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Practical PPP Molecular Orbital Calculations of Absorption Maxima of Quinones

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ABSTRACT

In order to calculate the excitation energies of linear para *acenoquinones (LPAs) more accurately by Pariser–Parr–Pople molecular orbital (PPP MO) method, the spectrochemical softness parameter* k *of a novel two centre electron repulsion integral new-γ are evaluated based on spectroactive portion (SP) in a molecular framework. SP is defined as the longest acene portion, including a quinonoid ring of LPAs. The calculated results using the new-γ are greatly improved compared with those using the conventional Nishimoto·Mataga γ function. © 1998 Elsevier Science Ltd. All rights reserved*

Keywords: PPP MO calculations, new-γ, linear *para* acenoquinone, first π–π^* absorption band, spectroactive portion.

INTRODUCTION

The absorption maxima wavelength of organic molecules calculated by the Pariser–Parr–Pople molecular orbital (PPP MO) method are often shorter [1] than the observed values, when molecules possessing a large π-conjugated system are treated, as for example, in calculations of the p-band of polycyclic aromatic hydrocarbons (PAHs) [2]. Such calculated results are improved by

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using a novel two-centre electron repulsion integral new-γ [1], instead of using the conventional Nishimoto•Mataga γ function (N•M-γ) [3] or the Ohno•Klopman γ function (O•K$-\gamma$) [4].

In our previous papers dealing with a series of fused polycyclic aromatic compounds [2, 5–7], reasonable methods to evaluate the spectrochemical softness parameter k in the new-γ were established. For the next step of the investigation, suitable values of k for practical calculations of the absorption maxima of organic molecules possessing various substituents were the necessary corollary. In this paper, the values of k suitable for quinone derivatives which contain an acene-like partial structure, namely, linear *para* acenoquinones (LPAs), are proposed. The structural formula of LPA is shown in Fig. 1, and the abbreviations as Q[n, n′] are used according to Itho's review [8].

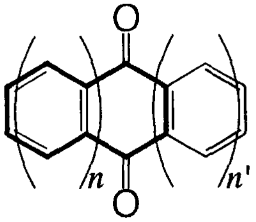
MO CALCULATIONS

PPP MO calculations were performed with a 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 used are shown in Tables 1 and 2, respectively [9–11]. Parameters of the core resonance integral β_{rs} in the variable β method are modified with the progress of iteration in the self-consistent-field (SCF) calculations as follows [12]:

$$\beta_{rs} = A_0 + A_1 \cdot P_{rs} \tag{1}$$

where P_{rs} is the bond order, which is given by

$$P_{rs} = 2 \sum_{\mu=1}^{\mathrm{HOMO}} c_{r\mu} c_{s\mu} \tag{2}$$



$Q[n, n']: n \geqq n'$

$SP(l) = n+1$

Fig. 1. Structural formula of LPAs; SP is represented using bold lines.

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 for PAHs [n or n′ for LPAs]*	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	−0.560	1.410	−0.180

where $c_{r\mu}[c_{s\mu}]$ is the LCAO coefficient of the molecular orbital. Parameters of β_{rs} for PAHs are used corresponding to the number of hexagons contained in the whole molecular framework [12]. For LPAs, however, parameters of β_{rs} are used corresponding to the repeating number $n\,[n']$ of fused six-membered rings in Fig. 1, ignoring the quinonoid ring.

For two centre electron repulsion integral γ_{rs} in the variable γ method, the following new-γ was used, as well as the conventional N•M-γ [3] in order to compare with the calculated results. For the input molecular geometry, the fixed bond length (1.4 Å) and fixed bond angle (120°) were used for all bonds, because the molecular geometry is modified with the progress of the SCF calculations.

