Improved CNDO/S Calculation of Electronic Spectra of Organic Compounds. I. New CNDO/S Calculation by Using an Improved Method of One-Center Electron Repulsion Integral

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Received December 7, 2005; accepted February 9, 2006; published online February 16, 2006

The NM-γ CNDO/S program previously developed by our group was modified by the introduction of a new one-center electron repulsion integral γ_{AA}^{new} approximation, namely, the γ_{AA}^{new}-CNDO/S method. The value of this γ_{AA}^{new} was evaluated according to the product values of the coefficient C with the γ_{AA} value proposed in our previous paper. This method using a new γ_{AA} was also found to improve the two-center electron repulsion integral γ_{AB} value with respect to the chemical softness proposed by Nishimoto and co-workers, together with the difference between HOMO and LUMO orbital energies. The results calculated by the present improved γ_{AA}^{new}-CNDO/S method demonstrated that not only the calculated absorption maxima wavelengths and ionization potentials, but also the order and the assignment of orbitals coincided very well with those based on the results of experiments investigating a variety of polyenes, cyanynes, and polycyclic aromatic hydrocarbons.

Key words CNDO/S; electronic spectrum; ionization potential; one-center electron repulsion integral

The semi-empirical CNDO/S, developed by Jaffé and co-workers,[1,2] and the ZINDO (so-called Zerner INDO/S)[3] methods are useful for the theoretical investigation of the electronic states and spectra of organic compounds. However, the usefulness of these methods for organic chemists is limited at present to the calculations of functional dyes, because the experimental absorption maxima wavelengths beyond approximately 400 nm are observed appreciably longer wavelengths, as compared to those of the ZINDO[3] and the conventional CNDO/S methods (referred to as NM-γ CNDO/S) used in our previous paper.[4] It is also known that the results of the absorption maxima wavelength calculated by the PPP method for π-electronic systems reflect substantial errors with the use of the NM-γ CNDO/S and ZINDO methods. The reason for the large discrepancy between the calculated and observed values suggests that the calculated absorption maxima wavelengths in the organic compounds of larger π-conjugated systems cannot be reproduced within the allowed ranges as the experimental value, because the results of the orbital energies calculated by these theoretical methods result in a large difference between HOMO and LUMO orbital energies.

Nishimoto[5] reported that the value of the ionization potential I_μ decreases, and that of the electron affinity A_μ increases with an increase in the number of mobile π-electrons in relatively large π-conjugated molecules. Moreover, they reported that this error produced by the conventional PPP method could be greatly improved by the reevaluation of the two-center electronic repulsion integral (New-γ), thus introducing the concept of chemical softness (referred to as New-γ PPP).[6—12] Furthermore, Nakayama and co-worker[13,14] also reported that the shortcomings of NM-γ CNDO/S calculations are appreciably absent among the results of the modified CNDO/S and ZINDO (referred to as New-γ CNDO/S and New-γ INDO/S) calculations, which introduce a New-γ using the concept of chemical softness for a number of polycyclic aromatic hydrocarbons. However, the New-γ CNDO/S and New-γ INDO/S methods cannot be applied to compounds other than π-conjugated aromatic hydrocarbons, because the New-γ values have not yet been determined with respect to the π-conjugated compounds containing various hetero atoms, namely, there is a variable k-function for each bonds C–N, C–O, N–N, *etc*.

In recent years, the time-dependent density functional theory (TD-DFT) has been considerably used for the analysis of the absorption spectra for the hydrocarbons.[15,16] However, the absorption maxima wavelengths obtained by this TD-DFT calculations are calculated appreciably longer wavelengths for larger π-conjugated compounds, as compared to the observed maxima wavelengths beyond *ca.* 400 nm. And this method is too time-consuming to be calculated to the absorption maxima wavelengths for larger π-conjugated compounds.

The goal of this investigation was to establish a general modified CNDO/S method of reproducing the observed absorption maxima wavelengths instead of reproducing the transition energies for all types of π-conjugated compounds, because very slight differences in the transition energies of larger π-conjugated molecules in turn produce very large differences in absorption wavelengths. Consequently, we expect that the large discrepancy between calculated and observed values could be substantially minimized by the reevaluation of the one-center repulsion integral related to the ionization potential (HOMO) and the electron affinity (LUMO). Needless to say, this new improvement provided by the one-center electron repulsion integral (γ_{AA}^{new}) enables the modification of the two-center electron repulsion integral (γ_{AB}) at the same time. In addition, the large error in the absorption maxima wavelength calculated by the abovementioned theoretical methods reflects sensitivity to the wavelength (nm) rather than to the transition energy (eV). Thus, we used wavelengths (nm) instead of transition energies (eV) as the dimension of the absorption maxima.

This paper addresses the following three points. First, the technique used for the reevaluation of the one-electron repulsion integral (γ_{AA}^{new}) in the π-conjugated systems of various

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type molecular structures is discussed. Second, we confirm that absorption maxima wavelengths experimentally observed to be located in relatively long wavelength regions reproduce fairly well those calculated by the modified CNDO/S method using the γ_{AA}^{new} value (designated as γ_{AA}^{new}-CNDO/S). Third, the calculated energies and sequences of orbitals using the γ_{AA}^{new}-CNDO/S method are compared with those of the experimentally determined orbitals. Furthermore, the ionization potentials (IPs), and the order and assignment of calculated orbitals showed relatively agreement with the experimental results.

