–10)] and simple cyanines [$Me_2N\text{-}(CH{=}CH)_{n-1}\text{-}CH{=}N^+Me_2$ (n = 1–9)]. In spite of success in the calculations of absorption wavelengths for such compounds, a quantitative criterion for the determination of the value of the chemical softness parameter has not yet been established. In order to achieve precise PPP MO calculations, a reasonable method to evaluate the parameter has to be investigated.

The spectroscopic characteristics of PAHs have been studied extensively.[5–7] π-Conjugate systems of electrons in PAHs extend with annellation of six membered rings. For example, extension of annellation in the series of acenes (**1**–**6**) gave the absorption maximum of the *p*-band (nomenclature by Clar:[5] corresponds to Platt's ^1L_a band[6]) at a longer wavelength as is shown in the observed plots in Fig. 1. Nishimoto and Forster calculated the absorption maxima of some PAHs using the conventional N•M-γ[8] and variable *β* approximation,[9] in which the parameter varied corresponding to the number of rings (Table 1). The calculated wavelengths of the *p*-band of acenes (**1**–**6**) using such parameters are shorter than the observed ones, and the discrepancies between them increase as the number of rings increases [Fig. 1 (N•M-γ)]. The defect of these calculations may be improved by using new-γ described as above. For example, precise CNDO/S-CI calculation of a particular PAH has been reported,[11] in which the electron repulsion part was modified.[12] However, precise calculations of various PAHs using such methods have not been reported. Therefore, for various PAHs, it should be important to evaluate the chemical softness parameter suitable for them.

Table 1 Parameters of the core resonance integral β_{rs} in the variable β method [$\beta_{rs} = A_0 + A_1 \cdot p$, where p is the bond order]

Number of rings	A_0	A_1
1[a]	−2.040	−0.510
2[a]	−1.900	−0.510
3[a]	−1.840	−0.510
4[a]	−1.820	−0.510
5 ≧[b]	−1.812	−0.510

[a] Ref. 9. [b] Ref. 10.

In this paper, we describe the character of π-conjugated system of PAHs in terms of the chemical softness under consideration with the absolute hardness proposed by Parr and Pearson.[13] In addition, we propose the method to evaluate the chemical softness parameter which is suitable for the PPP MO calculations of the *p*-band of PAHs using the absolute hardness as an index.

MO Calculations

PPP MO calculations were performed using variable *β* approximation[9] including the parameters shown in Table 1.[9,10] As for the two centre electron repulsion integral, either the N•M-γ[8] or the following new-γ[4] was used. Other PPP parameters used in this paper were a conventional set,[3,14] and 25 singly excited configurations were used in the CI calculations.

New-γ is represented in eqn. (1), where R_{rs} is the interatomic

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

distance between the *r*-th and *s*-th atoms in a molecule containing π-electrons; a_{rs} is given by eqn. (2), where $I_r[I_s]$ and

Table 2 Calculated and observed excitation energies of the *p*-band of acenes (**1**–**6**) and phenes (**7**–**38**)

