PERKIN 2

Precise PPP molecular orbital calculations of excitation energies of polycyclic aromatic hydrocarbons. Part 6.[1] Spectrochemical atomic softness parameter †

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The excitation energies of the α-, β-, and *p*-bands of benzo-annelated polyacenes were estimated by the Pariser–Parr–Pople (PPP) molecular orbital calculation method using a novel concept for evaluating the two-centre electron repulsion integral, new-γ^A, in which the spectrochemical atomic softness (SCAS) parameter k_r^A was taken into account. The value of k_r^A was determined using the concept of the spectroactive portion (SP) and allotted to each carbon atom. The calculated results using new-γ^A were excellent for the simultaneous calculations of the *p*-, α- and β-bands of benzo-annelated polyacenes and were better than those obtained from the conventional N·M-γ or the usual new-γ. The C–C bond lengths calculated using new-γ^A reproduced quantitatively the observed values.

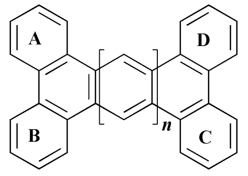
Introduction

The wavelengths calculated by the Pariser–Parr–Pople molecular orbital (PPP MO) method have been shown to be shorter than the observed values for molecules possessing a large π-conjugated system. A novel two-centre electron repulsion integral, new-γ, was proposed to improve the accuracy of the PPP calculations. New-γ has a spectrochemical softness (SCS) parameter k_{rs}.[2] For the calculations of the *p*-bands (nomenclature by Clar:[3] corresponds to Platt's ^1L_a band[4]) of polycyclic aromatic hydrocarbons (PAHs), we have established the proper methods to evaluate the SCS parameter k_{rs} in new-γ, as shown in our previous works.[1,5–8] In these works the π-conjugated system of linear polyacenes was defined to be an aromatic sextet resonance system (ASRS), and the SCS parameter was set to increase with the degree of annelation.[5] We showed that PAHs possessed a spectroactive portion (SP), which was defined to be the portion that contributes mainly to the electronic spectra of PAHs,[6,7] and the SPs of the *cata*-condensed PAHs were the longest acene-like portions in the molecular frameworks. The SCS parameters evaluated from the length of the SP reproduce well the values obtained from PPP calculations of the excitation energies of the *p*-band of *cata*-condensed PAHs[6,7] and non-alternant PAHs, such as a fluoranthene.[1]

The *p*-band is identified as a π–π* transition described by a mainly HOMO⟶LUMO transition, so it appears in the longest wavelength region except in the case of relatively small PAHs.[3] Clar named the absorption bands in the long wavelength region as the α-band (Platt's ^1L_b band[4]) and the β-band (Platt's ^1B_b band[4]), as well as the *p*-band.[3] The α-and the β-bands absorb shorter wavelength energy than the *p*-band except for in the case of small PAHs.[3]

We have applied the single SCS parameter k_{rs} to every C–C interaction of given PAHs for the calculation of excitation energies using new-γ.[1,5–8] The adopted k_{rs} values are suitable for the calculation of excitation energies of the *p*-band, but the k_{rs} values are not necessarily the most suitable for the calculation of excitation energies of the α- and/or the β-bands.

In this paper, we investigate the use of the SCS parameter k_{rs} in new-γ for the simultaneous calculation of the excitation energies of the α- and the β-bands, as well as of the *p*-band for typical *cata*-condensed PAHs, namely, benzo-annelated polyacenes (Fig. 1).



n = 0 – 3

Fig. 1 General formula of the benzo-annelated polyacenes. The benzo-annelated positions are indicated by the letters A–D.

MO calculations

PPP MO calculations were performed with the computer software revised PPP-PC,[9,10] in which the variable β approximation was adopted.[11] The conventional parameters set[9,12] was used as described in our previous papers.[1,5–8] New-γ was used for the two-centre electron repulsion integral. Conventional N·M-γ[13] was also applied for comparison with the calculated values for new-γ. Twenty-five lower singly excited configurations were used in the configuration interaction (CI) calculations.