Experimental

Method of CNDO/S Calculation The Fock matrix is expressed according to the CNDO/S method proposed by Jaffé *et al.*[1] as follows:

$$F_{\mu\mu} = -\frac{1}{2}(I_\mu + A_\mu) + \left[(P_{AA} - Z_A) - \frac{1}{2}(P_{\mu\mu} - 1)\right]\gamma_{AA} + \sum_{B\neq A}(P_{BB} - Z_B)\gamma_{AB} \tag{1}$$

$$F_{\mu\nu} = \frac{1}{2}(\beta_A^0 + \beta_B^0)S_{\mu\nu} - \frac{1}{2}P_{\mu\nu}\gamma_{AB} = \beta_{AB}^0 - \frac{1}{2}P_{\mu\nu}\gamma_{AB} \tag{2}$$

where I_μ and A_μ are the ionization potential and the electron affinity of a valence atomic orbital μ, respectively. $-1/2(I_\mu + A_\mu)$ is the "core integral" and β_A^0 is the "bonding parameter" of an atom A. γ_{AA} and γ_{AB} are the one-center and two-center electron repulsion integral, respectively. These γ_{AA} and γ_{AB} values are estimated according to the equation of Pariser[17] and the Nishimoto–Mataga equation,[18] respectively. $S_{\mu\nu}$ is the overlap integral between the valence atomic orbitals μ and ν, and is estimated by means of the following equation:

$$S_{\mu\nu} = S_{\mu\nu}^{\sigma} + 0.585 S_{\mu\nu}^{\pi} \tag{3}$$

When one or two of the orbitals are 3 d orbitals, $S_{\mu\nu}$ is estimated by means of Eq. 4 as follows[19]:

$$S_{\mu\nu} = 0.30 S_{\mu\nu}^{\mathrm{d}} \tag{4}$$

In the present calculations, the configuration interaction was treated by considering the lowest 60 singly excited configurations.[4]

Our previous CNDO/S program (NM-γ CNDO/S)[20] was corrected for by modifying the QCPE No. 141 program in our previous study, and the γ_{AA}^{new}-CNDO/S program used in the present investigation was modified by the introduction of a new one-electron repulsion integral, γ_{AA}^{new}, into the NM-γ CNDO/S program.

Method of TD-DFT Calculation The TD-DFT calculations taken into account in the 10 singlet excited states were performed together with 6–31G(d, p) basis set[21] and the combined Becke three-parameter hybrid exchange/Lee–Yang–Parr correlation functional (B3LYP).[22] All TD-DFT calculations were carried out using the GAUSSIAN03 Rev.C02 program package.[23]

All of the calculations in the present study were carried out on an NEC Parallel Cluster System at the Research Center for Green Science, Fukuyama University, and on an HIT HPC-IAX at our laboratory.

Evaluation of a New One-Center Electron Repulsion Integral γ_{AA}^{new} The estimated values in our previous NM-γ CNDO/S method were used as one-center electron repulsion integrals (γ_{AA}) and as two-center electron repulsion integrals (γ_{AB}) using the ionization potential (I_A) and the electron affinity (A_A) represented by the following equations (Eq. 5, Eq. 6):

$$\gamma_{AA} = I_A - A_A \tag{5}$$

$$\gamma_{AB} = \frac{e^2}{R_{AB} + 2e^2/(\gamma_{AA} + \gamma_{BB})} \tag{6}$$

According to the concept of the chemical softness mentioned above, the values of γ_{AA} decrease with increases in the spreading of the π-conjugated system. This spreading of the π-conjugated system reflects the degree of the delocalization of the mobile π-electron and is dependent on the molecular structure.

We considered that the degree of the delocalization of the mobile π-electron in the molecular structure (referred to as the coefficient C) reasonably expresses the close function $f(R_{av}, N)$ follows.

$$C = f(R_{av}, N) \tag{7}$$

where R_{av} and N are the average interatomic distance and the number of all atoms in the molecule, respectively.

The function, $f(R_{av}, N)$, shown in Eq. 7 is adjusted such that the calculated absorption maxima wavelengths are in fair agreement with the observed values for 43 different types of molecules.

Then, by the use of γ_{AA} (adopted in our previous paper) and the coefficient C, which varies with the molecular structure, a new γ_{AA}^{new} can be determined by solving Eq. 8, as follows.

$$\gamma_{AA}^{new} = C \times \gamma_{AA} \tag{8}$$

Parameters and Molecular Geometries The parameters used in this study, with the exception of the γ_{AA} of the oxygen atom listed in our previous paper,[4] are shown in Table 1. The structures of the 43 compounds used in this study are provided in Chart 1, and the geometries for all of the compounds examined here were optimized by applying the semi-empirical MNDO-AM1 method[25] using the MOPAC 97 program package.[26]

Results and Discussion

First, the coefficient C produced by γ_{AA}^{new} in Eq. 8 will be described below. Following that description will be a discussion of the correlation of the absorption maxima wavelengths calculated by the CNDO/S method using the γ_{AA}^{new} values of 43 compounds and the observed values (this approach to the CNDO/S calculation using γ_{AA}^{new} is referred to below simply as the γ_{AA}^{new}-CNDO/S method).