When the mobile π-electron polarization at 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 [1]

$$\gamma_{rs} = e^2/\left[\left(R_{rs} + 2ke^2/(I_r - A_s + I_s - A_r)\right]\right. \tag{3}$$

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. Essentially, k is a dimensionless parameter which indicates the relative magnitude of mobile π-electron polarization at the region between the rth and sth 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, except for benzene [2]. For example, the k values shown in Table 3 were suitable to calculate accurately the excitation energies of the p-band of acenes [5, 6].

RESULTS AND DISCUSSION

There are many reports concerning the electronic spectra of LPAs [8, 13]. For many organic colourants, the most important absorption band is the first π–π^* absorption band which usually appears in the longest wavelength region, though a weak n–π^* absorption band appears in the longest wavelength region for some LPAs. When the excitation energy of the first π–π^* absorption maximum of p-benzoquinone (Q[0, 0]), which is the parent compound of LPAs, is calculated by the PPP MO method using the N•M-γ, the calculated result can reproduce the observed one[†] (Table 1). With progress of the annellation toward higher LPAs, however, the calculated excitation energies of the first absorption maxima using the N•M-γ become larger compared with the observed ones [Table 4, Fig. 2 (- -△- -)].

The partial structure which contributes mainly to the electronic spectra of PAHs has been defined as the spectroactive portion (SP) [5, 6], and the spectrochemical softness parameter k in the new-γ for the calculations of excitation energies of the p-band of PAHs can be evaluated based on the size of SP. The electronic spectra of LPAs seem also to be governed by the partial structure of the molecule, namely, SP, in accordance with the description by Fabian *et al.* [15]. The first π–π^* absorption maxima of organic molecules are generally identified as a transition described by mainly HOMO→LUMO,

TABLE 3
Values of Spectrochemical Softness Parameter k Corresponding to SP Parameter l

Acene	*Benzene*	*Naphthalene*	*Anthracene*	*Naphthacene*	*Pentacene*	*Hexacene*	*Heptacene*
l	1	2	3	4	5	6	7
k	0.81	1.14	1.47	1.80	2.13	2.46	2.79

[†] For PAHs, extrapolated values from the liquid phase to the gas phase were used as observed excitation energies [2], using Clar's empirical expression [14]. For LPAs, however, the observed excitation energies in inert solvent are used 'as is', because the empirical expression for the extrapolation has not been established, to the best of our knowledge.

TABLE 4
The Observed and Calculated Excitation Energies of the First Absorption Maxima of LPAs

No.	*Abbreviation*	*l*	*k*	$\Delta E/eV$ calculated *new-γ*	$\Delta E/eV$ calculated *N•M-γ*	$\Delta E/eV$ *observed*[a]
1	Q[0, 0] (1,4-benzoquinone)	—	—	—	4.58	4.41[b]
2	Q[1, 0] (1,4-naphthoquinone)	2	1.14	3.74	3.85	3.76[b]
3	Q[2, 0]	3	1.47	2.96	3.28	2.95[b]
4	Q[3, 0]	4	1.80	2.46	2.95	2.58[b]
5	Q[4, 0]	5	2.13	2.14	2.80	—
6	Q[5, 0]	6	2.46	1.89	2.53	—
7	Q[6, 0]	7	2.79	1.71	2.29	—
8	Q[1, 1] (9,10-anthraquinone)	2	1.14	3.99	4.08	3.88[b]
9	Q[2, 1]	3	1.47	3.18	3.48	3.13[b]
10	Q[3, 1]	4	1.80	2.69	3.16	—
11	Q[4, 1]	5	2.13	2.36	2.89	—
12	Q[5, 1]	6	2.46	2.11	2.54	—
13	Q[2, 2]	3	1.47	3.16	3.48	3.17[b]
14	Q[3, 2]	4	1.80	2.71	3.20	2.72[c]
15	Q[4, 2]	5	2.13	2.40	2.89	—
16	Q[3, 3]	6	1.80	2.74	3.15	2.69[c]

[a] Ref. 8 and references cited therein.
[b] Hexane.
[c] Trichlorobenzene.

because the configuration energy between HOMO and LUMO is the smallest in all configuration energies. Observing the character of LACO coefficients of HOMO and LUMO of some LPAs, the acene character is maintained in the acene-like portion for HOMO, and the character of *p*-benzoquinone (Q[0, 0]) is maintained in the quinonoid ring for LUMO (Fig. 3). Thus, the first π-π* absorption band of LPAs is characterized as a charge transfer type transition from HOMO to LUMO. SP of LPAs is determined as the longest acene portion, including a quinonoid ring, namely, $n + 1$ in Fig. 1.

