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Practical PPP molecular orbital calculations of absorption maxima of quinones.
Part 2. Evaluation of the spectrochemical softness based on the absolute hardness[☆]

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Abstract

The first absorption maxima of linear *para* acenoquinones (LPAs) were calculated by the Pariser–Parr–Pople molecular orbital (PPP MO) method using a novel, two-centre electron repulsion integral new-γ. The spectrochemical softness parameter k in the new-γ was evaluated from the absolute hardness, η_{PPP} and η_{HMO}, which were obtained by the PPP MO and the HMO level approximations, respectively. The first absorption maxima calculated using the new-γ with k obtained from η_{PPP} are greatly improved to reproduce the observed values better than using the conventional Nishimoto·Mataga-γ function. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: PPP MO calculations; New-γ; Linear *para* acenoquinones; First π–π* absorption band; Absolute hardness

1. Introduction

The calculated wavelengths of the *p*-bands of the polycyclic aromatic hydrocarbons (PAHs) by the PPP MO method using a novel two-centre electron repulsion integral new-γ [1] have been improved to better reproduce the observed values [2–6] than using the conventional Nishimoto·Mataga-γ (N·M-γ) function [7]. The spectrochemical softness (SCS) parameter k in the new-γ can be evaluated from the spectroactive portion (SP), which is defined to be the main part of the molecule contributing to the electronic spectra of PAHs [3,4,6]. The k value evaluated from SP is also suitable for the calculation of the absorption maxima of linear *para* acenoquinones (LPAs) [8].

Another method to evaluate the k value, by estimation from the absolute hardness, η is suitable for the calculation of PAHs [2]. In this paper, we confirm that the evaluation of the k values from absolute hardness is suitable for the calculation of the absorption maxima of the LPAs; the structures of LPAs are shown in Fig. 1.

[☆] For Part 1, see Ref. [8]

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2. MO calculations

PPP MO calculations were performed using computer software PPP-PC [9,10], and 25 lower singly excited configurations were used in the CI calculations. Atom-type parameters and bond-type parameters are shown in Tables 1 and 2, respectively [9,11].

The new-γ was used for two-centre electron repulsion integral γ_{rs} in the variable γ method. The N·M-γ [7] was used for the comparison of the calculated values. The fixed bond length (1.4 Å) and fixed bond angle (120°) were used for all bonds for the input molecular geometry, because the molecular geometry is modified with progress of the reiterative, self-consistent-field (SCF) calculations.

When the mobile π-electron polarization in the region between the rth and sth atoms in a molecule is considered as follows,

$$r^{+} - s^{-} \text{ and } r^{-} - s^{+}$$

the new-γ is represented as Eq. (1):

$$\gamma_{rs} = e^{2}/\left[R_{rs} + 2k\mathrm{e}^{2}/I_{r} - A_{s} + I_{s} - A_{r}\right] \qquad (1)$$

where R_{rs} is the interatomic distance (in Å) between the rth and sth 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. The coefficient k is the relative magnitude of the dynamic polarizability of the mobile