Compound				ΔE_p/eV		
				Calc.		
No.	Name	$1/\eta_{HMO}$	k^a	New-γ	N·M-γ	Obs.[b]
1	Benzene	1.00	0.91	6.06	6.18	5.96
2	Naphthalene	1.62	1.11	4.41	4.42	4.38
3	Anthracene	2.41	1.38	3.35	3.48	3.38
4	Naphthacene	3.39	1.70	2.71	2.95	2.71
5	Pentacene	4.55	2.08	2.24	2.58	2.23
6	Hexacene	5.90	2.53	1.90	2.32	1.90
7	Phenanthrene	1.65	1.13	4.17	4.18	4.23
8	Chrysene	1.92	1.21	3.75	3.80	3.87
9	Picene	1.99	1.24	3.63	3.69	3.80
10	Benzo[*c*]picene	2.12	1.28	3.47	3.56	3.66
11	Benzo[*c*]phenanthrene	1.76	1.16	3.91	3.93	3.84
12	Benz[*a*]anthracene	2.21	1.31	3.54	3.63	3.53
13	Pentaphene	2.29	1.33	3.47	3.55	3.55
14	Dibenz[*a*,*j*]anthracene	2.03	1.25	3.69	3.73	3.60
15	Dibenz[*a*,*h*]anthracene	2.11	1.28	3.58	3.65	3.57
16	Benzo[*b*]chrysene	2.47	1.40	3.26	3.39	3.27
17	Dibenzo[*b*,*k*]chrysene	2.87	1.53	2.96	3.16	3.02
18	Benzo[*c*]pentaphene	2.33	1.35	3.38	3.49	3.42
19	Benzo[*b*]picene	2.42	1.38	3.29	3.41	3.34
20	Naphtho[1,2-*b*]chrysene	2.33	1.35	3.35	3.47	3.39
21	Naphtho[2,3-*c*]pentaphene	2.54	1.42	3.22	3.38	3.28
22	Benzo[*b*]naphtho[1,2-*k*]chrysene	2.74	1.48	3.05	3.23	3.10
23	Dibenzo[*b*,*n*]picene	2.52	1.41	3.21	3.34	3.37
24	Dibenzo[*c*,*m*]pentaphene	2.31	1.34	3.35	3.47	3.43
25	Benzo[*b*]naphtho[2,3-*m*]picene	2.73	1.48	3.07	3.25	3.09
26	Dinaphtho[1,2-*b*:1′,2′-*k*]chrysene	2.61	1.44	3.12	3.29	3.18
27	Benzo[*a*]naphthacene	3.06	1.59	2.89	3.09	2.83
28	Hexaphene	2.98	1.56	2.96	3.15	2.94
29	Heptaphene	3.07	1.59	2.94	3.14	2.97
30	Dibenzo[*a*,*l*]naphthacene	2.77	1.49	3.08	3.27	2.95
31	Dibenzo[*a*,*j*]naphthacene	2.79	1.50	3.06	3.24	2.95
32	Naphtho[2,1-*a*]naphthacene	3.30	1.67	2.75	2.97	2.72
33	Benzo[*b*]naphtho[2,3-*k*]chrysene	3.57	1.76	2.60	2.88	2.65
34	Benzo[*b*]naphtho[2,3-*n*]picene	3.21	1.64	2.81	3.05	2.75
35	Benzo[*a*]pentacene	4.11	1.93	2.40	2.70	2.37
36	Benzo[*b*]hexaphene	3.98	1.89	2.45	2.75	2.39
37	Dibenzo[*a*,*l*]pentacene	3.72	1.81	2.56	2.85	2.47
38	Benzo[*a*]hexacene	5.35	2.34	2.02	2.42	2.00

[a] Values of *k* in new-γ calculated by regressive expression (13). [b] Ref. 15.

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

$A_r[A_s]$ are the valence state ionization potential and the electron affinity, respectively. Thus, ka_{rs} is a parameter which indicates the relative magnitude of mobile π-electron polarization between the *r*-th and *s*-th atoms, namely, the chemical softness of π-electrons. When the value of *k* is 1.0, new-γ is equivalent to N·M-γ.

The structural formulae of 38 PAHs treated in this paper are represented in Fig. 2. The observed excitation energies of the *p*-band of PAHs in inert solvent were extrapolated to the gas phase using Clar's method,[5] in order to minimize solvent effects. The energies used are shown in Table 2.[15]

Results and discussion

Character of the π-conjugated system of PAHs

The longest absorption maxima of simple cyanines and linear polyenes are shown in Fig. 3. It is easily seen that there is an extraordinarily high similarity between Fig. 3 and observed plots in Fig. 1. Therefore, it is assumed that the character of π-conjugated system of acenes (**1**–**6**) resembles that of simple cyanines, and that of zig-zag phenes (**7**–**10**) resembles that of linear polyenes.