When the mobile π-electron polarization in the region between *r*-th and *s*-th atoms in a molecule is considered as follows, $-r^+-s^--$ and $-r^--s^+-$, new-γ is given by eqn. (1),

$$\gamma_{rs} = e^2/[(R_{rs} + 2k_{rs}e^2/(I_r - A_s + I_s - A_r)] \qquad (1)$$

where R_{rs} is the interatomic distance (Å) between the *r*-th and

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† Electronic supplementary information (ESI) available: further computational results. See http://www.rsc.org/suppdata/p2/b0/b009661j/

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Table 1 The numbers of nodal planes for four linear polyacenes

Compounds	HOMO−2	HOMO−1	HOMO	LUMO	LUMO+1	LUMO+2
Naphthalene	1	2	2	3	3	4
Anthracene	2	3	3	4	4	5
Naphthacene	*4*	3	4	5	6	*5*
Pentacene	*5*	4	5	6	7	*6*

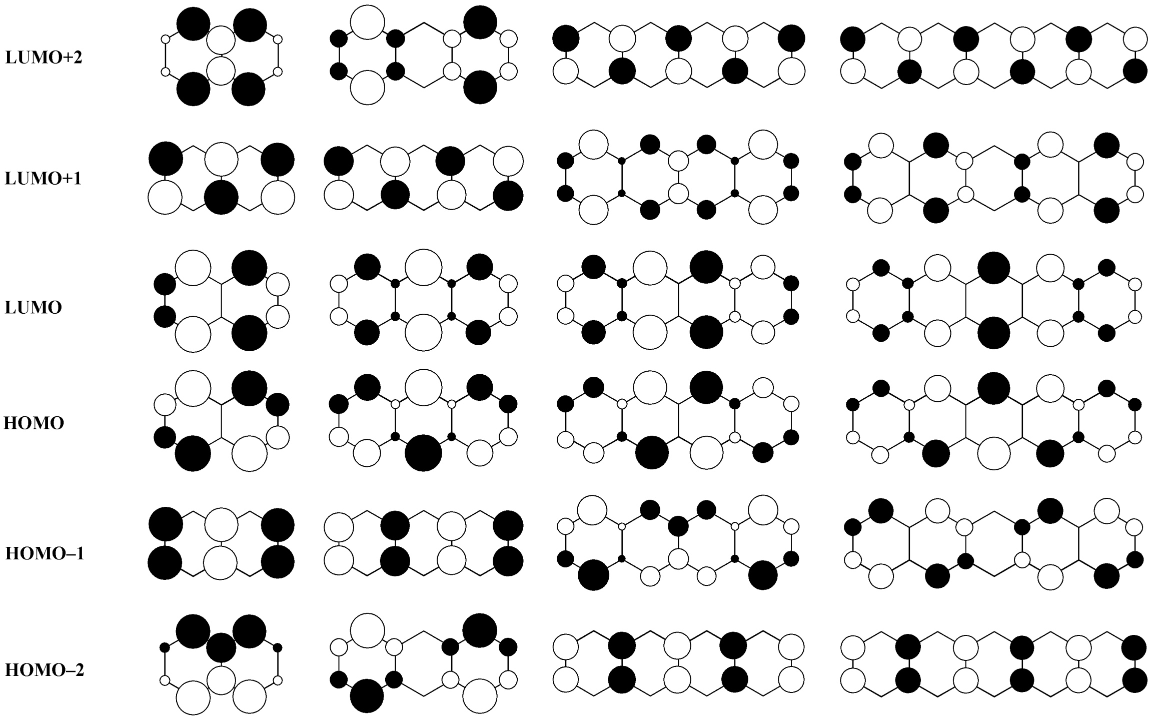

Fig. 2 The characters of HOMO−2, HOMO−1, HOMO, LUMO, LUMO+1, and LUMO+2 of polyacenes.

s-th atoms, e^2 is 14.397 eV Å^{-1}, $I_r[I_s]$ and $A_r[A_s]$ are the valence state ionization potential and the valence state electron affinity, respectively.[2] Essentially, k_{rs} is the relative magnitude of the dynamical polarizability of the mobile π-electrons in the region between the *r*-th and the *s*-th atoms, namely, the 'spectrochemical softness (SCS)' of the π-electrons. When the k_{rs} value is 1, new-γ is equivalent to N·M-γ. Large k_{rs} values are suitable for spectrochemically softer compounds such as polyacenes, but not benzene.[5]

The observed excitation energies of given PAHs in an inert solvent were extrapolated to those in the gas phase in order to minimize solvent effects.[14,15]

