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An MO Theoretical Study of Organic Dyes. II. Comparisons of the Electronic Spectra Calculated by PPP and *ab Initio* Methods with Various Levels of Theory

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An MO Theoretical Study of Organic Dyes. II. Comparisons of the Electronic Spectra Calculated by PPP and *ab Initio* Methods with Various Levels of Theory[#]

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Abstract

The electronic spectra of some typical aromatic hydrocarbons and organic colorants have been calculated by PPP–CI and *ab initio* methods with various levels of theory. A comparison of calculated results showed that simple PPP–CI calculation with suitable two–center electron repulsion integral sets is successful for the calculation of the π –electronic spectra of organic colorant with high accuracy and also for understanding the nature of their electronic spectra. One can compute molecules having the coronene size within a few seconds using a PC. Thus, this approach is useful for the combinatorial chemistry and for the design of organic colorants. Furthermore, the nature of the π –electronic spectra and the characteristic feature of the lowest excited states, such as ionic, covalent, diradical, etc., are clearly understood by PPP–CI calculations. On the other hand, in some cases, *ab initio* calculations provide erroneous results and the calculated excited state functions are very complicated. For example, the HOMO–LUMO transition is dispersed over among many excited states. The reason why a modified two–center electron repulsion integral set works satisfactorily is qualitatively discussed.

Keywords. Electronic spectra; organic colorants; PPP–CI calculation; TDDFT calculation; time–dependent density functional theory; two–center electron repulsion integral.

Abbreviations and notations

| | |
|--|---|
| AO, atomic orbital | PPP, Pariser–Parr–Pople |
| CI, configuration interaction | TDDFT, time–dependent density functional theory |
| CIS, configuration interaction with single excitations | TDHF, time–dependent Hartree–Fock |
| MO, molecular orbital | |

1 INTRODUCTION

One of the purposes of quantum color chemistry is to elucidate the nature of the electronic spectra and the electronic structure of (known and unknown) molecules and to calculate accurately the λ_{\max} 's of electronic transitions (absorption and emission), the intensities, directions of polarizations, hyperpolarizabilities, etc.

Regarding the accuracy, the calculated transition energy associated with the intense absorption

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bands in the visible regions should agree within $\pm 0.2\text{eV} = 1600\text{cm}^{-1}$ with the observed values, because when the calculated transition energy is larger by only 0.2 eV one expects incorrect color. For example, the transition energy of 2.40 eV corresponds to 517 nm (green, the complementary color is red) and that of 2.20 eV to 563 nm (yellow, the complementary color is blue).

In general, the following accuracy of quantum chemical calculation is desirable: for the calculated energy, the discrepancy with the experimental values must be less than kT (= 0.6 kcal/mol at 300 K), while for the optimized geometrical parameters, the accuracy of bond length must be better than $\pm 0.05 \text{ \AA}$ and that of bond angle better than $\pm 3^\circ$. The modern *ab initio* calculation fulfills the required accuracy for the optimized geometrical parameters. However, concerning the *ab initio* calculation of the electronic spectra, there are some serious problems to be solved, as shown in this paper. For example, when one uses the more sophisticated basis set 6-311++G**, one obtains many virtual excited states in the longest wavelength absorption regions.

The first chapter of quantum organic color chemistry would be the reasonable interpretation of the electronic spectra of organic colorants with simple theory based on reasonable theoretical models and concepts, and the PPP theory [1,2,3] is an interesting candidate for this purpose. The perfection would be the quantitative understanding of the electronic spectra of a given molecule and its electronic structure in the excited states by the *ab initio* theory, if it provides correct, reliable results.

It should be noted that all quantum chemical calculations for many electron systems are just approximation. Therefore, when one wants to obtain better result for energy by *ab initio* calculation, the wave function becomes very complicated, which prevents to image a clear-cut chemical picture. Fortunately, computer sometimes helps us with this serious problem by image processing of the calculated wave function.

Usually simple theory provides beautiful result and general rules, such as aromaticity and Woodward–Hoffmann rule for stereospecific reaction from HMO theory, three characteristic absorption bands of aromatic hydrocarbons from PPP theory, etc. The simple theory is based on the reasonable theoretical model which extracts the essential features of the investigated system.