Simple cyanines are described as charge resonance systems

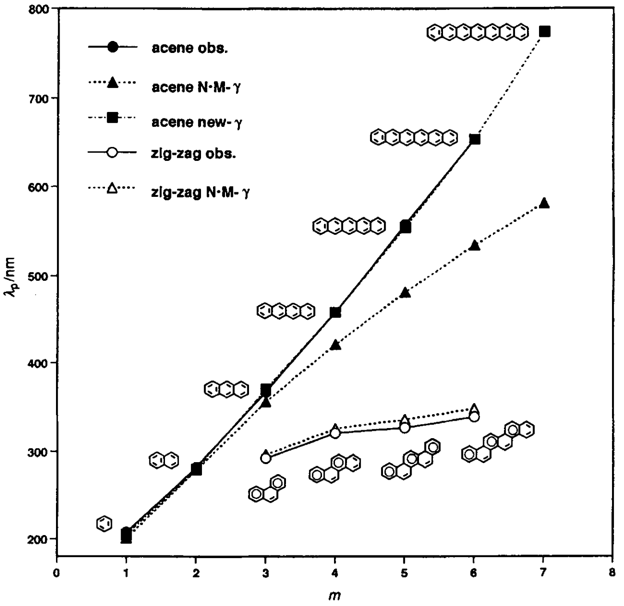


Fig. 1 Observed and calculated absorption wavelength *vs*. number of rings *m* in acenes or zig-zag phenes