Results and discussion

Character of the three absorption bands of the polyacenes

The *p*-band of polyacenes is identified as a π–π* transition described by a mainly HOMO⟶LUMO transition.[3] The α- and the β-bands are identified as π–π* transitions described by mainly HOMO−1⟶LUMO or HOMO⟶LUMO+1 transitions for small PAHs.[16] However, for large PAHs they are identified as a π–π* transition described by mainly HOMO−2⟶LUMO or HOMO⟶LUMO+2 transitions. The characters of HOMO−1 (and LUMO+1) for naphthalene and anthracene resemble those of HOMO−2 (and LUMO+2) for naphthacene and pentacene as shown in Fig. 2. Naphthacene and pentacene seem to exchange their character in HOMO−2 (and LUMO+2) for HOMO−1 (and LUMO+1) because they reverse their MO energies and their number of nodal planes (Table 1). The number of nodal planes of HOMO−2 (and LUMO+2) is less than that of HOMO−1 (and LUMO+1) for naphthacene and pentacene. The order of the MO levels of HOMO−1 (and LUMO+1) and HOMO−2 (and LUMO+2) for naphthacene and pentacene are inverted relative to those of naphthalene and anthracene. The characters of the three absorption bands of polyacenes are summarized in Table 2.

The α- and β-bands of A-, AB-, AC- and AD-annelated pentacenes (see Fig. 1) are also identified as π–π* transitions, which are thought of as mainly HOMO−2⟶LUMO or HOMO⟶LUMO+2 transitions, and those of ABC- and ABCD-annelated pentacenes are identified to be π–π* transitions described by mainly HOMO−1⟶LUMO or HOMO⟶LUMO+1 transitions.

Evaluation of the SCAS parameters for benzo-annelated polyacenes

The characters of the HOMO−1, HOMO, LUMO and LUMO+1 of benzo-annelated anthracene are shown in Fig. 3. The π-orbitals of the HOMO and LUMO are relatively localized in the anthracene portion. The distribution of the π-orbitals in the annelated benzene (branch) portion increases in HOMO−1 and LUMO+1. The character of the HOMO (and LUMO) of benzene appears in HOMO−1 and LUMO+1 on the branch portion of the benzo-annelated polyacenes.

On the other hand, for A-annelated pentacene, in which the α- and β-bands are identified as a π–π* transition described by mainly HOMO−2⟶LUMO or HOMO⟶LUMO+2 transitions, the character of the HOMO (and LUMO) of the benzene does not appear in HOMO−1 and LUMO+1 but rather in HOMO−2 and LUMO+2 on the branch portion, as shown in Fig. 4.

We applied a single value of the SCS parameter k_{rs} to every C–C interaction in a molecule for the calculation of the

Table 2 The transitional characters of the p-, α-, and β-bands of four linear polyacenes

	p-Band		α-Band		β-Band	
Compound	Transition	Oscillator Strength	Transition	Oscillator strength	Transition	Oscillator strength
Naphthalene	$H\longrightarrow L$	$f\neq 0$	$H\longrightarrow L+1$ and $H-1\longrightarrow L$	$f=0$	$H\longrightarrow L+1$ and $H-1\longrightarrow L$	$f\neq 0$
Anthracene	$H\longrightarrow L$	$f\neq 0$	$H\longrightarrow L+1$ and $H-1\longrightarrow L$	$f=0$	$H\longrightarrow L+1$ and $H-1\longrightarrow L$	$f\neq 0$
Naphthacene	$H\longrightarrow L$	$f\neq 0$	$H\longrightarrow L+2$ and $H-2\longrightarrow L$	$f=0$	$H\longrightarrow L+2$ and $H-2\longrightarrow L$	$f\neq 0$
Pentacene	$H\longrightarrow L$	$f\neq 0$	$H\longrightarrow L+2$ and $H-2\longrightarrow L$	$f=0$	$H\longrightarrow L+2$ and $H-2\longrightarrow L$	$f\neq 0$