Most organic colorants contain of π -conjugated systems. For π -conjugated system, the π -electron approximation is appropriate, where one assumes that strong σ -bonds form the framework of molecule and mobile π -electrons are responsible for electronic spectra in the longest wavelength region. The PPP method is the simplest theory for the calculation of the electronic spectra of the π -conjugated system based on the π -electron approximation. In spite of its simplicity, when one uses an appropriate two-center electron repulsion integral set, such as the modified Nishimoto–Mataga (NM) gamma [4,5], the PPP–CI calculation provides high accuracy results for the π -electronic spectra of organic colorants and for understanding the nature of their electronic spectra [6,7,8]. The reason why a modified NM gamma works nicely will be qualitatively discussed.

In order to assess the present performance of the *ab initio* calculations, it is helpful to compare the calculated electronic spectra by PPP method with those by *ab initio* methods at various levels of theory.

2 CALCULATION

We carried out *ab initio* CI calculations of the electronic spectra of some typical aromatic hydrocarbons and organic colorants, using various basis sets and various levels of theory (CIS, TDHF, TDDFT). Calculations are performed with the Gaussian–98 suite of programs [9]. In the *ab initio* calculations of the electronic spectra for π -conjugated system, there are some serious problems to be solved. One of them is that the basis sets used in *ab initio* methods were optimized for the ground states of molecules, but not for their excited states. Therefore, in some cases, we obtain unreasonable results as seen in Table 1, when one considers insufficiently the electron correlation effects at the excited states.

For a comparison, we carried out simple PPP–CI calculations based on a revised NM gamma [5] with variable beta approximation [10]. One of purposes of this paper is to show that the simple PPP–CI calculation is still accurate enough compared to *ab initio* calculations (CIS, TDHF, TDDFT) and provides a clear physical picture for the understanding of π -electronic spectra.

3 RESULTS AND DISCUSSION

3.1 Effective Two Electron Repulsion in a π -Conjugated System

In PPP–CI calculation, the evaluation of the following two electron repulsion integral,

$$\gamma_{\mu\nu} = \iint \chi_{\mu}^2(1) \left(e^2 / r_{12} \right) \chi_{\nu}^2(2) d\tau_1 d\tau_2 = f(R_{\mu\nu}) \quad (1)$$

is a very important task, where $R_{\mu\nu}$ is interatomic distance between the μ -th and ν -th atoms, χ_{μ} is $2p\pi$ AO of the μ -th atom and r_{12} is the distance between electrons 1 and 2. The calculated results greatly depend on the selection of $\gamma_{\mu\nu}$, because $\gamma_{\mu\nu}$ reflects an effective two electron repulsion in a given π -conjugated system.

NM gamma $\gamma_{\mu\nu}$ [4] is a simple formula representing the two-center electron repulsion integral, which is expressed by

$$\gamma_{\mu\nu} = e^2 / (R_{\mu\nu} + a_{\mu\nu}) \quad (2)$$

where $a_{\mu\nu}$ is given by

$$a_{\mu\nu} = 2e^2 / (I_{\mu} + I_{\nu} - A_{\mu} - A_{\nu}) \quad (3)$$

where I_μ and A_μ are valence state ionization potential and the electron affinity associated with the $2p\pi$ AO of the μ -th atom, respectively. In 1956, in order to reproduce the electronic spectra of benzene by PPP–CI calculation based on four orbitals model, I tried to look for a simple formula of electron repulsion integral, assuming that

$$\begin{aligned} \text{Limit}_{R \rightarrow 0} \gamma_{\mu\nu} &= \gamma_{\mu\mu} = I_\mu - A_\mu \\ \text{Limit}_{R \rightarrow \infty} \gamma_{\mu\nu} &= e^2 / R_{\mu\nu} \end{aligned} \quad (4)$$

First, I tried $\gamma_{\mu\nu} = e^2 / \sqrt{R_{\mu\nu}^2 + a_{\mu\nu}^2}$ which was obtained from a classical model, but the B_{1u} transition energy could not be reproduced by this formula (calculated: 5.2 eV, observed: 6.2 eV). Next, I tried $\gamma_{\mu\nu} = e^2 / (R_{\mu\nu} + a_{\mu\nu}) + g(R_{\mu\nu})$. In the first try, I put $g(R_{\mu\nu}) = 0$, then surprisingly I could reproduce the three absorption bands of benzene nicely with this simple formula. Thus NM gamma was accidentally obtained with an empirical formula.