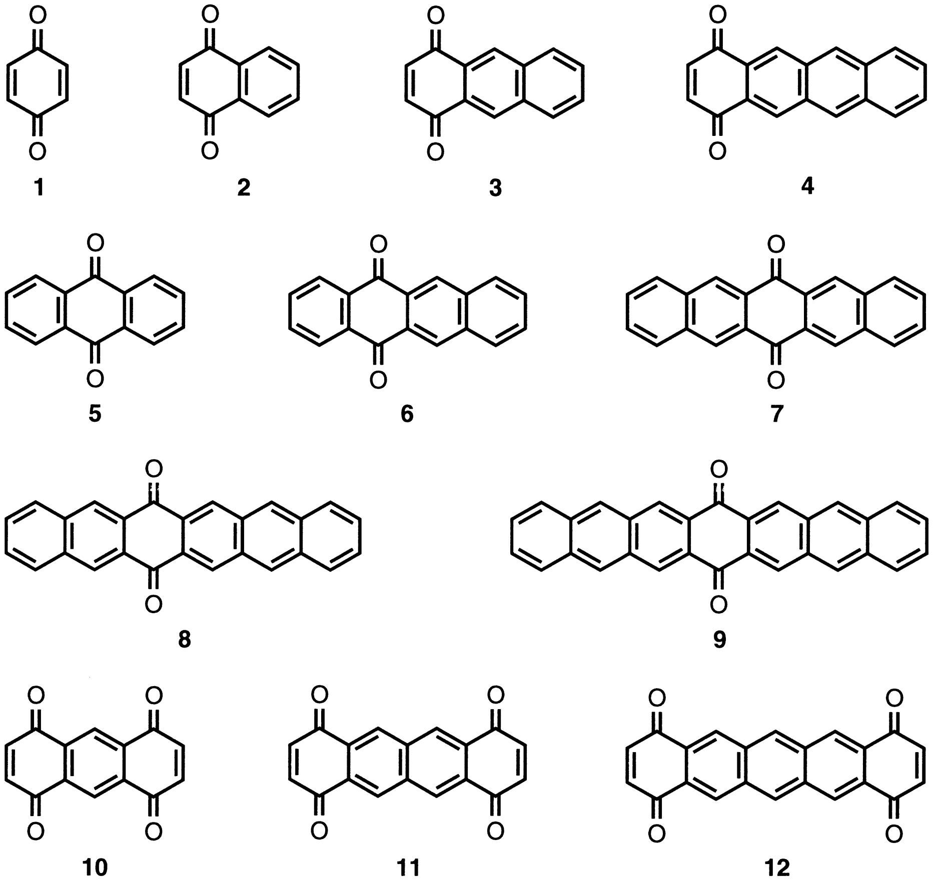

Fig. 1. Structural formulae of linear *para* acenoquinones.

π-electron in the region between the *r*th and *s*th atoms, namely, the 'spectrochemical softness' of the 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 compounds having chemically softer π-electrons, whereas small *k* values are suitable for chemically harder compounds [2].

For HMO calculations, the Coulomb integral and the resonance integral of the carbonyl oxygen atom and the adjacent carbon atom used are as follows [9]:

$$\alpha_{\mathrm{O}(=\mathrm{C})} = \alpha_{\mathrm{C}} + 2\beta_{\mathrm{C}} \qquad (2)$$

$$\alpha_{\mathrm{C}(=\mathrm{O})} = \alpha_{\mathrm{C}} + 0.2\beta_{\mathrm{C}} \qquad (3)$$

$$\beta_{\mathrm{C}=\mathrm{O}} = 1.414\beta_{\mathrm{C}} \qquad (4)$$

Table 1
Atom-type parameters

Atom	I_r	A_r	γ_{rr}
C	11.16	0.03	11.13
O=C (carbonyl oxygen)	17.70	2.47	15.23

Table 2
Bond-type parameters

Bond	Number of hexagons[a]	A_0	A_1	D_0	D_1
C–C	0	−2.040	−0.510	1.517	−0.180
C–C	1	−2.040	−0.510	1.517	−0.180
C–C	2	−1.900	−0.510	1.517	−0.180
C–C	3	−1.840	−0.510	1.517	−0.180
C–C	4	−1.820	−0.510	1.517	−0.180
C–C	⩾5	−1.812	−0.510	1.517	−0.180
C–C (=O)		−2.040	−0.510	1.517	−0.180
O=C		−2.440	−0.510	1.410	−0.180

[a] In molecules for PAHs and in acene units for LPAs.

3. Results and discussion

Parr and Pearson defined the absolute hardness η of a molecule as [10]:

$$\eta = (1/2)\left(\partial^2 E/\partial N^2\right)_v \qquad (5)$$

where E is the molecular electronic energy, N 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:

$$\eta = (1/2)(I - A) \qquad (6)$$

where I and A are the ionization potential and the electron affinity, respectively. Alternatively, as the first emphasized by Pearson [11], absolute hardness η can be defined in terms of the frontier orbital following Koopmans' theorem [12].

$$\eta = (1/2)(E_{\mathrm{LUMO}} - E_{\mathrm{HOMO}}) \qquad (7)$$

To obtain η, the MO theory can be employed at any level of approximation, for example, the HMO level [13], the MNDO level [14], and the ab initio level [15].

We earlier reported that the SCS parameter *k*, evaluated using the absolute hardness at the HMO level, η_{HMO} was suitable for the calculation of the excitation energies of the *p*-band of 38, *cata*-condensed PAHs [2]. The parameter *k* was evaluated using the regression expression (8) which was derived from the η_{HMO} of acenes (benzene to hexacene) and their k^{o} values. The k^{o} values were evaluated by trial and error PPP MO calculations using the new-γ to regenerate the observed excitation energies of the *p*-band. η_{HMO} and k^{o} values are shown in Table 3 and the regression expression (8) was obtained using the least squares method.