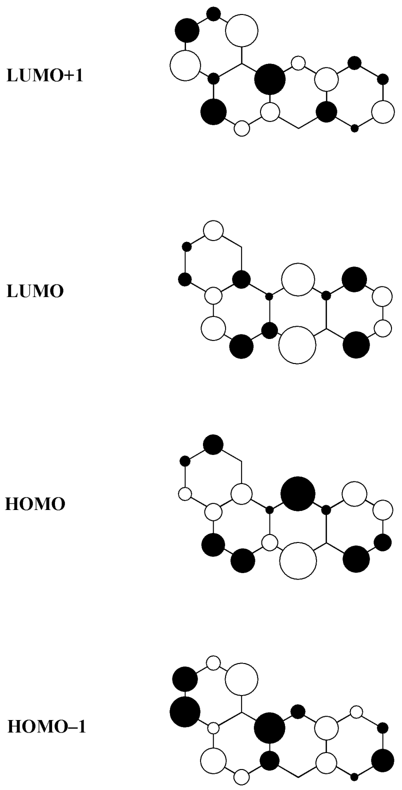

Fig. 3 The characters of HOMO−1, HOMO, LUMO, and LUMO+1 of benzo-annelated anthracene.

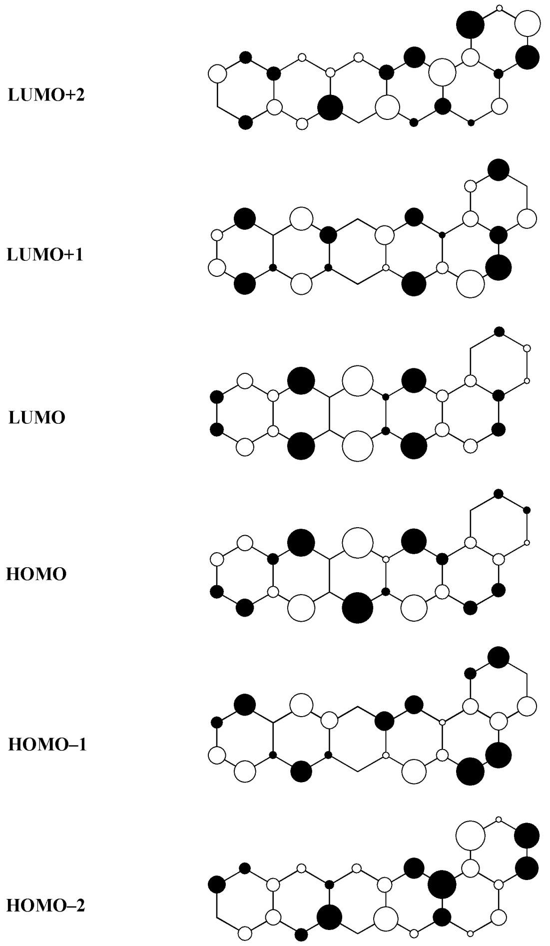

Fig. 4 The characters of HOMO−2, HOMO−1, HOMO, LUMO, LUMO+1, and LUMO+2 of benzo[*a*]pentacene.

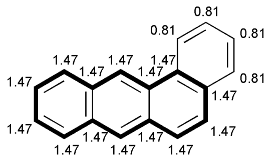

Fig. 5 The values of the SCAS parameter kr^A of benzo[*a*]anthracene; the SP is represented by bold lines.

excitation energies of the p-band of PAHs. However, different SCS parameters should be used for different C–C interactions in the calculation of the excitation energies of the α-band or the β-band. In other words, the different SCS parameters may be applicable to each chemically different region of a molecular framework. Therefore, the concept of a 'spectrochemical atomic softness' (SCAS) parameter k_r^A has been introduced. A different value of k_r^A should be evaluated for each chemically different carbon atom by considering the character of each carbon atom belonging to each region. The SCS parameter k_{rs} is taken to be the average of two SCAS parameters, k_r^A and k_s^A, as shown in eqn. (2).

$$k_{rs} = (k_r^A + k_s^A)/2 \qquad (2)$$

The value of k_r^A is evaluated for all the carbon atoms in the benzo-annelated polyacenes according to the characteristic region of the molecular framework. For example, the k_r^A value of the carbon atoms belonging to the anthracene portion is found to be suitable for anthracene (1.47) and the k_r^A value of the carbon atoms belonging to the residual unit of the benzo-annelated portion is found to be suitable for benzene (0.81) in benzo[*a*]anthracene (see Fig. 5). Thus, the k_r^A values suitable for each acene-like portion in benzo-annelated polyacenes are shown in Table 3, and were evaluated on the basis of the concept of the SP of the given molecules as in our previous works.[6,7] This evaluation method takes into consideration the characters of HOMO−2, HOMO−1, HOMO, LUMO, LUMO+1 and LUMO+2 of the molecules.