In the revised NM gamma [5], we made the following assumptions for the effective electron repulsion. We have considered two kinds of regions in the molecular potential field. One is the intra-atomic region which is associated with the one-center electron repulsion integral, representing repulsion between two electrons in the same $2p\pi$ -AO. Another one is the interatomic region which is associated with the two-center electron repulsion integral, representing repulsion between two electrons in different AO's. From the viewpoint of this model, it seems to be miraculous that the old NM gamma [4] includes two different type of integrals in the same formula.

In the intra-atomic region, the repulsion between two π -electrons in the same AO χ_μ at the μ -th atom can be expressed by the one-center electron repulsion integral $\gamma_{\mu\mu}$ which is given by the Pariser–Parr approximation [1],

$$r_{\mu\mu} = I_\mu - A_\mu \quad (5)$$

With this approximation, one can take into account the important electron correlation effect at the intra-atomic region.

In the interatomic region, two electrons repel each other at the polarizable many electron molecular potential field. There are many kinds of effects on the effective electron repulsion. Some of them may be as follows. The most important one is the electron correlation effect. With increase of the overlap integral between χ_μ and χ_ν , the electron correlation effect increases. Therefore this effect should have a maximum at the bond region. Next is the effect of dynamical Σ – Π interaction. This effect would have a maximum at the bond region.

The effect of deformation of the AO in molecule at the excited states will be also important. This can be described by the “atom in molecule” model. This effect have a maximum at the bond region. These three effects will decrease considerably the value of $\gamma_{\mu\nu}$ in the bond region (γ_{12}). NM gamma may reflect these effects adequately. As shown in the previous paper [10], when one use theoretical

gamma, where only the value of γ_{12} is subtracted by some amount, one can obtain satisfactorily results for the electronic spectra of aromatic hydrocarbons by PPP–CI calculation.

Fortunately, the semiempirical PPP calculation using NM gamma reproduced satisfactorily the interactions among the lowest singly excited configurations of benzene, naphthalene, anthracene, and their derivatives and provides accurate results for the electronic spectra of these compounds. However, as showed in the previous paper [5], NM gamma is not sufficient for very mobile π -electron systems, such as cyanines which are charge resonance systems, and merocyanines which are represented by strong intramolecular charge transfer systems. This is why we proposed a revised version of NM gamma expressed by Eq. (6). Introducing an extra parameter k , a modified NM gamma is written as

$$r_{\mu\nu} = e^2 / (R_{\mu\nu} + ka_{\mu\nu}) \quad (6)$$

The old NM gamma [4] is the case of $k = 1$. We designated k as the spectrochemical softness parameter, because k reflects the dynamical polarization in the mobile π -conjugated system. In the case when $1 < k$, we call soft, and for $k < 1$ hard. Hereafter, PPP calculation using $\gamma_{\mu\nu}$ expressed by Eq. (6) is designated by NM– k . For example, in case of $k = 1.5$, we write NM–1.5. When one obtains an adequate value for the parameter k for a prototype molecule, then one can use it to the analogues [6,7,8].

3.2 Three Characteristic Absorption Bands for Aromatic Hydrocarbons

Acceptable theoretical methods of quantum color chemistry should reproduce the observed three characteristic absorption bands of aromatic hydrocarbons classified by Clar [11], because they are the prototypes of π conjugated systems. A beautiful aspect of PPP–CI method is to explain their experimental data clearly by a four orbital model shown in the following.

Let us designate HOMO, LUMO, HOMO–1, and LUMO+1 of an alternant hydrocarbon as 1, 1', 2, and 2', respectively. Then their MO energies ε 's and MO's Ψ 's are expressed as follows, because in the PPP method there is an alternancy in the symmetry for aromatic hydrocarbons [12,13]:

$$\begin{aligned} \varepsilon_{2'} &= \varepsilon_0 - k_2 & \Psi_{2'} &= \sum^* a_{\mu} \chi_{\mu} - \sum^{\circ} a_{\nu} \chi_{\nu} \\ \varepsilon_{1'} &= \varepsilon_0 - k_1 & \Psi_{1'} &= \sum^* c_{\mu} \chi_{\mu} - \sum^{\circ} c_{\nu} \chi_{\nu} \\ \varepsilon_1 &= \varepsilon_0 + k_1 & \Psi_1 &= \sum^* c_{\mu} \chi_{\mu} + \sum^{\circ} c_{\nu} \chi_{\nu} \\ \varepsilon_2 &= \varepsilon_0 + k_2 & \Psi_2 &= \sum^* a_{\mu} \chi_{\mu} + \sum^{\circ} a_{\nu} \chi_{\nu} \end{aligned} \quad (7)$$