Table 3
The values of k° and the inverse of absolute hardness

Compound	Benzene	Naphthalene	Anthracene	Naphthacene	Pentacene	Hexacene
k^{o}	0.85	1.25	1.29	1.71	2.14	2.52
$1/\eta_{\mathrm{HMO}}$	1.00	1.62	2.41	3.39	4.55	5.90
$1/\eta_{\mathrm{PPP}}$	0.211	0.277	0.336	0.387	0.431	0.470

$$k = 0.33/\eta_{\mathrm{HMO}} + 0.58 \qquad (8)$$

Similarly, the regression expression (9) can be derived from η_{PPP}, the absolute hardness at the PPP MO level (refer to Table 2).

$$k = 6.19/\eta_{\mathrm{PPP}} - 0.55 \qquad (9)$$

The absolute hardness, η_{HMO} and η_{PPP}, and the excitation energies of the *p*-band for 38 *cata*-condensed PAHs are shown in Table 4. The excitation

Table 4
Calculated and observed excitation energies of the *p*-band of PAHs

Compound	E_p (eV)					
	Observed[a]	Calculated				
		N·M-γ[a]	New-γ			
			η_{HMO}[a]	(k)	η_{PPP}	(k)
Benzene	5.96	6.18	6.06	(0.91)	5.79	(0.76)
Naphthalene	4.38	4.42	4.41	(1.11)	4.40	(1.16)
Anthracene	3.38	3.48	3.35	(1.38)	3.30	(1.53)
Naphthacene	2.71	2.95	2.71	(1.70)	2.67	(1.85)
Pentacene	2.23	2.58	2.24	(2.08)	2.23	(2.12)
Hexacene	1.90	2.32	1.90	(2.53)	1.93	(2.36)
Phenanthrene	4.23	4.18	4.17	(1.13)	4.15	(1.22)
Chrysene	3.87	3.80	3.75	(1.21)	3.70	(1.38)
Picene	3.80	3.69	3.63	(1.24)	3.58	(1.41)
Benzo[*c*]picene	3.66	3.56	3.47	(1.28)	3.41	(1.47)
Benzo[*c*]phenanthrene	3.84	3.93	3.91	(1.16)	3.89	(1.31)
Benz[*a*]anthracene	3.53	3.63	3.54	(1.31)	3.49	(1.47)
Pentaphene	3.55	3.55	3.47	(1.33)	3.42	(1.51)
Dibenz[*a*,*j*]anthracene	3.60	3.73	3.69	(1.25)	3.64	(1.42)
Dibenz[*a*,*h*]anthracene	3.57	3.65	3.58	(1.28)	3.49	(1.58)
Benzo[*b*]chrysene	3.27	3.39	3.26	(1.40)	3.20	(1.59)
Dibenzo[*b*,*k*]chrysene	3.02	3.16	2.96	(1.53)	2.89	(1.73)
Benzo[*c*]pentaphene	3.42	3.49	3.38	(1.35)	3.32	(1.54)
Benzo[*b*]picene	3.34	3.41	3.29	(1.38)	3.23	(1.57)
Naphtho[1,2-*b*]chrysene	3.39	3.47	3.35	(1.35)	3.28	(1.55)
Naphtho[2,3-*c*]pentaphene	3.28	3.38	3.22	(1.42)	3.15	(1.62)
Benzo[*b*]naphtho[1,2-*k*]chrysene	3.10	3.23	3.05	(1.48)	2.98	(1.69)
Dibenzo[*b*,*n*]picene	3.37	3.34	3.21	(1.41)	3.14	(1.60)
Dibenzo[*c*,*m*]pentaphene	3.43	3.47	3.35	(1.34)	3.28	(1.54)
Benzo[*b*]naphtho[2,3-*m*)picene	3.09	3.25	3.07	(1.48)	3.00	(1.69)
Dinaphtho[l,2-*b*:1′,2′-*k*]chrysene	3.18	3.29	3.12	(1.44)	3.04	(1.65)
Benzo[*a*]naphthacene	2.83	3.09	2.89	(1.59)	2.84	(1.77)
Hexaphene	2.94	3.15	2.96	(1.56)	2.91	(1.74)
Heptaphene	2.97	3.14	2.94	(1.59)	2.88	(1.77)
Dibenzo[*a*,*l*]naphthacene	2.95	3.27	3.08	(1.49)	3.02	(1.69)
Dibenzo[*a*,*j*]naphthacene	2.95	3.24	3.06	(1.50)	3.00	(1.70)
Naphtho[2,l-*a*]naphthacene	2.72	2.97	2.75	(1.67)	2.70	(1.85)
Benzo[*b*]naphtho[2,3-*k*]chrysene	2.65	2.88	2.60	(1.76)	2.55	(1.93)
Benzo[*b*}naphtho[2,3-*n*]picene	2.75	3.05	2.81	(1.64)	2.76	(1.81)
Benzo[*a*]pentacene	2.37	2.70	2.40	(1.93)	2.37	(2.03)
Benzo[*b*]hexaphene	2.39	2.75	2.45	(1.89)	2.42	(2.39)
Dibenzo[*a*,*l*]pentacene	2.47	2.85	2.56	(1.81)	2.52	(1.95)
Benzo[*a*]hexacene	2.00	2.42	2.02	(2.34)	2.04	(2.00)

