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Precise PPP Molecular Orbital Calculations of Excitation Energies of Polycyclic Aromatic Hydrocarbons. Part 4[1] Evaluation of the Spectrochemical Softness using the Dewar-type Resonance Energy

Kimihiro Hiruta,[a] Sumio Tokita,[a]* & Kichisuke Nishimoto[b]

[a]Department of Applied Chemistry, Faculty of Engineering, Saitama University, 255 Shimo-Ohkubo, Urawa, Saitama 338, Japan
[b]Institute for Fundamental Chemistry, 34-4 Takano- Nishihiraki-cho, Sakyo-ku, Kyoto 606, Japan

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ABSTRACT

For Pariser-Parr-Pople molecular orbital (PPP MO) calculations of the excitation energies of the p*-band of polycyclic aromatic hydrocarbons (PAHs), the spectrochemical softness parameter* k *of a novel two centre electron repulsion integral new-*γ *were evaluated using Dewar-type resonance energies (*REs*). In many cases, the calculated results, using the new-*γ*, were improved compared with those using the conventional Nishimoto-Mataga* γ *(N·M-*γ*) function. The Dewar-type* REs *could be used as indices of the spectrochemical softness.* © *1997 Elsevier Science Ltd*

Keywords: PPP MO Calculations, New-γ, Polycyclic Aromatic Hydrocarbons, *p*-Band, Dewar-type Resonance Energy.

INTRODUCTION

The calculated wavelengths of large π-conjugated molecules by the Pariser-Parr-Pople molecular orbital (PPP MO) procedure are often improved by using a novel two-centre electron repulsion integral new-γ [2]. Throughout our previous studies, it has become apparent that the spectrochemical softness parameter in the new-γ could be evaluated based on the size of the

*Corresponding author.

spectroactive portion (SP), which contributes mainly to the electronic spectra of polycyclic aromatic hydrocarbons (PAHS) [1, 3], or the inverse of absolute hardness η [4]. The absolute hardness [5] is a well-known criterion of the aromaticity of PAHs [6], as well as the Dewar-type resonance energy *(RE)* [7]. Therefore, it is presumed that the spectrochemical softness parameter may be evaluated based on the Dewar-type *RE*.

In this paper, we propose an alternative method to evaluate the spectrochemical softness parameter, which is suitable for the PPP MO calculations of the *p*-band of PAHs using the Dewar-type *REs* as indices. The selected PAHs for calculations are increased to 112 compounds from 54 or 52 PAHs in our previous papers [1, 3].

MO CALCULATIONS

PPP MO calculations were performed with a computer software PPP-PC [8, 9] in which variable β approximation [10] and the conventional parameters set [8, 11] were used as in our previous papers [1, 3, 4]. For the two-centre electron repulsion integral, the following new-γ was used, with 25 lower singly excited configurations in the CI calculations. To compare with the calculated results, the conventional N·M-γ [12] was also used. The new-γ is represented as in eqn (1):

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

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

a_{rs} is given by eqn (2):

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

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.

Essentially, k is a dimensionless parameter which indicates the relative magnitude of the 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 N·M-γ. Large k values are suitable for chemically softer compounds such as acenes [4].

The observed excitation energies of the *p*-band of 54 *cata*-condensed PAHs (**1–54**) and 58 *peri*-condensed PAHs (**55–112**) (structural formulae are shown in Figs 1 and 2, respectively) in an inert solvent were extrapolated to the gas phase in order to minimize solvent effects [13].

RESULTS AND DISCUSSION

We adopted the Hess-Schaad *RE [RE(HS)]* [14], topological *RE [RE(TO)]* [15], and *RE* based on the Kekulé structure counts (*SC*) *[RE(SC)]* [16], as Dewar-type *RE* [17].