The transition energy $E(i \rightarrow j)$ associated with the single excitation $\psi(i \rightarrow j)$ for the singlet state is given by

$$E(1 \rightarrow 1') = -2k_1 - (11 | 1' 1') + 2(11' | 11') = E_1 \quad \Psi_1 = \Psi(1 \rightarrow 1') \quad (8)$$

$$E(1 \rightarrow 2') = -(k_1 + k_2) - (11|2'2') + 2(12'|12') = E_2 \quad \Psi_2 = \Psi(1 \rightarrow 2') \quad (9)$$

$$E(2 \rightarrow 1') = -(k_1 + k_2) - (22|1'1') + 2(12'|12') = E_3 \quad \Psi_3 = \Psi(2 \rightarrow 1') \quad (10)$$

$$E(2 \rightarrow 2') = -2k_2 - (22|2'2') + 2(22'|22') = E_4 \quad \Psi_4 = \Psi(2 \rightarrow 2') \quad (11)$$

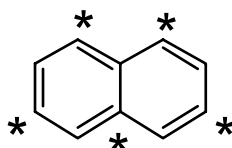


Figure 1. An example of aromatic hydrocarbon.

In the PPP method one obtains $E_2 = E_3$, because $(11|2'2')$ is equal to $(22|1'1')$ by the alternancy symmetry. Furthermore, since the symmetry of these two transitions is the same, they interact each other and split by

$$\Delta = \langle \Psi(1 \rightarrow 2') | H | \Psi(2 \rightarrow 1') \rangle = 2(12'|2'1') - (12'|1'2') \text{ as}$$

$$E_{2'} = E_2 - \Delta \quad \Psi_{2'} = (\Psi_2 - \Psi_3)/\sqrt{2} \quad (12)$$

$$E_{3'} = E_2 + \Delta \quad \Psi_{3'} = (\Psi_2 + \Psi_3)/\sqrt{2} \quad (14)$$

When one calculates the oscillator strength (intensity of absorption) of the transition associated with $\Psi_{2'}$, its value becomes zero (forbidden). It appears as a very weak absorption by the vibronic interaction. This weak band was designated as the α band by Clar [11]. On the other hand, the band associated with $\Psi_{3'}$ is very large (more intense than twice of that associated with Ψ_2) and it appears as a very strong absorption band. This band is designated as the β band [11].

The transition associated with Ψ_1 appears at a medium intensity absorption and is designated as the p -band [11]. Although the order of the transition energies is $E_1 < E_2 = E_3$, the configuration interaction between Ψ_2 and Ψ_3 makes to change the order. Let us define the transition energy difference as $D = E_2 - E_1$. When $D < \Delta$, the order becomes as $E_{2'} < E_1 < E_{3'}$. This is the case of benzene, naphthalene, phenanthrene, etc. On the other hand, when $\Delta < D$, the order is $E_1 < E_{2'} < E_{3'}$. This is the case of polyacenes, except benzene and naphthalene.

Since $\Psi(i \rightarrow j)$ for the singlet state is expressed by

$$\Psi(i \rightarrow j) = (\psi_i(1)\psi_j(2) + (\psi_j(1)\psi_i(2)))/\sqrt{2} \quad (14)$$

one obtains by the substitution of Eq. (7) into Eq. (14), in the PPP scheme, the following results; Ψ_1 and $\Psi_{3'}$ are ionic, but $\Psi_{2'}$ is non-ionic, respectively.