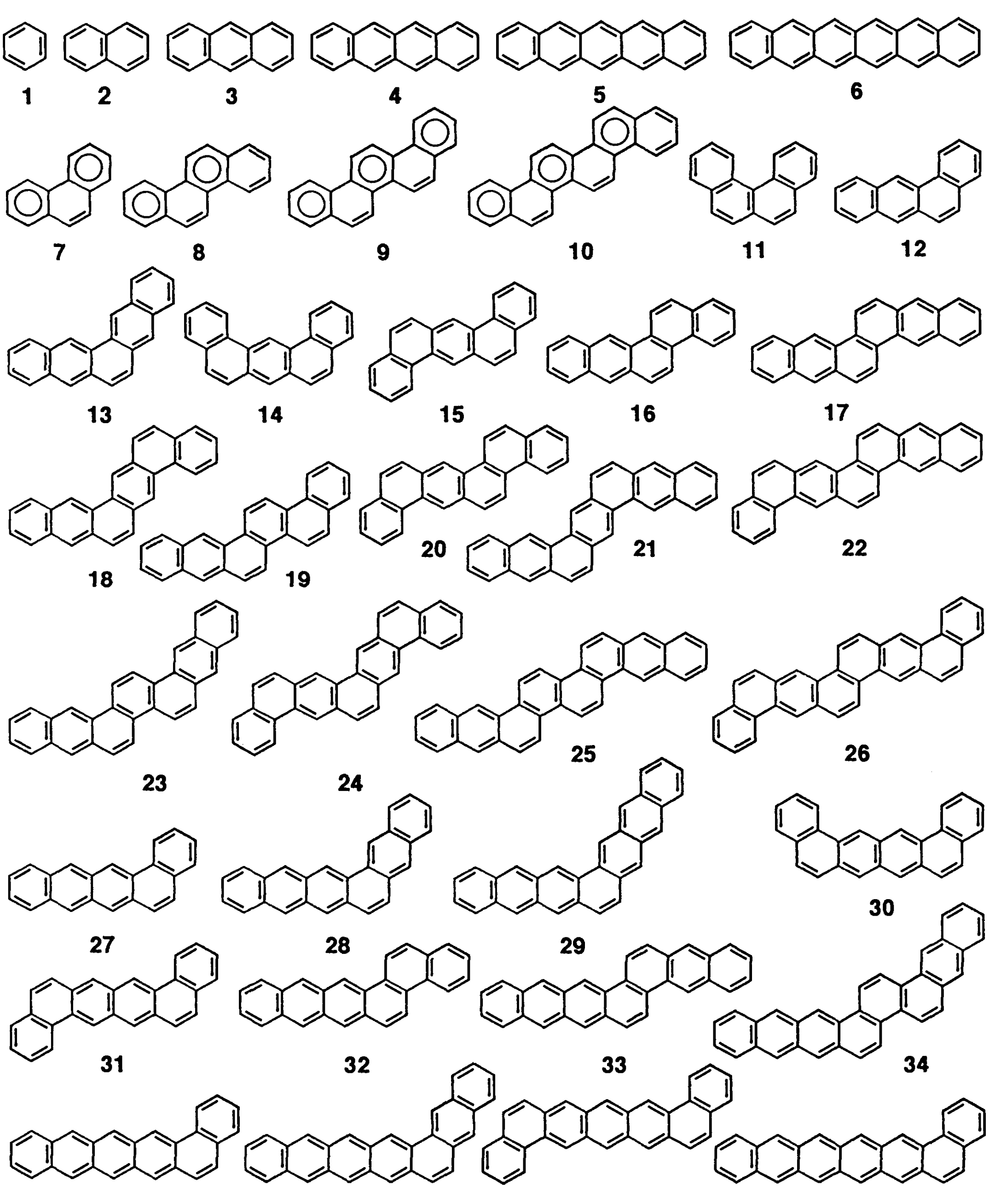


Fig. 2 Structural formulae of acenes (**1**–**6**) and phenes (**7**–**38**)

[Fig. 4 (I)],[4] so that π-electrons move almost freely in the whole molecular framework. π-Electrons in acenes also move almost freely in the whole molecular framework, but they do not possess a particular charge at a ground state. The mobilities of π-electrons of acenes arise from the migration of the aromatic sextet in the molecular framework, as proposed by Clar.[5,16] Thus we define the π-conjugated system of acenes as an 'aromatic sextet resonance system' [Fig. 4 (II)]. The values of the chemical softness parameter k for simple cyanines were set larger (chemically softer) than that of benzene which was a standard of chemical softness.[4] It is easily presumed that large k values are suitable for acenes except for benzene in the calculations of excitation energies of the p-band, because they would be chemically soft compounds. In fact, the calculated energies coincided with the observed ones when the large k values shown in Table 3 were used.

On the other hand, linear polyenes can be qualitatively described by a bond alternation structure [Fig. 4 (III)], so that their π-electrons are not so mobile as those of simple cyanines at a ground state.[4] Similarly, π-electrons of zig-zag phenes are also not so mobile as those of acenes at a ground state, because they have a tendency to localize in a particular portion of the molecular framework, as if they constitute an alternation of the aromatic sextet [Fig. 4 (IV)]. Thus, we define the π-conjugated system of zig-zag phenes as an 'aromatic sextet alternation system'. They would be chemically hard compounds. In fact, the calculated energies using N•M-γ (namely, $k = 1.0$ in new-γ) correspond well with the observed ones [Fig. 1 (N•M-γ)].

On the correlation between the chemical softness and the absolute hardness

Parr and Pearson defined the absolute hardness η of a molecule as in eqn. (3),[13] where E is the molecular electronic energy, N