RE (HS) is defined as in eqn (3):

$$RE(HS) = E_\pi(\text{conjugated molecule}) - \sum n_i E_i \tag{3}$$

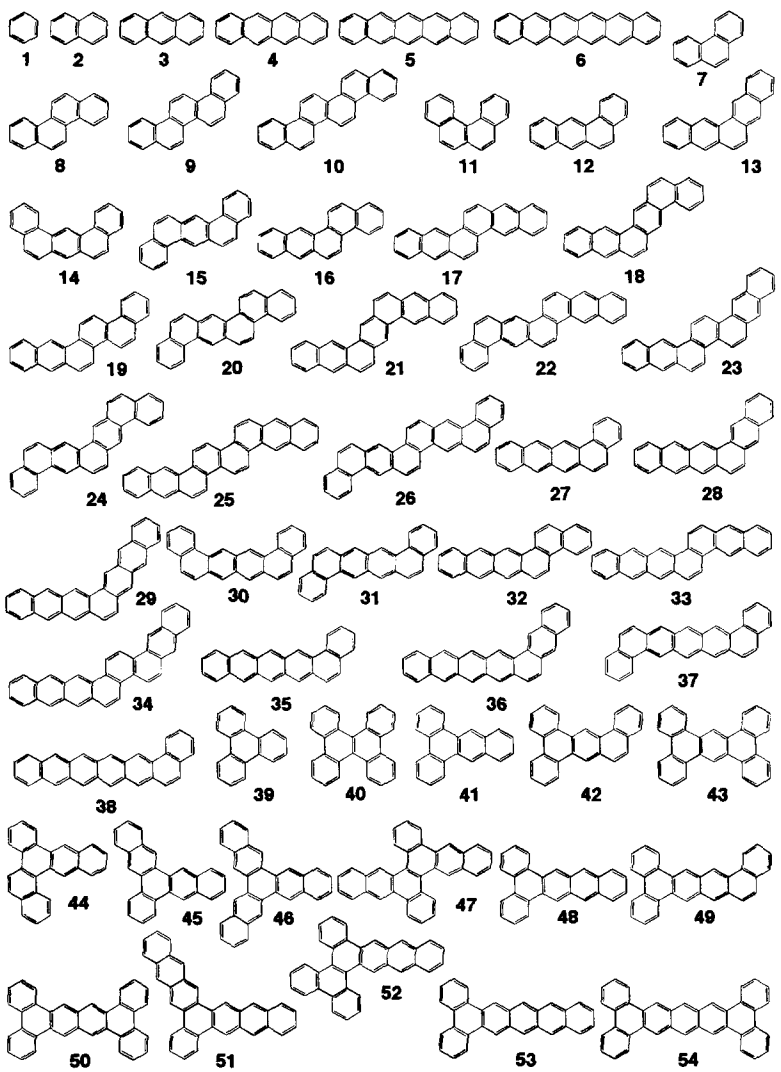

Fig. 1. Structural formulae of *cata*-condensed PAHs (1–54).

where E_π (conjugated molecule) is the Hückel π-electron energy of the conjugated model, and n_i and E_i represent the number of bonds of a particular type in a polyene and the corresponding energy parameter, respectively [14].

RE(TO) is defined as

$$RE(TO) = E_\pi(\text{conjugated molecule}) - E_\pi(\text{reference structure}) \quad (4)$$