3.3 Electronic Spectra of Naphthalene

The calculated results for the electronic spectra of naphthalene are summarized in Table 1. It should be noted that as shown in Table 1, all *ab initio* CI calculations using various basis sets and

various levels of theory (CIS, TDHF, TDDFT) used in the present study gave the results that the wavelength of the p band (B_{2u}) (the experimental value is 275 nm) is longer than that of the α band (B_{3u}) (the experimental value is 310 nm), where the p , α , and β bands refer to Clar's notation [11]. This is due to the insufficient evaluation of electron correlation effect. Moreover, when one uses the more sophisticated basis set 6–311++G**, TDDFT calculation provides many virtual excited states among p and β bands (Table 1). Hashimoto, Nakano, and Hirao [14] reported that MRMP–CASSCF reproduced fairly well the experimental data. Simple PPP–CI calculation based on the four orbital model provides fairly good results (308 nm for the weak α band, 281 nm for the medium intensity p band, and 222 nm for the strong β band) (Table 1).

The fluorescence of naphthalene is coming from the lowest B_{3u} state. Therefore, above mentioned *ab initio* CI calculations with usual level of theory predicts an incorrect assignment for the fluorescent state of naphthalene. The photochemical reaction of naphthalene also proceeds, of course, via the lowest excited states. Therefore, in the quantum chemical study of the photochemistry and the fluorescence of naphthalene by *ab initio* calculations, one should pay attention to the selection of method.

Table 1. Calculated electronic spectra of naphthalene with various levels of theory: Transition energy, ΔE in eV (in parenthesis, corresponding wavelength λ in nm), oscillator strength f , $\log \epsilon$ for observed intensity.

| Assignment ^a | CIS/3–21G* | | TDHF/3–21G* | | TDDFT/3–21G* | |
|-----------------------------|---------------------|------|---------------------|------|---------------------|------|
| | $\Delta E(\lambda)$ | f | $\Delta E(\lambda)$ | f | $\Delta E(\lambda)$ | f |
| p -band (B_{2u}) | 5.67 (219) | 0.09 | 5.35 (232) | 0.08 | 4.80 (258) | 0.06 |
| α -band (B_{3u}) | 5.75 (216) | 0.00 | 5.56 (223) | 0.00 | 4.80 (258) | 0.00 |
| β -band (B_{3u}) | 7.71 (161) | 2.39 | 7.19 (172) | 1.56 | 6.42 (193) | 1.23 |

| Assignment ^a | TDDFT/6–31G* | | TDDFT/6–311–G** | |
|-----------------------------|---------------------|------|---------------------|------|
| | $\Delta E(\lambda)$ | f | $\Delta E(\lambda)$ | f |
| p -band (B_{2u}) | 4.46 (278) | 0.06 | 4.35 (285) | 0.05 |
| α -band (B_{3u}) | 4.53 (274) | 0.00 | 4.44 (279) | 0.00 |
| — | | | 5.26 (236) | 0.00 |
| — | | | 5.50 (226) | 0.00 |
| — | | | 5.57 (223) | 0.00 |
| — | | | 5.60 (221) | 0.00 |
| β -band (B_{3u}) | 6.11 (198) | 1.21 | 5.86 (212) | 1.25 |

| Assignment ^a | Obs ^b | | NM–1.0 | |
|-----------------------------|---------------------|-----------------|---------------------|------|
| | $\Delta E(\lambda)$ | $\log \epsilon$ | $\Delta E(\lambda)$ | f |
| α -band (B_{3u}) | 4.00 (310) | 2.37 | 4.03 (308) | 0.00 |
| p -band (B_{2u}) | 4.51 (275) | 3.75 | 4.42 (281) | 0.20 |
| β -band (B_{3u}) | 5.63 (220) | 5.01 | 5.58 (222) | 1.96 |

^a For the band assignment, Clar's notation [11] is used

^b Ref. [11]

3.4 Electronic Spectra of Some Other Aromatic Hydrocarbons

The calculated electronic spectra of some aromatic hydrocarbons are summarized in Table 2. One expects that in larger π -electron systems, such as coronene, the dynamical polarization effect becomes significant. As seen from Table 2, the electronic spectra of coronene is much improved by the use of NM-1.3.