$$\eta = (1/2)(\partial^2 E/\partial N^2)v \qquad (3)$$

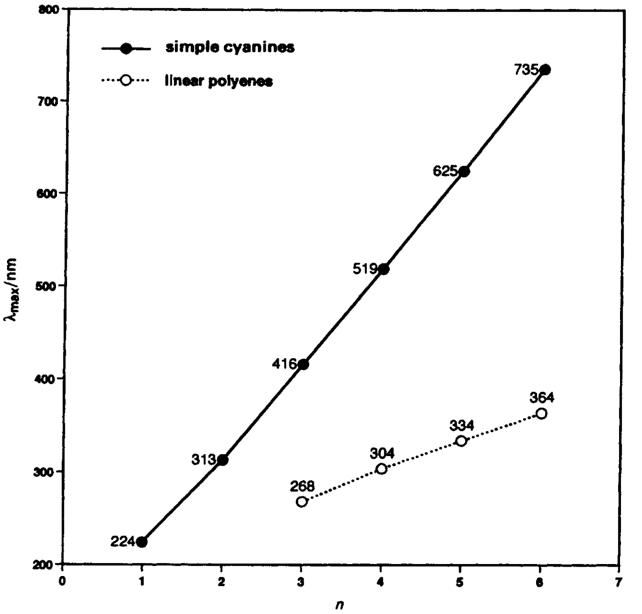
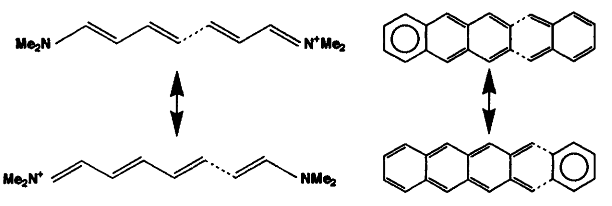
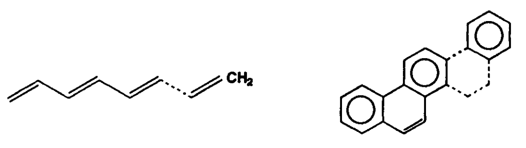


Fig. 3 Plot of observed absorption wavelength *vs.* n of simple cyanines, $Me_2N\text{–}(CH{=}CH)_{n-1}\text{–}CH{=}N^+Me_2$, and n of linear polyenes, $H\text{–}(CH{=}CH)_n\text{–}H$



(I) charge resonance

(II) aromatic sextet resonance



(III) bond alternation

(IV) aromatic sextet alternation

Fig. 4 π-Conjugated system of simple cyanines (I), acenes (II), linear polyenes (III) and zig-zag phenes (IV)

Table 3 Values of k to regenerate experimental absorption maxima of the p-band by PPP MO calculations and the inverse of absolute hardness in acenes (**1**–**6**)

	1	2	3	4	5	6
k	0.85	1.25	1.29	1.71	2.14	2.52
$1/\eta_{HMO}$	1.00	1.62	2.41	3.39	4.55	5.90

is the number of electrons, and v is the external potential due to the nuclei. The corresponding operational definition is the corresponding finite difference expression (4), where I and A are

$$\eta = (1/2)(I - A) \tag{4}$$

the ionization potential and the electron affinity, respectively. Alternatively, as has been first emphasized by Pearson,[17] the absolute hardness can be defined in terms of frontier orbitals following Koopmans' theorem[18] (5). To obtain η, the MO

$$\eta = (1/2)(E_{LUMO} - E_{HOMO}) \tag{5}$$

Table 4 Calculated and observed bond lengths of anthracene (**3**) and phenanthrene (**7**)

		Bond length		
			Calc.	
Compound	Bond[a]	Obs.[b]	N·M-γ	New-γ
3	*a*	1.368[c]	1.375	1.376[e]
	b	1.419	1.423	1.421
	d	1.436	1.431	1.429
	dd	1.428	1.424	1.425
	e	1.399	1.405	1.406
7	*a*	1.381[d]	1.386	1.387[f]
	b	1.398	1.409	1.408
	c	1.383	1.387	1.387
	d	1.405	1.413	1.413
	dd	1.404	1.410	1.411
	e	1.448	1.443	1.442
	l	1.372	1.368	1.368
	m	1.390	1.438	1.437
	n	1.457	1.415	1.414

[a] See Fig. 7. [b] X-ray data. [c] Ref. 27. [d] Ref. 28. [e] Used k = 1.38. [f] Used k = 1.13.

theory may be employed at any level of approximation, for example, the HMO level,[19] the MNDO level,[20] and the *ab initio* level.[21] In the HMO level, since for benzenoid PAHs $E_{LUMO} = -E_{HOMO}$ (6), expression (5) reduces to eqn. (7). The absolute

$$\eta_{HMO} = -E_{HOMO} \tag{7}$$

hardness is a good measure of aromaticity of PAHs,[20,22,23] and correlated well with Dewar-type resonance energy,[24] *e.g.* Hess–Schaad resonance energy,[25] or topological resonance energy.[26]