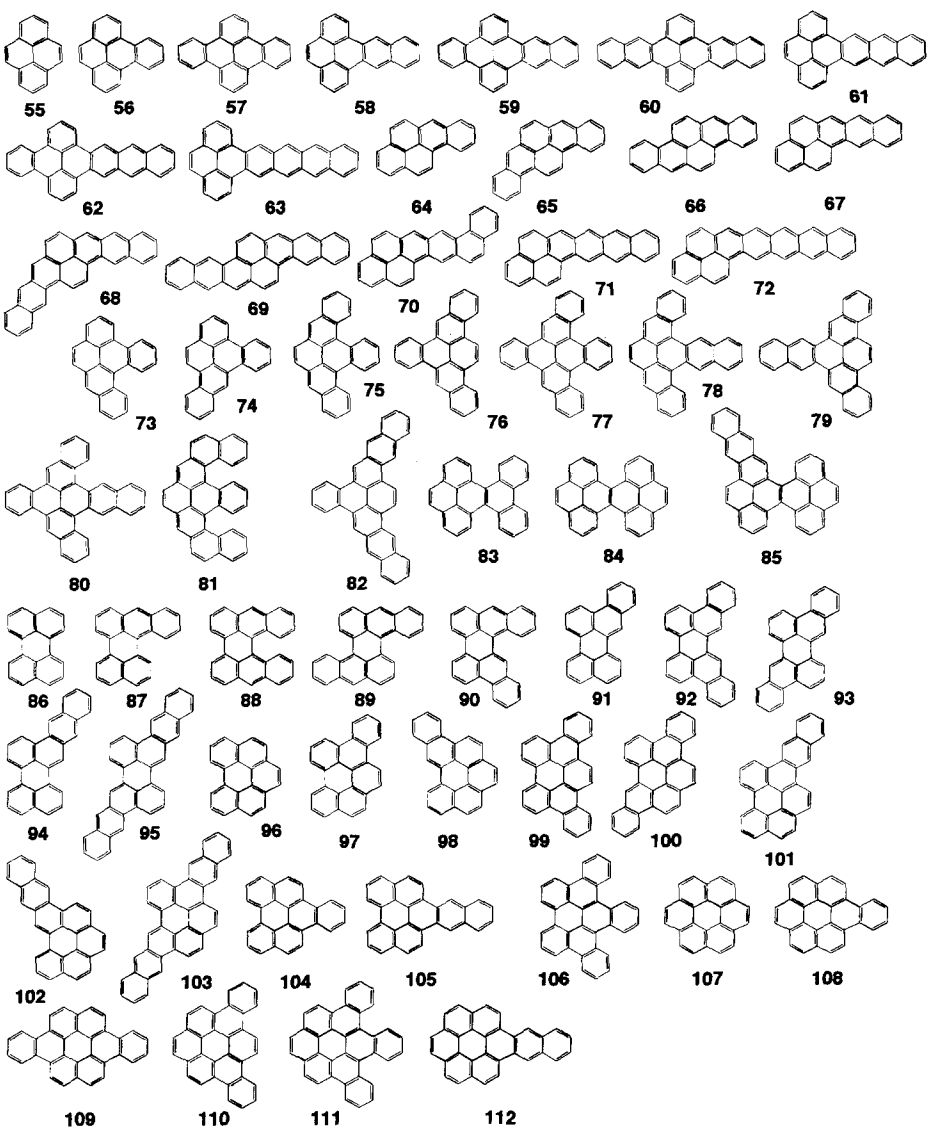

Fig. 2. Structural formulae of *peri*-condensed PAHs (55–112).

where E_π (reference structure) is the Hückel π-electron energy of the reference structure of a given molecule, which differs from E_π (conjugated molecule) in the absence of the contribution coming from the cyclic electron delocalization [15].

The aromaticity model of Herndon *et al.* [18] is a simple valence bond resonance model on the Kekulé structure counts of PAHs [16], and the *SC* can relatively easily be obtained for any PAHs [18]. The *RE(SC)* is defined by the following expression:

$$RE(SC) = 2.729 \log_{10} SC \tag{5}$$

Since the total *REs* of molecules of different sizes cannot be compared, *RE* per π-electrons (*REPE*) is usually used to this end. The values of k were evaluated using the regression expressions (6)–(8), which were derived from the *REPE* of six acenes [benzene to hexacene] and their k° values [evaluated by trial-and-error PPP MO calculations using the new-γ to regenerate the observed excitation energies of the *p*-band] and are shown in Table 1 using the least squares method.