As regards the theoretical study of the ionization potential (IP), Koopmans' theorem is well-known to be useful as a good approximation.[27] In the present study, the molecular orbital energies calculated by the γ_{AA}^{new}-CNDO/S method will be compared with the observed IP values by application of Koopman's theorem. The order and assignment of calculated molecular orbital energies will also be compared with those of orbitals established by experiments.

Determination of the Coefficient *C* in Eq. 8 It has been reported that the p absorption band can be assigned to the π-electron transition from the HOMO to the LUMO. Then, as the p absorption bands obtained by NM-γ CNDO/S calculations agree with the observed p-bands, the optimum coefficients (C_{opt}) giving the most suitable values for a new γ_{AA}^{new} were determined for a variety of 43 compounds, *i.e.*, 7 polyenes, 5 cyanines, 6 merocyanines, 6 acenes, and 19 phenes (Chart 1). The C_{opt} values were used to obtain the most suitable function $f(R_{av}, N)$ to determine the desired coefficient C in Eq. 8. In the results, the C_{opt} is plotted as the ordinate, and the average interatomic distance (R_{av}) is plotted as the abscissa (Fig. 1). As shown in Fig. 1, it was clearly demonstrated that the C_{opt} values for all of the Polyenes were approximately 0.9, and the γ_{AA}^{new} values were found to be almost independent of the one-center electron repulsion integral of the Polyenes. On the other hand, the C_{opt} values for the other compounds, with the exception of merocyanines, decreased with increasing R_{av} values. This finding suggests that the function $f(R_{av}, N)$ could be expressed in the form of a logarithm function of R_{av}. A plot of C_{opt} against the average interatomic distance R_{av} for all compounds showed spreading around the central acenes. These results regarding the determination of the desired C introduced into the NM-γ CNDO/S method suggest that the degree of π-electron delo-

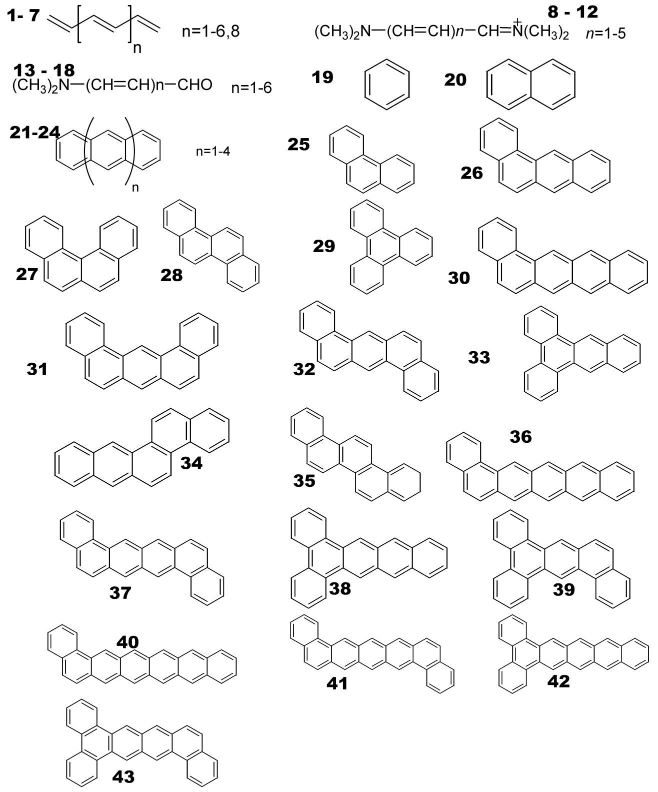


Chart 1. Compounds Used

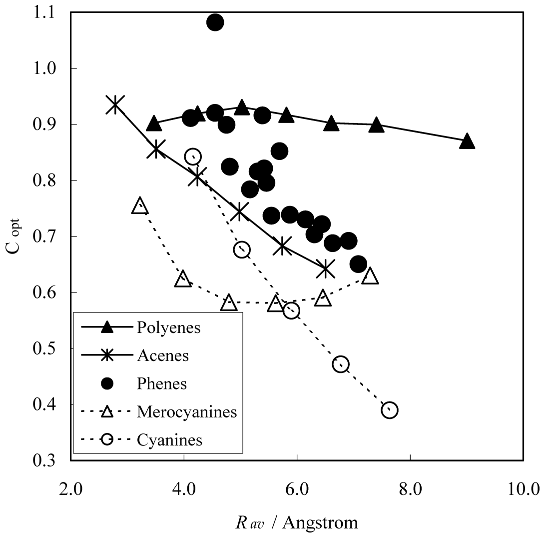


Fig. 1. Correlation between the Optimum Coefficient C_{opt} and the Average Interatomic Distance R_{av}

calization for each compound can be expressed as the logarithmic values of the R_{av} and the degree of difference between the average interatomic distance (R_{ac}) for acenes and that (R_{av}) for other compounds, except for acenes. However, R_{ac} is the average interatomic distance of acenes compounds, which contain the same number of atoms (N) as the target compound, *i.e.*, $R_{ac}=eN+f$.