Pearson defined the softness of a molecule as the inverse of its hardness.[17] In HMO approximation, E_{LUMO} and E_{HOMO} of linear polyenes are given by eqns. (8) and (9), respectively, where

$$E_{LUMO} = \alpha - 2\beta \sin[\pi/2(n + 1)] \tag{8}$$

$$E_{HOMO} = \alpha + 2\beta \sin[\pi/2(n + 1)] \tag{9}$$

n is the number of carbon atoms. Then expression (5) is rewritten as eqn. (10). If the π-conjugated system of polyene is sufficiently

$$\eta = -2\beta \sin[\pi/2(n + 1)] \tag{10}$$

extended and chemically soft, namely, $(n + 1)$ is large and therefore $[\pi/2(n + 1)] << 1$, expression (10) can be rewritten as eqn. (11) and hence eqn. (12). The extension of the π-conjugated

$$\eta \approx -2\beta[\pi/2(n + 1)] \tag{11}$$

$$1/\eta \approx (-1/\beta\pi)(n + 1) \tag{12}$$

system $(n + 1)$, namely, the chemical softness of a molecule, is approximately proportional to the inverse of absolute hardness, if the bond alternation is not taken into account.

On the other hand, Clar noted that HOMO→LUMO excitation is identified as the p-band in PAHs.[5] The relationship between the inverse of the absolute hardness $1/\eta_{HMO}$ and the number of rings m of acenes (**1**–**6**) and zig-zag phenes (**7**–**10**) is shown in Fig. 5. A high degree of similarity is recognized between Fig. 5 and observed plots in Fig. 1. These figures indicate that the chemical softness parameter k in new-γ can be evaluated using the inverse of absolute hardness as an index.

Calculations of excitation energies

From the values of k shown in Table 3 and the inverse of

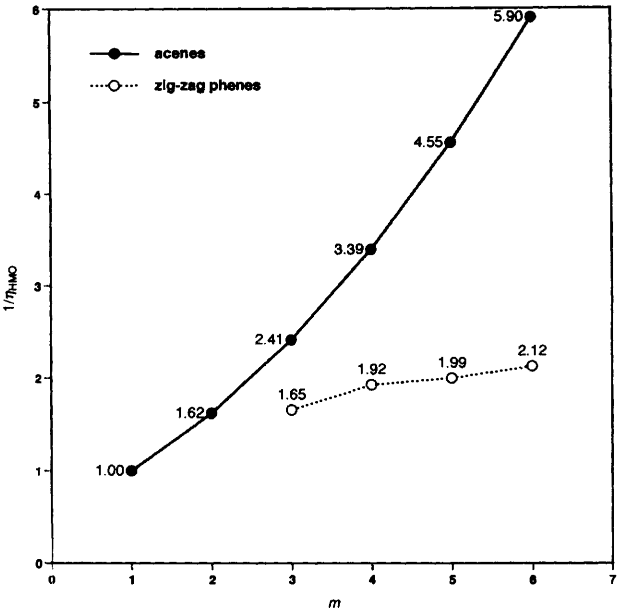


Fig. 5 Inverse of the absolute hardness ($1/\eta_{HMO}$) *vs.* number of rings *m* in acenes and zig-zag phenes

absolute hardness $1/\eta_{HMO}$ of acenes (**1–6**), the following regressive expression (13) was derived using least-squares method.

$$k = 0.33/\eta_{HMO} + 0.58 \qquad (13)$$

The excitation energies of the *p*-band of acenes (**1–6**) were calculated using the values of *k* derived from expression (13) (Table 2 and Fig. 1). The absorption wavelength of the *p*-band of heptacene which has not been isolated in a pure state because of its high reactivity[16] is calculated to be 774 nm using new-γ (parameter *k* is evaluated as 3.04 in a similar manner as above). This predicted wavelength (774 nm) may be more reasonable than the value predicted by N•M-γ (581 nm), judging from the curve depicted in Fig. 1. For the aromatic sextet resonance system, the calculated absorption wavelength of the *p*-band is greatly influenced by the value of *k*.