$$k = -51.81;\ REPE(HS) + 4.07 \tag{6}$$

$$k = -82.21;\ REPE(TO) + 4.43 \tag{7}$$

$$k = -31.88;\ REPE(SC) + 5.22 \tag{8}$$

In Table 2, the excitation energies of the *p*-band of 112 PAHs calculated using the new-γ containing such k values (new-γ^{HS}, new-γ^{TO} and new-γ^{SC} respectively) are shown, in comparison with the calculated results using the N·M-γ or the new-γ^{η} (new-γ based on the inverse of absolute hardness of a molecule described in our previous paper [4]. In many cases, the calculated

TABLE 1
The Values of k° and *REPE* of Acenes

Compound	*Benzene*	*Naphthalene*	*Anthracene*	*Naphthacene*	*Pentacene*	*Hexacene*
k°	0.85	1.25	1.29	1.71	2.14	2.52
REPE(HS)	0.065	0.055	0.047	0.042	0.038	0.036
REPE(TO)	0.045	0.039	0.034	0.031	0.029	0.027
REPE(SC)	0.137	0.130	0.117	0.106	0.097	0.089

TABLE 2
Calculated and Observed Excitation Energies of the *p*-Band of PAHs

Compound		E_p/eV					
		Obs.	*Calc.*				
No.	*Name*		*N-M-γ*	*New-γ*^{n}	*New-γ*^{HS}	*New-γ*^{TO}	*New-γ*^{SC}
1	Benzene	5.96	6.18	6.06	5.66	5.66	5.98
2	Naphthalene	4.38	4.42	4.41	4.39	4.38	4.42
3	Anthracene	3.38	3.48	3.35	3.27	3.27	3.32
4	Naphthacene	2.71	2.95	2.71	2.66	2.66	2.68
5	Pentacene	2.23	2.58	2.24	2.24	2.24	2.23
6	Hexacene	1.90	2.32	1.90	1.96	1.96	1.92
7	Phenanthrene	4.23	4.18	4.17	4.15	4.15	4.16
8	Chrysene	3.87	3.80	3.75	3.72	3.73	3.82
9	Picene	3.80	3.69	3.63	3.60	3.61	3.72
10	Benzo[*c*]picene	3.66	3.56	3.47	3.46	3.46	3.61
11	Benzo[*c*]phenanthrene	3.84	3.93	3.91	3.89	3.89	3.93
12	Benz[*a*]anthracene	3.53	3.63	3.54	3.49	3.48	3.59
13	Pentaphene	3.55	3.55	3.47	3.38	3.38	3.49
14	Dibenz[*a,j*]anthracene	3.60	3.73	3.69	3.64	3.65	3.74
15	Dibenz[*a,h*]anthracene	3.57	3.65	3.58	3.53	3.54	3.66