Table 2. Calculated electronic spectra of some aromatic hydrocarbons: transition energy, ΔE in eV (in parenthesis, corresponding wavelength λ in nm), oscillator strength f , $\log \epsilon$ for observed intensity.

| Assignment ^a | TDDFT/3-21G* | | Obs. ^b | | NM-1.0 | | NM-1.3 | |
|-----------------------------------|--------------------------|------|--------------------------|-----------------|--------------------------|------|--------------------------|------|
| | ΔE (λ) | f | ΔE (λ) | $\log \epsilon$ | ΔE (λ) | f | ΔE (λ) | f |
| Anthracene | | | | | | | | |
| <i>p</i> -band (B _{2u}) | 3.61 (344) | 0.06 | 3.31 (374) | 3.7 | 3.49 (355) | 0.31 | | |
| α -band (B _{3u}) | 4.18 (297) | 0.00 | – | – | 3.61 (343) | 0.00 | | |
| β -band (B _{3u}) | 5.60 (221) | 1.93 | 4.88 (254) | 5.2 | 4.83 (257) | 2.54 | | |
| β' -band (B _{3u}) | | | 5.56 (223) | 4.1 | 5.90 (210) | 0.79 | | |
| Phenathrene | | | | | | | | |
| α -band | 4.31 (288) | 0.00 | 3.67 (338) | 2.3 | 3.90 (317) | 0.00 | | |
| <i>p</i> -band | 4.60 (270) | 0.07 | 4.27 (290) | 4.2 | 4.27 (291) | 0.35 | | |
| β -band | 5.15 (241) | 0.14 | 4.92 (252) | 4.8 | 5.02 (247) | 1.65 | | |
| β' -band | 5.41 (229) | 0.76 | 5.02 (247) | 4.7 | 5.18 (240) | 1.06 | | |
| Coronene | | | | | | | | |
| α -band (B _{2u}) | 3.48 (356) | 0.00 | 3.02 (410) | 2.76 | 3.16 (392) | 0.00 | 2.97 (417) | 0.00 |
| <i>p</i> -band (B _{1u}) | 3.73 (332) | 0.00 | 3.63 (342) | 4.85 | 3.50 (354) | 0.00 | 3.45 (359) | 0.00 |
| β -band (E _{1u}) | 4.42 (280) | 1.39 | 4.06 (305) | 5.50 | 4.31 (287) | 2.55 | 4.00 (310) | 2.42 |

^a For the band assignment, Clar's notation [11] is used

^b Ref. [11]

3.5 Electronic Spectra of Some Interesting Organic Colorants

For the molecule having a strong intramolecular charge transfer system, such as merocyanine, we expect such molecule to be soft. That is the case of $1 < k$. In Table 3 we present the calculated electronic spectra of some interesting organic colorants having an intramolecular charge transfer system. In *ab initio* calculation of electronic spectra, TDDFT (time dependent density functional theory) is recommended by many authors, because it adequately considers the electron correlation effect.

However, as seen from Table 3, the λ_{\max} of electronic spectra of anthraquinone calculated with TDDFT/3-21G* is too long compared with that of observed ones (calculated: 410 nm, observed: 329 nm). Furthermore, TDDFT/3-21G* predicts very small substituent effect on the spectra of anthraquinone, (only 20 nm red shift by 1-NH₂ substitution (experimental data: 144 nm red shift, PPP-CI; 129 nm red shift) and 2 nm blue shift by 2-NH₂ substitution (experimental data: 131 nm red shift, PPP-CI; 95 nm red shift)). On the other hand, our simple NM- k calculation provides satisfactory results for overall spectra.

Table 3. Calculated electronic spectra of some interesting organic colorants I–V; transition energy, ΔE in eV (in parenthesis, corresponding wavelength λ in nm), oscillator strength f , $\log \epsilon$ for observed intensity.^a