On the other hand, the calculated energies of the zig-zag phenes (**7–10**) using new-γ correspond well with the observed ones (Table 2). The calculated energies using N•M-γ are also close to the observed ones. For the aromatic sextet alternation system, the calculated absorption wavelength of the *p*-band is only slightly influenced by the value of *k*.

From these calculations of acenes and zig-zag phenes, expression (13) is expected to be suitable for the calculations of various PAHs. The excitation energies of the *p*-band of an additional 28 phenes (**11–38**) were calculated using the values of *k* derived from expression (13). The calculated energies using new-γ correspond well with the observed ones (Table 2).

The plots of calculated energies *vs.* the observed ones of the above 38 PAHs are shown in Fig. 6 (*a*: using N•M-γ; *b*: using new-γ). From these Figures, it is intuitively understood that the calculated energies using new-γ are greatly improved compared with the ones using N•M-γ. To evaluate the degree of improvement quantitatively, statistical parameters[23] for the linear relationship between the calculated and the observed energies, $y[E_{calc.}] = a \times x[E_{obs.}] + b$, are shown in Fig. 6, where *a* is a slope, *b* is an intercept, and *r* is a correlation coefficient of the regressive expression, respectively. In the ideal case, the values of *a* and *r* approach 1, and the value of *b* approaches 0. These statistical parameters also support the improvement of the calculated energies using new-γ compared with the ones using N•M-γ.

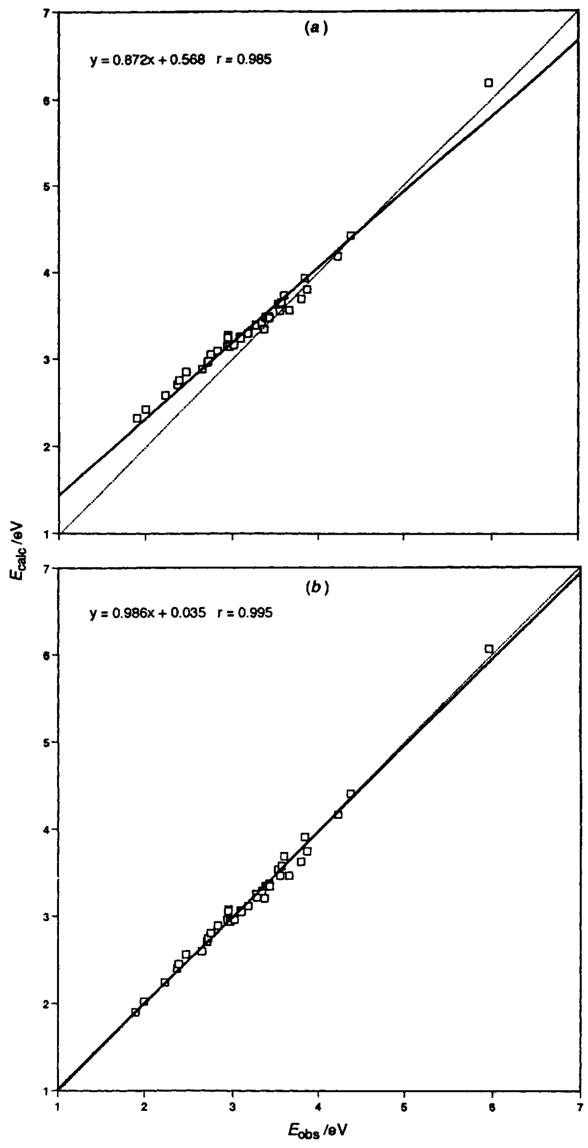


Fig. 6 Observed excitation energies *vs.* the calculated ones using (*a*) N•M-γ, (*b*) new-γ

Calculated bond lengths

Carbon–carbon bond lengths R_{CC} of conjugated system can be evaluated from the expression[9] (14), where *p* is the bond order.

$$R_{CC} = 1.517 - 0.180p \qquad (14)$$

The calculated bond lengths of anthracene (**3**) and phenanthrene (**7**) using new-γ or N•M-γ are shown in Table 4 together with observed data.[27,28] Agreements between calculated results and observed data are quite good, except for the phenanthrene *m* and *n* bonds. The accuracy of these calculated bond lengths is comparable to those of precise *ab initio* calculations,[29] or even better.