We have defined the SP parameter l for calculations of the excitation energies of the *p*-band of PAHs [5, 6]. For acenes, the values of l correspond to the number of hexagons in the whole molecular framework, as shown in Table 3, because the SP of acenes is the whole molecular framework. For other generalized PAHs, the values of l correspond to the number of hexagons contained in SP, and the values of k were evaluated based on the values of l as acenes [5, 6].

Similarly, for LPAs, the values of l correspond to the number of hexagons contained in SP shown in Fig. 1. The relationship between the values of l and k for PAHs may be applied to that for LPAs. Therefore, for calculations of the excitation energies of the first π–π* absorption maxima of 15 LPAs

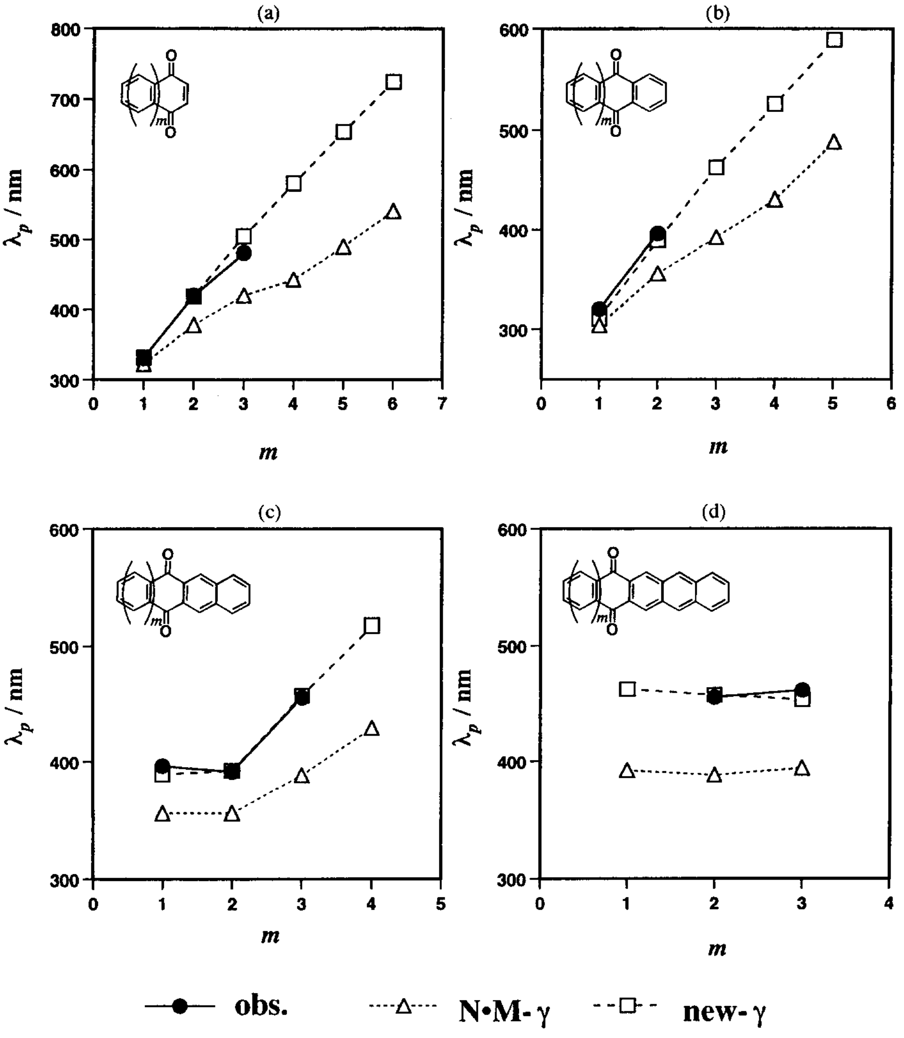


Fig. 2. The calculated and absorption wavelength of the first absorption maxima of LPAs.