I. Azulene

| State ^b | TDDFT/3–21G* | | Obs. ^c | | NM–1.0 | | NM–1.1 | |
|--------------------|--------------------------|-------------|--------------------------|-----------------|--------------------------|-------------|--------------------------|-------------|
| | ΔE (λ) | f | ΔE (λ) | $\log \epsilon$ | ΔE (λ) | f | ΔE (λ) | f |
| S ₁ | <u>2.54 (489)</u> | <u>0.01</u> | 2.13 (580) | 2.54 | <u>2.08 (595)</u> | <u>0.04</u> | <u>1.92 (646)</u> | <u>0.03</u> |
| S ₂ | 3.89 (319) | 0.00 | 3.64 (341) | 3.64 | <u>3.54 (350)</u> | <u>0.01</u> | <u>3.39 (366)</u> | <u>0.01</u> |
| S ₃ | <u>4.94 (251)</u> | <u>0.06</u> | — | — | <u>4.81 (258)</u> | <u>0.60</u> | <u>4.66 (266)</u> | <u>0.58</u> |
| S ₄ | <u>5.40 (230)</u> | <u>1.08</u> | 4.54 (273) | 4.74 | <u>4.81 (258)</u> | <u>2.07</u> | <u>4.67 (265)</u> | <u>2.01</u> |
| S ₅ | 6.15 (202) | 0.00 | — | — | — | — | — | — |
| S ₆ | 6.35 (195) | 0.25 | — | — | — | — | — | — |

II. Indigo

| State ^b | TDDFT/3–21G* | | Obs. ^c | | NM–1.0 | | NM–1.5 | |
|--------------------|--------------------------|-------------|--------------------------|-----------------|--------------------------|-------------|--------------------------|-------------|
| | ΔE (λ) | f | ΔE (λ) | $\log \epsilon$ | ΔE (λ) | f | ΔE (λ) | f |
| S ₁ | <u>2.49 (497)</u> | <u>0.27</u> | 2.05 (605) | 4.10 | <u>2.16 (574)</u> | <u>0.72</u> | <u>2.10 (590)</u> | <u>0.71</u> |
| S ₂ | <u>2.98 (416)</u> | <u>0.00</u> | 2.75 (450) | 2.95 | <u>2.93 (395)</u> | <u>0.00</u> | <u>2.68 (463)</u> | <u>0.00</u> |
| S ₃ | 3.02 (411) | 0.00 | 3.59 (345) | 3.85 | <u>3.87 (320)</u> | <u>0.00</u> | <u>3.56 (348)</u> | <u>0.48</u> |
| S ₄ | 3.46 (358) | 0.00 | — | — | 3.94 (315) | 0.50 | 3.58 (346) | 0.00 |
| S ₅ | 3.79 (328) | 0.00 | 4.35 (285) | 4.40 | <u>5.19 (239)</u> | <u>0.79</u> | <u>4.75 (261)</u> | <u>0.74</u> |
| S ₆ | <u>4.19 (296)</u> | <u>0.14</u> | — | — | — | — | — | — |
| S ₇ | 4.34 (286) | 0.00 | — | — | — | — | — | — |
| S ₈ | 4.50 (276) | 0.08 | — | — | — | — | — | — |
| S ₉ | 4.73 (262) | 0.28 | — | — | — | — | — | — |
| S ₁₀ | <u>4.91 (252)</u> | <u>0.58</u> | — | — | — | — | — | — |

III. Anthraquinone

| State ^b | TDDFT/3–21G* | | Obs. ^d | | NM–1.0 | |
|--------------------|--------------------------|-------------|--------------------------|-----------------|--------------------------|-------------|
| | ΔE (λ) | f | ΔE (λ) | $\log \epsilon$ | ΔE (λ) | f |
| S ₁ | <u>3.02 (410)</u> | <u>0.00</u> | 3.77 (329) | 3.8 | <u>3.74 (331)</u> | <u>0.23</u> |
| S ₂ | 3.36 (369) | 0.00 | — | — | 3.79 (327) | 0.00 |
| S ₃ | 4.02 (308) | 0.00 | — | — | 3.88 (320) | 0.00 |
| S ₄ | <u>4.17 (298)</u> | <u>0.12</u> | 4.59 (270) | 4.3 | <u>4.38 (283)</u> | <u>0.69</u> |
| S ₅ | 4.17 (298) | 0.00 | 4.96 (250) | 4.8 | <u>5.04 (246)</u> | <u>1.03</u> |
| S ₆ | 4.62 (268) | 0.00 | — | — | — | — |
| S ₇ | <u>4.82 (257)</u> | <u>0.16</u> | — | — | — | — |