By observing the calculated bond lengths in detail, the character of the π-conjugated system in each compound is revealed (Table 5). For anthracene (**3**), the discrepancy of bond lengths between **b** and **a** using new-γ (*k* = 1.38) decreases compared with the one using N•M-γ (namely, *k* = 1.0 in new-γ), and that between **d** and **a** also decreases. Thus, the bond alternation decreases when the calculation is performed using new-γ with a large *k* value (chemically soft), so that the character of aromatic sextet resonance system of compound **3** is reproduced well.

Table 5 Difference between some bond lengths in anthracene (**3**), phenanthrene (**7**), pentacene (**5**) and picene (**9**)

		Difference	
Compound	Bond[a]	N·M-γ	New-γ[b]
3	*b–a*	0.048	0.045
	d–a	0.056	0.053
7	*e–l*	0.075	0.074
	m–l	0.070	0.069
5	*b–a*	0.057	0.045
	d–a	0.064	0.054
	d–e	0.040	0.030
	f–e	0.023	0.016
9	*u–f*	0.064	0.061
	e–f	0.069	0.067
	g–f	0.062	0.058

[a] See Fig. 7. [b] Used *k* shown in Table 2.

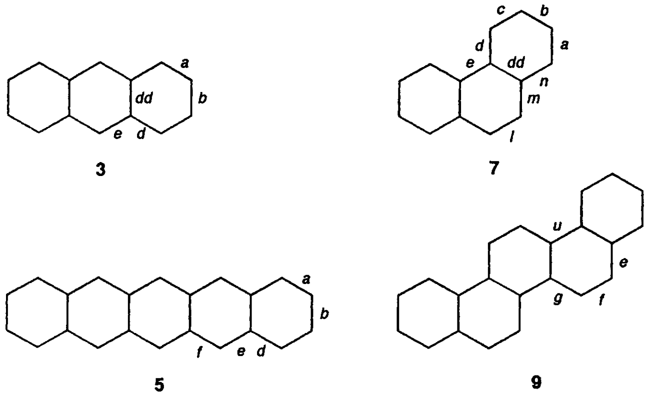


Fig. 7 Bonds of compound **3**, **5**, **7** and **9**

In the case of phenanthrene (**7**), the bond alternation slightly increases when using N·M-γ compared with using new-γ (k = 1.13). Thus, the character of the aromatic sextet alternation system of compound **7** is reproduced well when using new-γ with a small k value (chemically hard).

For pentacene (**5**) and picene (**9**), these characters of the π-conjugated system become significantly apparent.

Conclusions

In order to describe the character of the π-conjugated system of PAHs, we defined that of acenes as an 'aromatic sextet resonance system', and that of zig-zag phenes as an 'aromatic sextet alternation system'. The calculated excitation energy of the *p*-band of the former was greatly influenced by the value of chemical softness parameter k in new-γ, while that of the latter was only slightly influenced. The parameter k was evaluated using the inverse of absolute hardness as an index. The calculated excitation energies of the *p*-band of 38 PAHs using new-γ were greatly improved compared with the calculated ones using N·M-γ. To the best of our knowledge, this is the first example of precise semiempirical MO calculations of excitation energies of various PAHs using new-γ.

Besides the absolute hardness, the other indices suitable for the evaluation of the chemical softness parameter for the calculations of PAHs might exist. Investigations to find the other indices are now in progress.

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Paper 4/07756C
Received 20*th December* 1994
Accepted 9*th March* 1995