Therefore, the function $f(R_{av}, N)$ in Eq. 8 can be adequately approximated by the following two equations.

$$C=a\log R_{av}+b|R_{ac}-R_{av}|^{c}+d \tag{9}$$

Table 1. CNDO/S Parameters (eV)[a]

Atom	Core integral		γ_{AA}	β_A^0
	s	p		
H	7.175		12.85	−12.0
C	14.960	5.805	10.93	−17.5
N	20.485	8.480	11.88	−26.0
O	27.255	10.965	13.00[b]	−30.0

a) ref. 5, *b*) ref. 24

$$R_{ac}=eN+f \tag{10}$$

The desired C reproducing the observed absorption maxima wavelengths, namely, the parameters $a{\sim}f$ in Eq. 9 and Eq. 10, is determined by the nonlinear least-squares method, such as to minimize the difference between the desired C and the C_{opt}. The γ_{AA}^{new} can be obtained by the solution of Eq. 11 and Eq. 12.

$$C=-1.533\log R_{av}+0.415|R_{ac}-R_{av}|^{0.703}+1.563 \tag{11}$$

$$R_{ac}=0.141N+1.164 \tag{12}$$

The product values of the desired C with the γ_{AA} value listed in Table 1 are used as the value of γ_{AA}^{new} introduced for the present γ_{AA}^{new}-CNDO/S method.

Comparison of the Absorption Maxima Wavelengths Calculated by the γ_{AA}^{new}-CNDO/S Method with the Observed Values The absorption maxima wavelength values calculated by γ_{AA}^{new}-CNDO/S, NM-γ CNDO/S and TD-DFT methods for 43 compounds, and those calculated by the New-γ PPP method for 29 compounds with the exception of polyenes and merocyanines are shown in Table 2 together with the observed values. The plots of the results calculated by the γ_{AA}^{new}-CNDO/S, NM-γ CNDO/S and TD-DFT methods against those observed values are shown in Fig. 2. Figure 2 clearly show a linear relationship between the observed values and those calculated by γ_{AA}^{new}-CNDO/S method; this relationship was satisfactorily maintained for all of the compounds examined in the wavelength region extending from approximately 210 to 730 nm, but the results obtained with the NM-γ CNDO/S and TD-DFT calculations gave only a poor linear relationship, especially in the wavelength region above *ca.* 400 nm.

In this study, the linear regressions for the results calculated by the γ_{AA}^{new}-CNDO/S, the NM-γ CNDO/S and the TD-DFT methods were obtained using Eqs. 13, 14 and 15. The slope and the intercept were calculated according to the following methods, *i.e.*, the γ_{AA}^{new}-CNDO/S method:

$$\lambda_{\mathrm{calcd}}=0.9420\lambda_{\mathrm{obsd}}+21.0163;\quad r^2=0.9704;\quad n=43 \tag{13}$$

the NM-γ CNDO/S method:

$$\lambda_{\mathrm{calcd}}=0.6469\lambda_{\mathrm{obsd}}+101.9277;\quad r^2=0.9212;\quad n=43 \tag{14}$$

and the TD-DFT method:

$$\lambda_{\mathrm{calcd}}=0.9804\lambda_{\mathrm{obsd}}-11.5765;\quad r^2=0.7099;\quad n=43 \tag{15}$$

Those results showed that the linear relationship obtained by our γ_{AA}^{new}-CNDO/S calculations was closer to the values of 1.0 and 0.0 (*i.e.*, the slope and the intercept, respectively) than were those obtained by the NM-γ CNDO/S calculations.

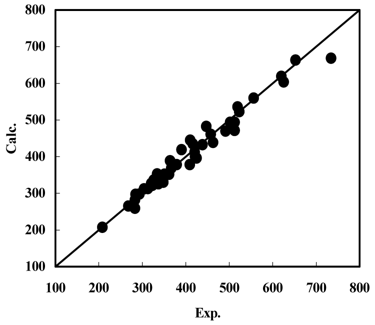
Table 2. Calculated and Observed Absorption Wavelengths (nm) of the p-Band for a Series of Polyenes (**1**—**7**), Cyanines (**8**—**12**), Merocyanines (**13**—**18**), Acenes (**19**—**24**), and Phenes (**25**—**43**)