16	Benzo[*b*]chrysene	3.27	3.39	3.26	3.22	3.22	3.35
17	Dibenzo[*b,k*]chrysene	3.02	3.16	2.96	2.91	2.91	3.05
18	Benzo[*c*]pentaphene	3.42	3.49	3.38	3.32	3.31	3.46
19	Benzo[*b*]picene	3.34	3.41	3.29	3.26	3.25	3.41
20	Naphtho[1,2-*b*]chrysene	3.39	3.47	3.35	3.32	3.32	3.49
21	Naphtho[2,3-*c*]pentaphene	3.28	3.38	3.22	3.13	3.13	3.30
22	Benzo[*b*]naphtho[1,2-*k*]chrysene	3.10	3.23	3.05	3.02	3.01	3.19
23	Dibenzo[*b,n*]picene	3.37	3.34	3.21	3.14	3.14	3.29
24	Dibenzo[*c,m*]pentaphene	3.43	3.47	3.35	3.30	3.30	3.48
25	Benzo[*b*]naphtho[2,3-*m*]picene	3.09	3.25	3.07	3.02	3.05	3.20
26	Dinaphtho[1,2-*b*:1′,2′-*k*]chrysene	3.18	3.29	3.12	3.08	3.06	3.30
27	Benzo[*a*]naphthacene	2.83	3.09	2.89	2.85	2.86	2.94
28	Hexaphene	2.94	3.15	2.96	2.90	2.89	2.99
29	Heptaphene	2.97	3.14	2.94	2.82	2.83	2.91
30	Dibenzo[*a,l*]naphthacene	2.95	3.27	3.08	3.06	3.05	3.19
31	Dibenzo[*a,j*]naphthacene	2.95	3.24	3.06	3.04	3.03	3.17
32	Naphtho[2,1-*a*]naphthacene	2.72	2.97	2.75	2.74	2.73	2.83
33	Benzo[*b*]naphtho[2,3-*k*]chrysene	2.65	2.88	2.60	2.58	2.59	2.68
34	Benzo[*b*]naphtho[2,3-*n*]picene	2.75	3.05	2.81	2.78	2.78	2.90
35	Benzo[*a*]pentacene	2.37	2.70	2.40	2.41	2.41	2.45
36	Benzo[*b*]hexaphene	2.39	2.75	2.45	2.44	2.44	2.50
37	Dibenzo[*a,l*]pentacene	2.47	2.85	2.56	2.58	2.57	2.67
38	Benzo[*a*]hexacene	2.00	2.42	2.02	2.09	2.09	2.10
39	Triphenylene	4.36	4.15	4.15	4.15	4.15	4.08
40	Dibenzo[*g,p*]chrysene	3.43	3.63	3.58	3.57	3.60	3.69
41	Benzo[*b*]triphenylene	3.56	3.75	3.71	3.70	3.71	3.76
42	Naphtho[1,2-*b*]triphenylene	3.68	3.77	3.73	3.70	3.72	3.78
43	Tetrabenz[*a,c,h,j*]anthracene	3.71	3.81	3.80	3.79	3.80	3.79
44	Naphtho[2,3-*g*]chrysene	3.27	3.52	3.41	3.38	3.40	3.55
45	Benzo[*h*]pentaphene	3.63	3.72	3.69	3.63	3.65	3.72