Calculations of excitation energies

The excitation energies of the α-, β- and p-bands of benzo-annelated polyacenes were calculated by the PPP MO method

Table 3 The k_r^A values suitable for the carbon atoms belonging to each acene-like portion

	Benzene-like	Naphthacene-like	Anthracene-like	Naphthalene-like	Pentacene-like	Hexacene-like
k_r^A	0.81	1.14	1.47	1.80	2.13	2.46

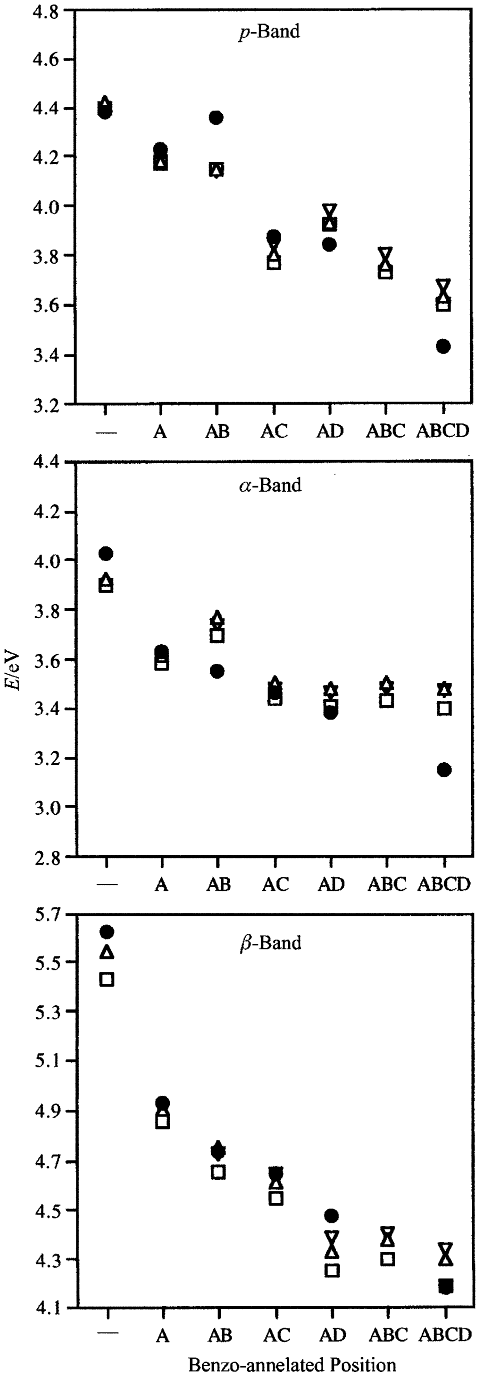

Fig. 6 The excitation energies of the *p*-, α-, and β-bands of benzo-annelated naphthalene obtained from PPP calculations using N·M-γ (–△–), new-γ (–□–), and new-γ^A (–▽–), compared with the observed values (–●–).