Compd.	Exp. log ε	γ_{AA}^{new}-CNDO/S log ε	NM-γ CNDO/S log ε	TD-DFT log ε	New-γ PPP log ε	Compd.	Exp. log ε	γ_{AA}^{new}-CNDO/S log ε	NM-γ CNDO/S log ε	TD-DFT log ε	New-γ PPP log ε
1	268.0[a]	265.6	256.8	251.8		**23**	556.0[c]	559.7	460.7	617.9	556.0[f]
	4.54	4.88	4.88	4.75				4.25	4.28	3.36	
2	304.0[a]	312.2	293.0	294.1		**24**	652.5[c]	663.6	512.9	766.1	649.1[f]
		4.99	5.00	4.89				4.26	4.31	3.28	
3	334.0[a]	353.3	323.0	332.6		**25**	293.1[c]	298.2	284.5	287.8	299.5[f]
	5.14	5.07	5.09	5.00				4.03	4.02	3.51	
4	364.0[a]	389.1	349.3	367.9		**26**	351.2[c]	352.6	327.1	361.8	355.2[f]
	4.56	5.14	5.15	5.08				4.13	4.13	3.44	
5	390.0[a]	419.4	371.1	400.5		**27**	322.9[c]	321.3	314.2	327.6	316.3[f]
	4.56	5.19	5.20	5.14				3.39	3.38	3.05	
6	410.0[a]	444.8	389.1	430.7		**28**	320.4[c]	327.3	309.3	324.0	324.5[f]
	5.03	5.23	5.25	5.20				4.29	4.29	3.16	
7	447.0[a]	482.7	416.6	484.4		**29**	284.4[c]	297.3	291.4	293.5	298.7[f]
		5.31	5.33	5.25				0.00	0.00	0.00	
8	312.5[b]	313.2	289.7	271.4	313.7[e]	**30**	438.1[c]	432.8	384.6	463.7	436.5[f]
	4.81	4.72	4.71	4.70	4.86			4.18	4.18	3.37	
9	416.0[b]	435.4	355.8	334.9	408.5[e]	**31**	344.4[c]	338.0	321.7	351.2	341.5[f]
	5.08	4.89	4.88	4.88	5.00			3.75	3.71	3.17	
10	519.0[b]	535.8	414.0	392.9	500.8[e]	**32**	347.3[c]	348.1	324.9	359.3	352.2[f]
	5.32	5.00	5.00	5.00	5.10			4.34	4.36	3.03	
11	625.0[b]	603.6	468.3	447.4	600.7[e]	**33**	348.3[d]	330.3	320.8	353.3	338.7[f]
	5.47	5.09	5.09	5.10	5.19			3.79	3.78	3.10	
12	734.5[b]	668.5	519.4	499.5		**34**	379.1[d]	378.7	347.8	390.3	382.6[f]
	5.55	5.17	5.15	5.18				4.30	4.31	3.56	
13	283.0[b]	259.4	243.6	242.2		**35**	326.3[c]	336.7	317.0	326.7	333.3[f]
	4.57	4.64	4.63	4.49				4.46	4.48	3.85	
14	361.5[b]	352.1	286.3	294.6		**36**	523.1[c]	522.8	442.2	583.5	527.6[f]
	4.71	4.77	4.83	4.70				4.22	4.24	3.31	
15	421.5[b]	400.6	320.7	342.4		**37**	420.3[c]	412.1	369.5	442.4	417.4[f]
	4.75	4.93	4.95	4.83				4.19	4.14	3.36	
16	462.5[b]	438.8	350.0	387.2		**38**	424.6[c]	396.2	374.4	451.3	416.0[f]
	4.81	5.01	5.04	4.90				4.05	4.05	3.15	
17	491.5[b]	469.8	373.1	429.5		**39**	336.9[c]	325.9	320.2	356.2	337.8[f]
	4.83	5.08	5.11	4.96				3.86	3.86	2.50	
18	512.5[b]	493.9	393.0	469.4		**40**	619.9[c]	619.1	495.4	721.2	619.9[f]
	4.86	5.14	5.17	4.99				4.24	4.29	3.25	
19	208.0[c]	207.1	202.9	196.3	210.5[f]	**41**	501.9[c]	493.7	424.2	552.4	499.9[f]
		0.00	0.00	0.00				4.20	4.23	3.27	
20	283.1[c]	282.2	268.4	276.2	281.8[f]	**42**	512.3[c]	471.7	429.6	568.3	504.0[f]
		4.01	3.98	3.52				4.20	4.22	3.16	
21	366.8[c]	368.9	337.2	374.1	373.4[f]	**43**	409.2[c]	378.1	360.7	430.9	398.6[f]
		4.16	4.13	3.51				3.91	4.00	3.08	
22	457.5[c]	461.0	400.8	487.7	460.9[f]						
		4.24	4.24	3.44							

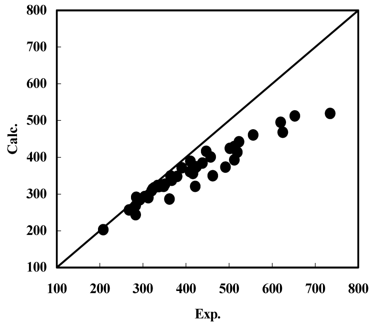
a) ref. 28, *b*) ref. 29, *c*) ref. 30, *d*) ref. 31, *e*) ref. 12, *f*) ref. 7

However, the coefficient of determination (r^2) for the relationship obtained by the TD-DFT calculations was smaller than that (r^2) obtained by the improved γ_{AA}^{new}-CNDO/S calculations. In the results of TD-DFT calculations, the experimental maxima wavelengths beyond *ca.* 400 nm were observed appreciably shorter wavelengths for the hydrocarbons and were observed extremely longer wavelengths for cyanines and merocyanines. In addition, the TD-DFT method is too time-consuming to be calculated to the analysis of absorption spectra compared with the γ_{AA}^{new}-CNDO/S and ZINDO methods. For example, the desired computational times for the γ_{AA}^{new}-CNDO/S and the TD-DFT calculations were, respectively, 0.39 s and 10457.9 s for the compound 33 (36 atoms) and were 0.70 s and 17209.3 s for the compound 41 (48 atoms). These findings clearly show that the improved γ_{AA}^{new}-CNDO/S method presented here provides an excellent general approach to the calculation of the absorption spectra of all types of organic compounds.