IV. 1–NH₂–anthraquinone

| State ^b | TDDFT/3–21G* | | Obs. ^e | | NM–1.0 | | NM–1.6 | |
|--------------------|--------------------------|-------------|--------------------------|-----------------|--------------------------|-------------|--------------------------|-------------|
| | ΔE (λ) | f | ΔE (λ) | $\log \epsilon$ | ΔE (λ) | f | ΔE (λ) | f |
| S ₁ | <u>2.88 (430)</u> | <u>0.11</u> | 2.61 (474) | m ^f | <u>2.92 (425)</u> | <u>0.24</u> | <u>2.69 (460)</u> | <u>0.23</u> |
| S ₂ | 3.09 (401) | 0.00 | — | — | 3.85 (322) | 0.08 | 3.50 (355) | 0.02 |
| S ₃ | 3.47 (358) | 0.00 | — | — | 3.91 (317) | 0.09 | 3.58 (347) | 0.06 |
| S ₄ | <u>4.04 (307)</u> | <u>0.00</u> | 4.00 (310) | s ^f | <u>4.36 (284)</u> | <u>0.19</u> | <u>4.08 (304)</u> | <u>0.57</u> |
| S ₅ | 4.20 (295) | 0.02 | — | — | <u>4.66 (266)</u> | <u>0.45</u> | <u>4.24 (292)</u> | <u>0.06</u> |
| S ₆ | <u>4.27 (290)</u> | <u>0.08</u> | 5.00 (248) | s ^f | <u>5.31 (234)</u> | <u>0.50</u> | <u>4.84 (256)</u> | <u>0.64</u> |
| S ₇ | 4.79 (259) | 0.00 | — | — | — | — | — | — |
| S ₈ | <u>4.80 (258)</u> | <u>0.12</u> | — | — | — | — | — | — |

V. 2–NH₂–anthraquinone

| State ^b | TDDFT/3–21G* | | Obs. ^e | | NM–1.0 | | NM–1.6 | |
|--------------------|--------------------------|-------------|--------------------------|-----------------|--------------------------|-------------|--------------------------|-------------|
| | ΔE (λ) | f | ΔE (λ) | $\log \epsilon$ | ΔE (λ) | f | ΔE (λ) | f |
| S ₁ | <u>3.04 (408)</u> | <u>0.05</u> | 2.69 (461) | m ^f | <u>3.21 (386)</u> | <u>0.18</u> | <u>2.91 (426)</u> | <u>0.16</u> |
| S ₂ | 3.07 (404) | 0.00 | 3.53 (351) | w ^f | <u>3.80 (326)</u> | <u>0.02</u> | <u>3.50 (355)</u> | <u>0.10</u> |
| S ₃ | 3.41 (364) | 0.00 | — | — | 3.90 (318) | 0.09 | 3.60 (345) | 0.05 |
| S ₄ | 4.11 (302) | 0.01 | 4.07 (305) | s ^f | <u>4.32 (287)</u> | <u>0.43</u> | <u>4.00 (310)</u> | <u>0.50</u> |
| S ₅ | <u>4.26 (291)</u> | <u>0.04</u> | — | — | <u>4.58 (271)</u> | <u>0.79</u> | <u>4.20 (296)</u> | <u>0.66</u> |
| S ₆ | <u>4.50 (275)</u> | <u>0.32</u> | — | — | <u>5.11 (243)</u> | <u>0.79</u> | <u>4.76 (261)</u> | <u>0.32</u> |

^a In Table, n→ π^* transitions are neglected^b The calculated data mentioned by underline corresponds to observed ones.^c Ref [15]; ^d Ref [16]; ^e Ref [17]; ^f w: weak, m: medium, s: strong

4 CONCLUSIONS

The present study demonstrated that simple PPP–CI calculations with a suitable two–center electron repulsion integral is successful for the calculation of the π –electronic spectra of organic colorants with high accuracy and also for understanding the nature of their electronic spectra. One can compute molecules having the coronene size in a few seconds using a PC. Thus, this method is useful for the combinatorial chemistry in the theoretical design of organic colorants. Furthermore, the nature of the π –electronic spectra and the characteristic feature of the lowest excited states, such as ionic, covalent, diradical and the type of electronic transitions, etc. are clearly understood using PPP–CI calculations. On the other hand, in some cases, *ab initio* calculations provide erroneous results. And also, the calculated *ab initio* excited state functions are very complicated. For example, a configuration associated with the HOMO–LUMO transition is dispersed over among many excited states.

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Biographies

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