[a] Ref. [2].

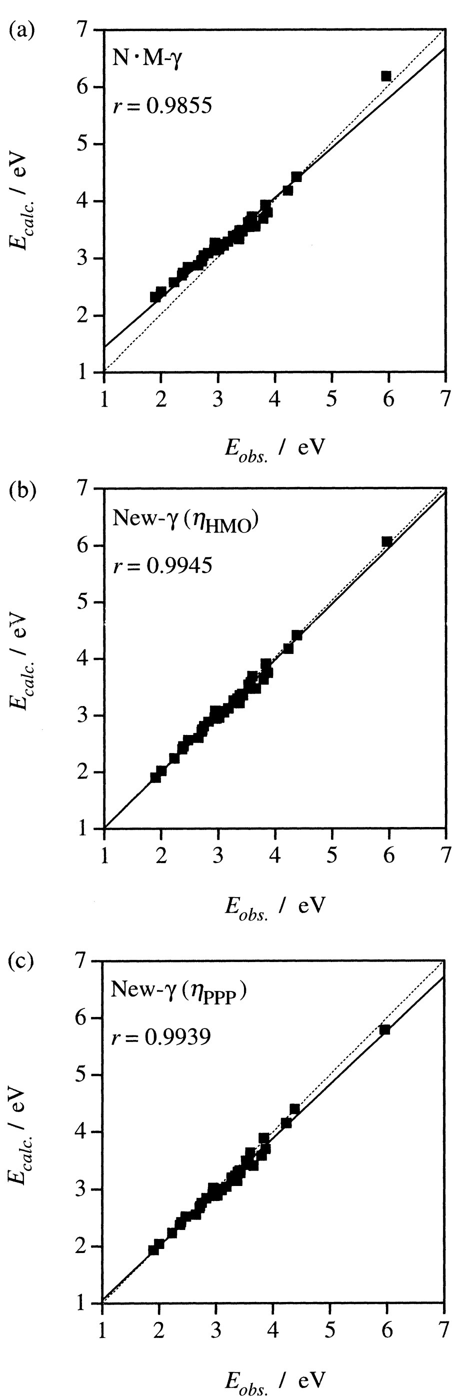

Fig. 2. Observed excitation energies vs. calculated excitation energies for 38 *cata*-condensed PAHs using (a) N·M-γ, (b) new-γ (η_{HMO}), and (c) new-γ (η_{PPP}).