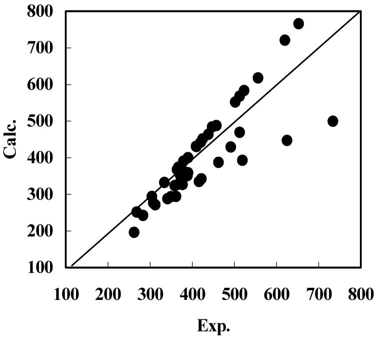
Nishimoto and co-workers[7—12] previously studied the absorption maxima wavelengths calculated by the New-γ PPP method for a total of 29 compounds consisting of 4 cyanines and 25 aromatic hydrocarbons (*i.e.*, they did not determine the results for 7 polyenes and 7 merocyanines from among the 43 compounds used in this study). We carried out a comparison of their results and those of our group, as calculated by the New-γ PPP method. The linear regressions for the results calculated according to our γ_{AA}^{new}-CNDO/S method and those calculated by the New-γ PPP and the TD-DFT methods were obtained by solving Eqs. 16, 17 and 18. The result calculated by our γ_{AA}^{new}-CNDO/S method was in good agreement with the observed values; it was clearly observed that the slope and the intercept of the linear relationship were



(a) γ_{AA}^{new} – CNDO/S (This work)



(b) NM–γCNDO/S



(c) TD–DFT (Time–dependent B3LYP/6–31G(d,p))

Fig. 2. Correlation between the Calculated and Observed Absorption Wavelengths (nm) of 7 Polyenes, 5 Cyanines, 6 Merocyanines, 6 Acenes, and 19 Phenes

closer to 1.0 and 0.0, respectively, than those obtained by the New-γ PPP and the TD-DFT methods.

In brief, the γ_{AA}^{new}-CNDO/S results can be described as follows.

$$\lambda_{\text{calcd}}=0.9828\lambda_{\text{obsd}}+3.9843; \quad r^2=0.9849; \quad n=29 \tag{16}$$

Moreover, the New-γ PPP results were as follows.

$$\lambda_{\text{calcd}}=0.9660\lambda_{\text{obsd}}+12.4075; \quad r^2=0.9960; \quad n=29 \tag{17}$$

Finally, the TD-DFT results were as follows.

$$\lambda_{\text{calcd}}=1.1985\lambda_{\text{obsd}}-92.0579; \quad r^2=0.8033; \quad n=29 \tag{18}$$

On the other hand, Nakayama and co-worker have already reported that the lowest excitation energies (eV) calculated by the New-γ CNDO/S and New-γ INDO/S methods for 7 polyenes and 123 polycyclic aromatic hydrocarbons were in fair agreement with the observed eVs; these methods were deemed more appropriate than the NM-γ CNDO/S method for the calculations of excitation energies.

Table 3. Calculated and Observed the Longest Wavelengths (nm) of Polyenes (**1**—**7**), Acenes (**19**—**24**), and Phenes (**25**—**43**)

Compd.	Exp.	γ_{AA}^{new}-CNDO/S	New-γ CNDO/S	New-γ INDO/S	TD-DFT
1	268.0[a]	265.6	272.3[b]	264.9[b]	251.8
2	304.0[a]	312.2	319.0[b]	307.3[b]	294.1
3	334.0[a]	353.3	359.7[b]	342.7[b]	332.6
4	364.0[a]	389.1	395.9[b]	372.7[b]	367.9
5	390.0[a]	419.4	426.8[b]	402.6[b]	400.5
6	410.0[a]	444.8	451.1[b]	414.3[b]	430.7
7	447.0[a]	482.7	486.9[b]	436.8[b]	484.4
19	262.1[c]	255.8	259.3[e]	259.3[e]	223.4
20	307.6[c]	306.5	305.4[e]	300.1[e]	276.2
21	366.8[c]	368.9	352.5[e]	346.3[e]	374.1
22	457.5[c]	461.0	429.3[e]	400.8[e]	487.7
23	556.0[c]	559.7	505.8[e]	470.0[e]	617.9
24	652.5[c]	663.6	574.5[e]	531.5[e]	766.1
25	341.5[c]	329.6	330.0[e]	318.0[e]	306.1
26	380.3[c]	358.5	351.4[e]	340.9[e]	361.8
27	366.8[c]	353.2	348.8[e]	334.1[e]	336.9
28	358.3[c]	344.5	344.6[e]	330.9[e]	324.0
29	349.2[c]	331.1	358.2[e]	341.2[e]	309.0
30	438.1[c]	432.8	425.9[e]	403.0[e]	463.7
31	388.6[c]	362.7	365.8[e]	347.1[e]	358.2
32	389.9[c]	364.0	368.5[e]	349.7[e]	359.3
33	371.2[c]	349.1	373.5[e]	356.4[e]	353.3
34	379.1[d]	378.7	368.1[e]	359.7[e]	390.3
35	376.8[d]	354.9	343.5[e]	328.4[e]	341.1
36	523.1[c]	522.8	497.5[e]	461.1[e]	583.5
37	420.3[c]	412.1	420.3[e]	398.4[e]	442.4
38	424.6[c]	396.2	433.0[e]	409.6[e]	451.3
39	382.6[c]	353.7	381.9[e]	359.5[e]	356.2
40	619.9[c]	619.1	565.6[e]	522.7[e]	721.2
41	501.9[c]	493.7	488.7[e]	450.2[e]	552.4
42	512.3[c]	471.7	498.7[e]	459.7[e]	568.3
43	409.2[c]	378.1	425.5[e]	402.0[e]	430.9