(**2–16**) using the new-γ, the values of k shown in Table 4 are used based on the values of l of each compound.

The calculated results shown in Table 4 are greatly improved compared with those using the conventional N•M-γ. The relationship between the number of fused six-membered rings m and the observed or the calculated wavelengths using the new-γ, as well as the calculated wavelengths using the N•M-γ, are shown in Fig. 2. From these figures, it can be seen that the calculated wavelengths using the new-γ reproduce well the observed values. For compounds which have not yet been synthesized, the calculated values using the new-γ are certainly more reasonable than those using the N•M-γ.

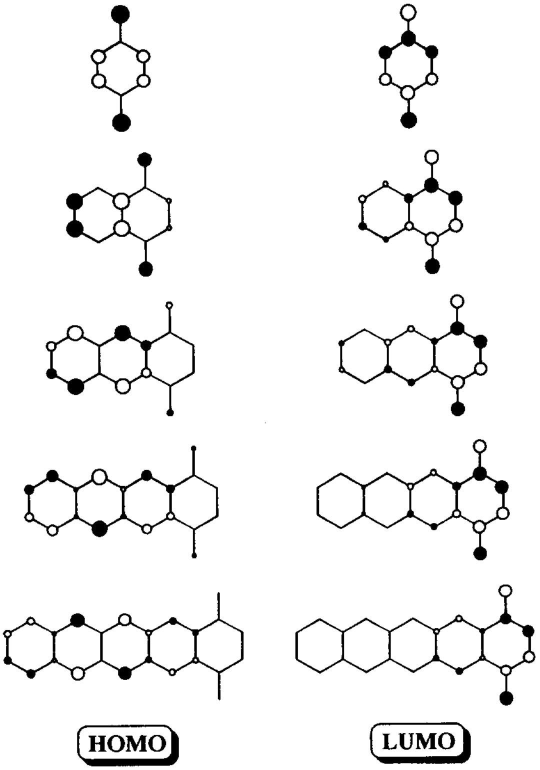


Fig. 3. The LCAO coefficients of HOMO and LUMO of some LPAs.

We have previously reported that the spectrochemical softness parameter k in the new-γ for the calculations of excitation energies of the p-band of PAHs could be evaluated based on the absolute hardness [2] or Dewar-type resonance energies [7], as well as the SP of a molecule. The values of absolute hardness [$\eta = (E_{\mathrm{LUMO}} - E_{\mathrm{HOMO}})/2$] [16] of LPAs, however, are too small compared with those of PAHs possessing the same molecular framework except for two carbonyl groups; when the MO energy levels of LPAs are compared with those of PAHs, lowering of the MO energy level of the LUMO is larger than that of the HOMO. Thus, when the regression expression [$k = 0.33/\eta + 0.58$] [2] to evaluate the parameter k based on the absolute hardness established for PAHs is applied for LAPs, the values of k are overestimated. The absolute hardness therefore seems not to be a suitable criterion to practically evaluate the parameter k for LPAs, as far as using the regression expression established for PAHs. On the other hand, the conventional method to evaluate the Dewar-type resonance energies for compounds containing hetero atoms, or possessing various substituents, has not been yet established, so that Dewar-type resonance energies are also not suitable for the criteria to evaluate the parameter k for LPAs. In conclusion, using SP as criterion to evaluate the parameter k for LPAs seems to be the most suitable method at the present stage.

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