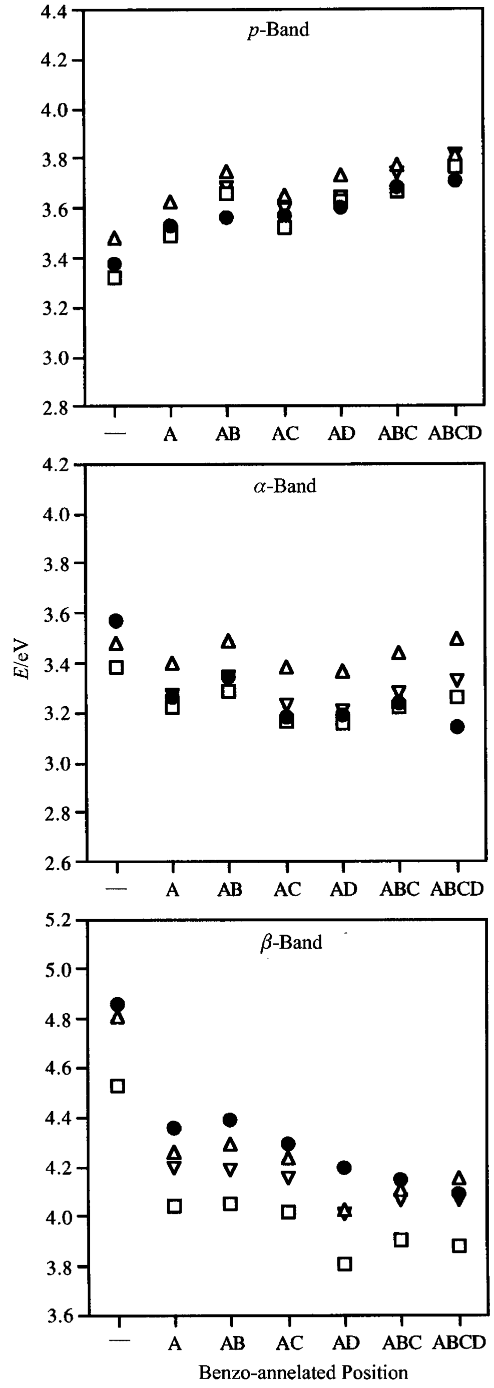

Fig. 7 The excitation energies of the *p*-, α-, and β-bands of benzo-annelated anthracene obtained from PPP calculations using N·M-γ (–△–), new-γ (–□–), and new-γ^A (–▽–), compared with the observed values (–●–).

using N·M-γ, new-γ including the single SCS parameter k_{rs} for every C–C interaction, and new-γ^A including the concept of SCAS described in the previous section. The calculated and the observed values are shown in Figs. 6–9.

The calculated results for the *p*-band using the usual new-γ reproduced the observed data better than using N·M-γ for many compounds.[6] The calculated results using new-γ^A are nearly equal to those obtained using new-γ, which reflects the character of the *p*-band. Thus, the *p*-band is mainly governed by the size of the SP (the longest acene-like portion), and the k_{rs} values included in new-γ^A are equal to those included in the usual new-γ.

The calculated results for the α-band using new-γ^A are nearly equal to those found by using the usual new-γ, though the former energies are somewhat larger than the latter ones. These results are somewhat improved, reproducing the observed values better than the use of N·M-γ.

In contrast, the calculated results for the β-band using N·M-γ

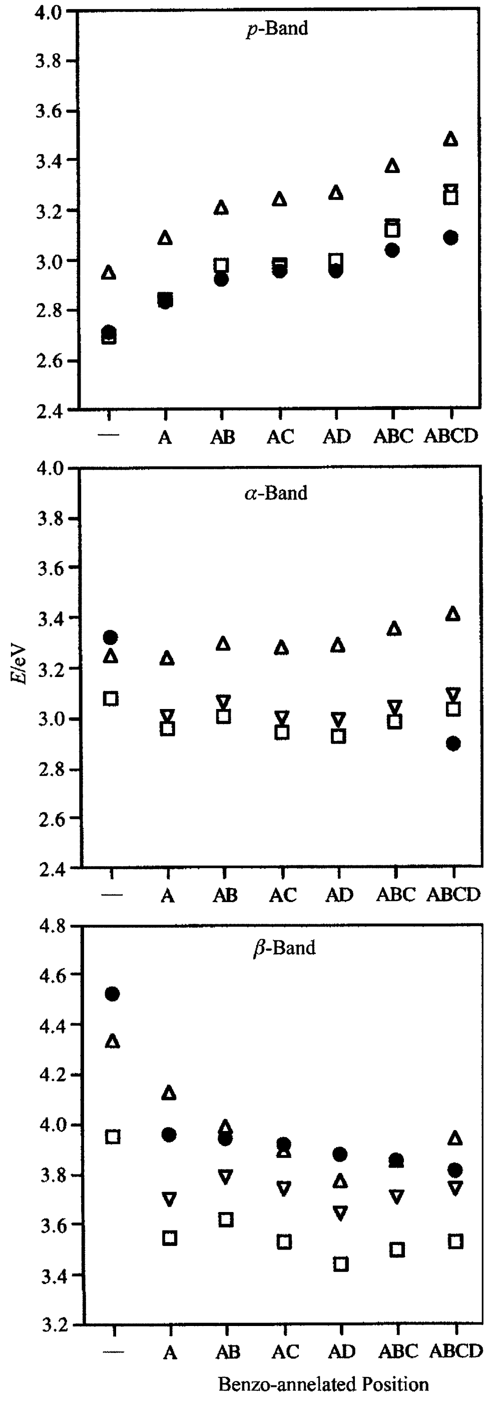

Fig. 8 The excitation energies of the *p*-, α-, and β-bands of benzo-annelated naphthacene obtained from PPP calculations using N·M-γ (–△–), new-γ (–□–), and new-γ^A (–▽–), compared with the observed values (–●–).