a) ref. 28, *b*) ref. 13, *c*) ref. 30, *d*) ref. 31, *e*) ref. 14

In order to improve the NM-γ CNDO/S method, Nakayama and co-worker[13,14] used the lowest excitation energies (eV) for polycyclic aromatic hydrocarbons, but we used the p-bands of the observed absorption maxima wavelengths for all of the calculated compounds. As shown in Table 3, the results calculated by the γ_{AA}^{new}-CNDO/S, the New-γ CNDO/S, the New-γ INDO/S and the TD-DFT methods were compared with the longest wavelengths for the 7 polyenes and 25 polycyclic aromatic compounds used in this study. The linear regressions between the observed and calculated values were obtained using Eqs. 19, 20, 21 and 22. The reproducibility of the observed values was best indicated by the results of the γ_{AA}^{new}-CNDO/S calculation, because the slope and the intercept of the linear relationship were as close as possible to the desired values 1.0 and 0.0, respectively. As clearly shown in Table 3, the results obtained by the New-γ CNDO/S and the New-γ INDO/S methods were calculated using appreciably shorter wavelengths than the observed maxima wavelengths beyond *ca.* 450 nm. To the contrary, the results of the TD-DFT method were calculated using extremely longer wavelengths than the observed values beyond *ca.* 450 nm.

The results obtained by the γ_{AA}^{new}-CNDO/S calculations were as follows:

$$\lambda_{\text{calcd}}=1.0126\lambda_{\text{obsd}}-10.2906; \quad r^2=0.9566; \quad n=32 \tag{19}$$

Moreover, those obtained by the New-γ CNDO/S and the New-γ INDO/S calculations were as follows:

$$\lambda_{\mathrm{calcd}}=0.8267\lambda_{\mathrm{obsd}}+63.6734; \quad r^2=0.9193; \quad n=32 \tag{20}$$

$$\lambda_{\mathrm{calcd}}=0.7871\lambda_{\mathrm{obsd}}+65.3567; \quad r^2=0.8111; \quad n=32 \tag{21}$$

Finally, those obtained by the TD-DFT calculations were as follows:

$$\lambda_{\mathrm{calcd}}=1.4083\lambda_{\mathrm{obsd}}-158.3031; \quad r^2=0.9813; \quad n=32 \tag{22}$$

Furthermore, Nakayama and co-worker[13)] reported that the α, β, and p absorption bands for 6 polycyclic aromatic hydrocarbons were in fair agreement with the observed values. Here, we compared the results calculated by the three methods described above. Table 4 clearly shows that the results of our γ_{AA}^{new}-CNDO/S calculation were identical to the observed values of the three absorption bands. This finding indicates that the γ_{AA}^{new}-CNDO/S method is an excellent method for the theoretical calculations of the absorption spectra and that the approximation of this method depend solely on the shape of entire molecule. However, it should be noted that the New-γ CNDO/S method proposed by Nakayama and co-worker has at least one serious disadvantage, namely, a different variable *k*-function must be determined for each bond (*e.g.*, C–C, C–O, C–N, N–N, *etc.*) in a molecule of interest.

Table 4. Calculated and Observed Absorption Wavelengths (nm) of α-, p-, and β-Bands of Polyacenes

Compd.	Band	Exp.[a)]	γ_{AA}^{new}-CNDO/S	NM-γ CNDO/S	New-γ CNDO/S[a)]	New-γ INDO/S[a)]
19	α	262	255.8	255.4	259.0	259.0
	p	207	207.1	202.9	189.1	202.3
	β	187	186.8	187.7	186.2	174.1
20	α	308	306.5	304.2	305.8	300.6
	p	283	282.2	268.4	268.6	273.7
	β	221	228.4	219.8	222.2	209.0
21	p	367	368.9	337.2	351.0	344.8
	α	347	348.8	342.6	339.5	331.9
	β	255	262.5	246.9	250.8	238.3
22	p	458	461.0	400.8	430.3	401.8
	α	373	339.5	370.8	322.5	301.0
	β	274	293.6	271.4	298.4	281.6
23	p	556	559.7	460.7	510.2	437.7
	α	407	407.3	349.8	376.8	350.5
	β	299	369.0	329.4	354.9	332.6
24	p	653	663.6	512.9	579.1	536.8
	α	443	428.1	371.8	428.5	397.2