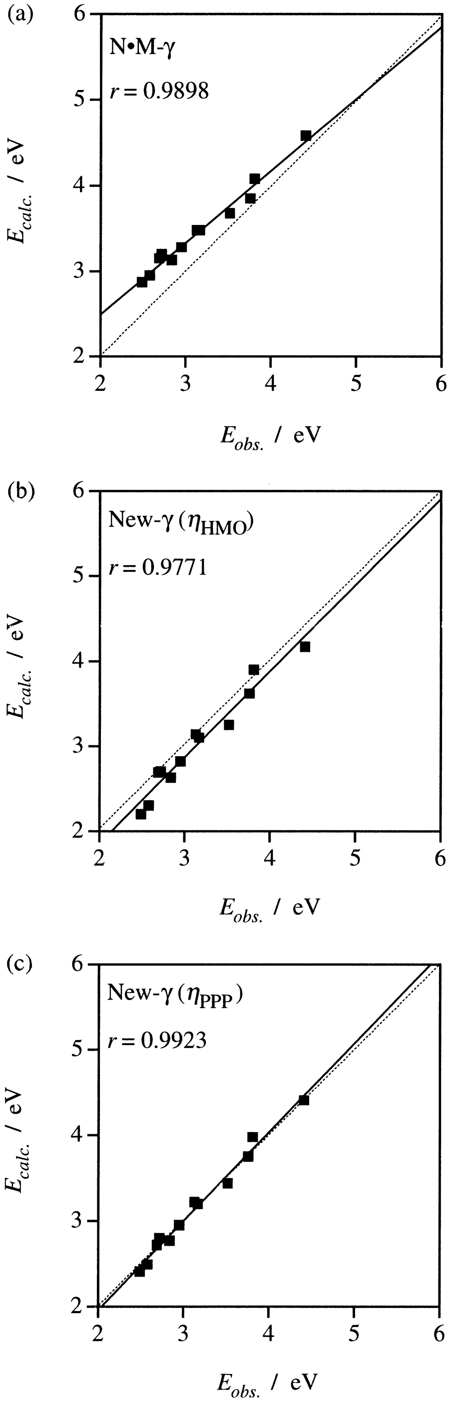

Fig. 3. Observed excitation energies vs. calculated excitation energies for 12 LPAs using (a) N·M-γ, (b) new-γ (η_{HMO}), and (c) new-γ (η_{PPP}).

Table 5
Calculated and observed excitation energies of the first absorption maxima of LPAs

Compound	E_P (eV)					
	Observed	Calculated				
		N·M-γ	New-γ			
			η_{HMO}	(k)	η_{PPP}	(k)
1	4.41	4.58	4.17	(1.67)	4.41	(1.22)
2	3.76	3.85	3.62	(1.43)	3.75	(1.22)
3	2.95	3.28	2.82	(1.74)	2.95	(1.49)
4	2.58	2.95	2.30	(2.19)	2.49	(1.72)
5	3.81	4.08	3.90	(1.29)	3.98	(1.16)
6	3.13	3.48	3.14	(1.55)	3.22	(1.41)
7	3.17	3.48	3.10	(1.58)	3.20	(1.42)
8	2.72	3.20	2.70	(1.83)	2.80	(1.61)
9	2.69	3.15	2.69	(1.91)	2.72	(1.65)
10	3.52	3.68	3.25	(1.67)	3.44	(1.32)
11	2.84	3.13	2.63	(1.85)	2.77	(1.54)
12	2.49	2.87	2.20	(2.28)	2.41	(1.73)

energies were calculated using the new-γ containing k values evaluated by Eqs. (8) and (9) and the N·M-γ. The correlation coefficients r of the regressive expression of $E_{\mathrm{obs.}}$ vs. $E_{\mathrm{calc.}}$ are shown in Fig. 2. The calculated values using the new-γ are shown, clearly, the observed ones better than the ones using the N·M-γ. η_{HMO} is more favorable to an index to evaluate the k values than η_{PPP}, as decided from the r value.

The wavelengths of the first absorption maxima for 12 kinds of LPAs were calculated by the PPP method using the new-γ with the k values evaluated from η_{HMO} and η_{PPP} using Eqs. (8) and (9). The structures of the LPAs (Fig. 1) and the calculated results (Table 5 and Fig. 3) show that the new-γ reproduces the observed values better than using the N·M-γ. The r value obtained using η_{PPP} is better for reproduction of observed wavelengths than that secured using η_{HMO}. The results are different from those of PAHs, as mentioned above.

The absolute hardness, η_{HMO}, is affected by Coulomb integral and resonance integral of the carbonyl oxygen atom; these parameters are arbitrarily estimated and may not be suitable for calculation of the η_{HMO} for the LPAs. On the other hand, the parameters used in the PPP MO calculations are corrected to the most suitable values in the course of the reiterative SCF calculations. Therefore, the calculated η_{PPP} value seems to be more reliable than the η_{HMO} value as an index for the evaluation of SCS parameters in the new-γ.

4. Conclusions

In conclusion, the absolute hardness of the PPP MO level, η_{PPP}, is more effective for the evaluation of the SCS parameter in the new-γ than the absolute hardness at the HMO level, η_{HMO}, particularly in the calculation of the wavelengths of the first absorption maxima of LPAs. The η_{PPP} value may be suitable as an index for the practical PPP MO calculation of many organic molecules containing hetero atoms. Investigations to confirm the above assumption are now in progress.

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