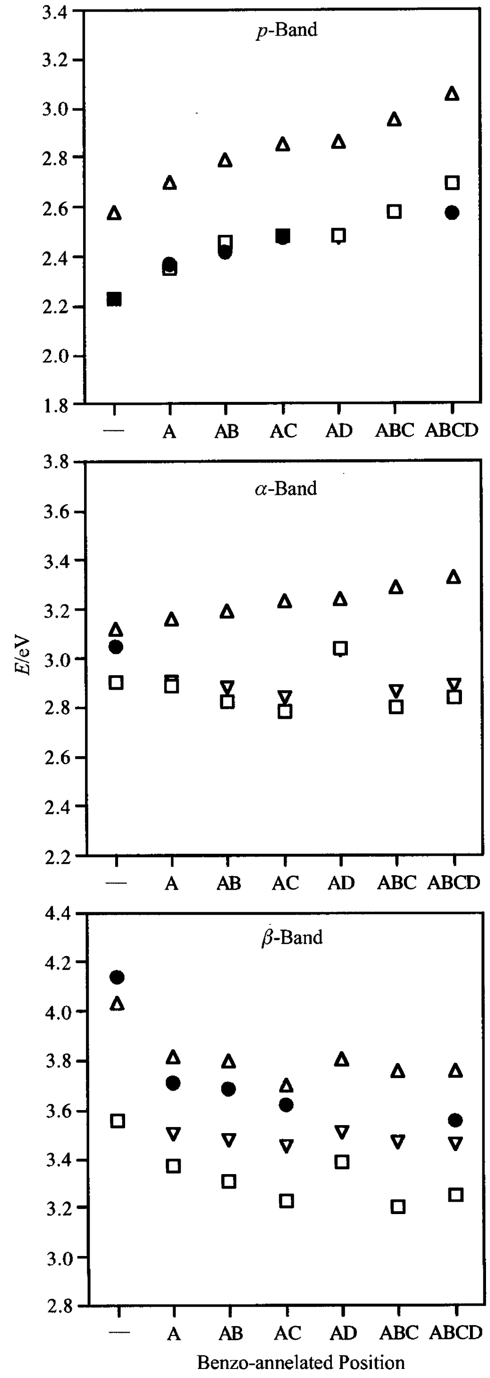

Fig. 9 The excitation energies of the *p*-, α-, and β-bands of benzo-annelated pentacene obtained from PPP calculations using N·M-γ (–△–), new-γ (–□–), and new-γ^A (–▽–), compared with the observed values (–●–).

are similar to the observed data, compared with those obtained using the usual new-γ. Thus, the k_{rs} values included in the usual new-γ are too large (soft) to calculate accurately the excitation energies of the β-band. The calculated results using new-γ^A are improved compared with those obtained using the usual new-γ, though the reproduction of the observed values is somewhat inferior to those in the case of the N·M-γ.

In conclusion, the reproduction of the observed wavelengths by PPP calculations using new-γ^A, which includes the concept of the SCAS parameter, is better for the simultaneous calculation of the *p*-band, the α-band and the β-band of benzo-annelated polyacenes than that obtained using the usual new-γ or N·M-γ.

The statistical parameters for the linear relationship between the calculated and the observed energies (slopes, intercepts, and correlation coefficients of the regressive expression) also support the results described above.

Calculated bond lengths

The carbon–carbon bond lengths, R_{cc}, of a conjugated system can be evaluated from eqn. (3),[11]

$$R_{cc} = 1.517 - 0.180\,p_{rs} \qquad (3)$$

where p_{rs} is the bond order. The observed[17,18] and calculated bond lengths of some PAHs using new-γ^A or N·M-γ are presented in the electronic supplementary information (ESI, Table S2) with those calculated by the *ab initio* method with the 6-31G* basis set (Gaussian 94[19]). The characters of each bond of the molecules are reproduced quantitatively by the PPP MO calculations as well as by the *ab initio* method. The plots of calculated *vs.* observed bond lengths of the C–C bonds of the molecules are found in the ESI (Fig. S3) with the correlation coefficients (*r*) of each calculation, although the latter results may be improved by taking into account electron correlation.

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