a) ref. 13

Correlation of the HOMO Calculated by the γ_{AA}^{new}-CNDO/S Method with the Observed First Ionization Potentials The objective of the major improvement of the NM-γ CNDO/S method described in the present investigation was to include the difference between the HOMO and LUMO orbital energies, namely, the one-center electron repulsion integral γ_{AA}. In turn, the appropriate evaluation of this integral leads to a much improved IP; moreover, the two-center electron repulsion integral γ_{AB} which relates the chemical softness was improved. Thus, the orbital energies (HOMO) calculated by the γ_{AA}^{new}-CNDO/S and NM-γ CNDO/S methods could be compared with respect to the observed values of the first ionization potentials (referred to as the first IP); the calculated results are shown in Table 5. As shown in Table 5, the results calculated by the γ_{AA}^{new}-CNDO/S method were closer to the values of the observed first IPs than were the results calculated by the NM-γ CNDO/S method. The linear regressions for the results calculated by the γ_{AA}^{new}-CNDO/S and NM-γ CNDO/S methods were obtained by Eqs. 23 and 24. The slope and the intercept of the linear relationship obtained by the γ_{AA}^{new}-CNDO/S method were closer to the desired respective values 1.0 and 0.0 than were those obtained by the NM-γ CNDO/S method, as can be seen in the following examples, first, Eq. 23 shows the results obtained by the γ_{AA}^{new}-CNDO/S method:

$$\mathrm{IP}_{\mathrm{calcd}}=0.9787\mathrm{IP}_{\mathrm{obsd}}+0.8046; \quad r^2=0.9771; \quad n=26 \tag{23}$$

Then, Eq. 24 shows the results obtained by the NM-γ CNDO/S method:

$$\mathrm{IP}_{\mathrm{calcd}}=0.9106\mathrm{IP}_{\mathrm{obsd}}+1.9866; \quad r^2=0.9866; \quad n=26 \tag{24}$$

On the other hand, the order and assignment of molecular orbitals calculated by the γ_{AA}^{new}-CNDO/S method could also be compared with the observed orbitals already determined experimentally. These results are not summarized in the Table. However, the results of the γ_{AA}^{new}-CNDO/S calculation were found to coincide very well with the observed results obtained for all of the compounds studied, as well as NM-γ CNDO/S method. Therefore, these findings clearly indicated that our improved γ_{AA}^{new}-CNDO/S method is especially well

Table 5. Calculated and Observed Vertical π Ionization Potentials (eV) of Polyene (**1**), Acenes (**19**—**24**), and Phenes (**25**—**43**)

Compd.	Exp.	γ_{AA}^{new}-CNDO/S	NM-γ CNDO/S	Compd.	Exp.	γ_{AA}^{new}-CNDO/S	NM-γ CNDO/S
1	8.29[a)]	8.71	8.77	**31**	7.40[b)]	8.12	8.21
19	9.24[b)]	9.88	9.93	**32**	7.38[b)]	8.04	8.18
20	8.15[b)]	8.67	8.78	**33**	7.39[b)]	8.17	8.22
21	7.41[b)]	7.94	8.10	**34**	7.20[c)]	7.83	7.98
22	6.97[b)]	7.48	7.67	**35**	7.50[c)]	8.16	8.29
23	6.61[b)]	7.16	7.38	**36**	6.61[b)]	7.24	7.45
24	6.36[b)]	6.92	7.18	**37**	6.96[b)]	7.64	7.81
25	7.86[b)]	8.53	8.64	**38**	6.96[b)]	7.72	7.80
26	7.41[b)]	8.02	8.15	**39**	7.40[b)]	8.22	8.25
27	7.61[b)]	8.25	8.30	**40**	6.36[b)]	7.00	7.23
28	7.59[b)]	8.22	8.34	**41**	6.64[b)]	7.32	7.51
29	7.87[b)]	8.63	8.68	**42**	6.62[b)]	7.38	7.49
30	6.96[b)]	7.57	7.75	**43**	6.99[b)]	7.80	7.87

a) ref. 32, *b)* ref. 30, *c)* ref. 31

suited for the calculations of both the absorption maxima wavelengths and the ionization potentials, as well as the order and the assignment of the molecular orbitals.

Conclusion

The present improvements of the NM-γ CNDO/S method were carried out by the introduction of a new one-center electron repulsion integral (γ_{AA}^{new}) approximation. The value of a new γ_{AA}^{new} was evaluated by the product values of the coefficient C with the γ_{AA} value proposed in our previous paper. This approach led to the improvement of the NM-γ CNDO/S calculations, which very successfully reproduced the electronic spectra wavelengths observed experimentally for 7 polyenes, 5 cyanines, and 6 merocyanines containing hetero atoms, as well as those of 25 polycyclic aromatic hydrocarbons. Furthermore, the calculated orbital energies obtained by the present γ_{AA}^{new}-CNDO/S calculations were found to coincide very well with the first IPs and the order and the assignment of molecular orbitals obtained experimentally for the one polyene and the 25 polycyclic aromatic hydrocarbons described above.

It is expected that our γ_{AA}^{new}-CNDO/S calculations using the γ_{AA}^{new} value introduced in the present study will be extensively applicable for the calculation of the electronic absorption spectra, the first IPs, and the order and the assignment of molecular orbitals for a wide variety of organic compounds.

Investigation into the potential usefulness of our method of the γ_{AA}^{new}-CNDO/S calculation are currently underway. These studies are using as target molecules a number of organic compounds containing hetero atoms, as well as the 123 polycyclic aromatic hydrocarbons reported by Nakayama and co-worker. The results of these investigations will be reported in the near future.

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