TABLE 2 *contd.*

Compound		E_p/eV					
		Obs.	*Calc.*				
No.	*Name*		*N·M-γ*	*New-γ^{n}*	*New-γ^{HS}*	*New-γ^{TO}*	*New-γ^{SC}*
46	Naphtho[2,3-*h*]pentaphene	3.62	3.71	3.69	3.65	3.65	3.71
47	Tetrabenzo[*b,g,k,p*]chrysene	2.97	3.24	3.06	3.03	3.11	3.72
48	Dibenzo[*a,c*]naphthacene	2.92	3.21	3.06	3.05	3.06	3.18
49	Tribenzo[*a,c,j*]naphthacene	3.03	3.37	3.23	3.21	3.23	3.39
50	Tetrabenzo[*a,c,j,l*]naphthacene	3.08	3.48	3.37	3.36	3,39	3.56
51	Benzo[*j*]heptaphene	2.93	3.25	3.10	3.04	3.05	3.14
52	Dibenzo[*g,p*]naphtho[2,3-*b*]chrysene	2.73	3.06	2.83	2.84	2.87	3.05
53	Dibenzo[*a,c*]pentacene	2.42	2.79	2.52	2.55	2.56	2.65
54	Tetrabenzo[*a,c,l,n*]pentacene	2.57	3.05	2.81	2.84	2.87	3.06
55	Pyrene	3.83	3.59	3.50	3.47	3.49	3.59
56	Benzo[*e*]pyrene	3.85	3.72	3.67	3.65	3.68	3.72
57	Dibenzo[*fg,op*]naphthacene	3.93	3.80	3.79	3.78	3.80	3.73
58	Dibenzo[*de,qr*]naphthacene	3.74	3.67	3.64	3.61	3.63	3.67
59	Dibenzo[*fg,st*]pentacene	3.69	3.68	3.65	3.63	3.65	3.69
60	Dibenzo[*hi,uv*]hexacene	3.77	3.61	3.56	3.51	3.54	3.63
61	Dibenzo[*de,uv*]pentacene	2.95	3.23	3.08	3.04	3.06	3.20
62	Dibenzo[*fg,xw*]hexacene	2.97	3.23	3.07	3.06	3.09	3.25
63	Dibenzo[*de,yz*]hexacene	2.47	2.81	2.54	2.55	2.57	2.67
64	Benzo[*def*]chrysene	3.34	3.21	3.07	3.05	3.07	3.19
65	Benzo[*rst*]pentaphene	3.27	3.09	2.91	2.90	2.93	3.07
66	Benzo[*b,def*]chrysene	2.90	2.87	2.65	2.66	2.68	2.80
67	Naphtho[8,1,2-*arq*]naphthacene	2.86	2.92	2.68	2.68	2.69	2.80
68	Benzo[*xyz*]heptaphene	2.89	2.84	2.56	2.56	2.58	2.69
69	Naphthaceno[12,1,2-*arq*]naphthacene	2.32	2.45	2.11	2.18	2.19	2.25
70	Benzo[*a*]naphtho[2,1,8-*hij*] naphthacene	2.90	2.98	2.75	2.77	2.78	2.94
71	Naphtho[8,1,2-*avu*]pentacene	2.44	2.67	2.34	2.37	2.37	2.45
72	Naphtho[8,1,2-*azy*]hexacene	2.11	2.45	2.03	2.10	2.12	2.15
73	Dibenzo[*def,p*]chrysene	3.23	3.27	3.14	3.21	3.17	3.32
74	Naphtho[1,2,3,4-*def*]chrysene	3.43	3.39	3.27	3.26	3.30	3.46
75	Naphtho[1,2,3,4-*rst*]pentaphene	3.23	3.20	3.06	3.04	3.07	3.22
76	Dibenzo[*h,rst*]pentaphene	3.33	3.27	3.12	3.11	3.16	3.37
77	Benzo[*h*]naphtho[1,2,3,4-*rst*] pentaphene	3.37	3.37	3.26	3.23	3.28	3.45
78	Anthra[1,2,3,4-*rst*]pentaphene	3.29	3.19	3.09	3.04	3.06	3.18
79	Benzo[*rst*]naphtho[2,3-*h*]pentaphene	3.40	3.32	3.20	3.17	3.19	3.37
80	Dinaphtho[3,2,1-*fg*:1′,2′,3′-*st*] pentaphene	3.15	3.30	3.20	3.16	3.19	3.36
81	Dibenzo[*a,o*]naphtho[1,2,3,4-*rst*] pentaphene	3.10	3.22	3.10	3.08	3.10	3.29
82	Dibenzo[*i,xyz*]heptaphene	2.97	3.00	2.76	2.76	2.78	2.96
83	Benzo[g]naphtho[8,1,2-*pqr*]chrysene	3.43	3.38	3.25	3.25	3.30	3.48
84	Tetrabenzo[*de,hi,mn,qr*]naphthacene	3.21	3.20	3.01	3.00	3.07	3.31
85	Anthra[1,2,3-*de*]tribenzo[*hi,mn,qr*] naphthacene	2.71	2.82	2.53	2.56	2.62	2.83

continued

TABLE 2 *contd.*

Compound		E_p/eV					
		Obs.	Calc.				
No.	Name		N·M-γ	New-γ^{η}	New-γ^{HS}	New-γ^{TO}	New-γ^{SC}
86	Perylene	2.97	3.05	2.86	2.85	2.91	3.02
87	Benzo[*a*]perylene	2.58	2.64	2.38	2.40	2.46	2.53
88	Dibenzo[*a,o*]perylene	2.37	2.32	2.01	2.08	2.12	2.16
89	Dibenzo[*a,f*]perylene	2.38	2.37	2.06	2.12	2.16	2.21
90	Dibenzo[*a,n*]perylene	2.62	2.64	2.38	2.41	2.46	2.57
91	Benzo[*b*]perylene	2.96	3.05	2.86	2.86	2.92	3.06
92	Dibenzo[*fg,ij*]pentaphene	2.97	3.03	2.84	2.86	2.90	3.08
93	Dibenzor[*fg,qr*]pentacene	3.01	3.06	2.87	2.88	2.80	3.11
94	Dibenzo[*de,st*]pentacene	2.93	2.97	2.77	2.75	2.79	2.92
95	Dibenzo[*jk,yz*]heptacene	2.94	2.93	2.70	2.69	2.72	2.87
96	Benzo[*ghi*]perylene	3.35	3.38	3.28	3.27	3.31	3.43
97	Dibenzo[*b,pqr*]perylene	3.43	3.44	3.36	3.35	3.40	3.50
98	Dibenzo[*b,ghi*]perylene	3.20	3.24	3.11	3.10	3.14	3.32
99	Tribenzo[*fg,ij,rst*]pentaphene	3.49	3.53	3.47	3.46	3.51	3.58
100	Benzo[*st*]naphtho[2,1,8-*fghi*]pentacene	3.23	3.25	3.13	3.13	3.18	3.37
101	Benzo[*qr*]naphtho[2,1,8-*hijk*] pentacene	3.39	3.38	3.28	3.25	3.29	3.46
102	Benzo[*uv*]naphtho[2,1,8-*defg*] pentacene	2.90	3.03	2.84	2.83	2.87	3.06
103	Benzo[*yz*]naphtho[2,1,8-*hujk*] heptacene	2.87	2.99	2.78	2.78	2.82	3.03
104	naphtho[1,2,3,4-*ghi*]perylene	3.12	3.12	2.97	2.99	3.04	3.24
105	Anthra[1,2,3,4-*ghi*]perylene	2.86	2.95	2.74	2.75	2.81	3.01
106	Dibenzo[fg,ij]naphtho[1,2,3,4-*rst*] pentaphene	3.06	3.16	3.02	3.04	3.11	3.32
107	Coronene	3.78	3.47	3.45	3.34	3.45	3.45
108	Benzo[*a*]coronene	3.45	3.36	3.29	3.28	3.32	3.43
109	Dibenzo[*a,j*]coronene	3.27	3.16	3.04	3.06	3.12	3.33
110	Dibenzo[*a,g*]coronene	3.45	3.35	3.28	3.28	3.32	3.44
111	Tribenzo[*a,g,j*]coronene	3.20	3.22	3.14	3.14	3.18	3.35
112	Naphtho[2,3-*a*]coronene	3.08	3.19	3.04	3.04	3.08	3.29

excitation energies are improved compared with the calculated values using the N·M-γ, and are well correlated with the observed values.

The calculated results are evaluated quantitatively by the statistical parameters for the linear relationship between the observed energies and those calculated, viz., $E_{calc} = a \cdot E_{obs.} + b$ (Table 3), where a is the slope, b is the intercept, and r is the correlation coefficient of the regression expression, respectively; s is a standard deviation of the discrepancies between the calculated and observed energies.

In the ideal case, the values of a and r approach to 1, and the values of b and s approach to 0. The parameters r and s using the new-γ^{HS}, new-γ^{TO} and

TABLE 3
The Statical Parameter of the Regression Expression Between the Calculated and the Observed Excitation Energies of the *p*-Band of PAHs (1–112)

Statistical Parameter	*N·M-γ*	*new-γ*			
		η	*HS*	*TO*	*SC*
a	0.842	0.988	0.928	0.925	0.934
b	0.596	–0.025	0.148	0.179	0.270
r	0.960	0.970	0.970	0.971	0.965
s	0.160	0.136	0.133	0.131	0.144

new-γ^{SC} are improved compared with those using the N·M-γ, as well as those using the new-γ^{η}, though the values of parameters *a* and *b* using the new-γ^{η} are somewhat favourable compared with those using the new-γ^{HS}, new-γ^{TO} or new-γ^{SC}.

As noted above, it has become obvious that the Dewar-type *REs* can be used as indices of the spectrochemical softness. The computer program of precise PPP MO calculations, which combines an evaluating process of the spectrochemical softness parameter of the new-γ based on these indices, can be easily prepared.

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