Singlet and Triplet Excited State Energy Ordering in Cyclopenta-Fused Polycyclic Aromatic Hydrocarbons (CP-PAHs) Suitable for Energy Harvesting: An Exact Model and TDDFT Study

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ABSTRACT: We calculated the ground and low-lying excited states of cyclopenta-fused polycyclic aromatic hydrocarbons (CP-PAHs) using exact diagonalization in full configuration interaction (CI) within the model Pariser–Parr–Pople Hamiltonian as well as a time-dependent density functional theory technique. The CP-PAHs include acenaphrylene, isomers of pyracylene, cycloocta-pentalene, and three isomers of dicyclopentacyclo-octenes (DCPCO). We used the inherent symmetries of these systems to calculate the energy ordering of the lowest singlet (S1) and lowest triplet excited (T1) states with respect to the ground state (S0). The calculation shows that the lowest dipole allowed singlet absorption varies from 0.43 to 1.42 eV for most of these systems. Such an optical absorption range is very promising in harvesting solar radiation ranging from the visible to near-infrared region improving the efficiency of photovoltaic device application. The calculated optical gaps for pyracylene, acenaphrylene, acenaphthylene, isomers of pyracylene, cycloocta-pentalene, and three isomers of DCPCO are in very good agreement with experimental results reported in the literature. The calculated S1−T1 energy gaps (ΔS1T1) in cycloocta-pentalene and in the DCPCO isomers are very small ranging from 0.01 to 0.2 eV, which is highly desirable in improving their electroluminescence efficiency in light-emitting device applications.

1. INTRODUCTION

In the field of electronic and optoelectronic devices, organic conjugated systems have received major attention as they are cheap and easy to fabricate. These conjugated systems serve the purpose of an active material in designing photovoltaic devices with well-defined molecular architectures. Conjugated systems with a low band gap (<2 eV) that can absorb solar radiation extending into the red and near-infrared (NIR) region are strongly desirable to improve the power conversion efficiency of organic solar cells (OSCs). For single junction OSCs, an optical band gap of about 1.3−1.7 eV is expected to be optimal.1,2 So, the lowest dipole allowed singlet (S1) excited state energy will predict the optical gap of the system. Similarly, the energy ordering of the lowest triplet (T1) with respect to S1 is very crucial so that population transfer from T1 to S1 can be achieved through reverse intersystem crossing (RISC). According to spin statistics in the noninteracting limit, the upper bound of singlet exciton formation is 25% in organic solar cells.3,4 Generation of singlets is still small with respect to triplets, even in the interacting picture. The efficiency of electroluminescence in OLEDs can be enhanced through RISC as, according to Kasha, emission occurs from the lowest dipole allowed singlet state (S1) only.5

In general, for conjugated systems, the lowest triplet energy E(T1) is lower than the lowest singlet energy E(S1), however in the process of RISC, it is very desirable to have a S1−T1 energy gap that is of the order of kT (0.025 eV) so that S1 can be populated thermally. There are some experimental reports on such conjugated systems with very small S1−T1 energy gaps (0.04 eV).6−10 In recent times, theoretical and computational investigations have also predicted some conjugated systems with small S1−T1 energy gaps.11−14 In those cases, the S1−T1 energy gap has been calculated using time-dependent density functional theory (TDDFT), single configuration interaction (SCI), and the full CI technique. Gierschner et al. reported carbozole–paraterphenyl systems with donor–acceptor (D–A) substituents.11 Kohler et al. reported a planar and twisted conformation of long conjugated oligomers.12 Theoretical prediction at INDO level reported an S1−T1 energy gap of 0.8 eV in pentamers.13 Prodhon et al. carried out a full CI calculation on model polyenes and showed that the best system with a very low S1−T1 gap involves D substitution in one half of the carbons and A substitution in the other half of the carbon atoms in the polynene chain.14 The energy ordering of S1 and T1 is also very important in photodynamic therapy. In this technique, ground state (gs) triplet oxygen collides with an S1 photosensitizer to give rise to singlet oxygen forming the T1 excited state. The production of reactive singlet oxygen kills the tumor cell in living organs.15

In this work, we calculated the ground and excited states of seven cyclopenta-fused polycyclic aromatic hydrocarbons (CP-PAHs). These CP-PAHs were considered for our calculation as they have been the recipients of a huge amount of attention due to their strong electron affinities, chemical reactivities, and...
Because of their high electron affinities they have been used in several optoelectronic applications including organic photovoltaics and field-effect transistors. Moreover, CP-PAHs have been proven to be a biologically important species. They have been used as DNA intercalators in chemotherapy to prevent DNA replication in cancer cells. A theoretical understanding of the electronic structures of these CP-PAHs would be helpful in explaining their applicability. The strong electron−electron correlation in these systems plays a very important role in determining the energy ordering of these CP-PAHs. So, from the theoretical point of view, it is very important to calculate the nature of the gs and the energy ordering of the excited states to predict their suitability in optoelectronics. These molecules are acenapthylene (a), pyracylene (b), an isomer of pyracylene called cycloocta-pentalene (c), dicyclo-pentacyclo-octenes (DCPCO) (d−f), and cycloocta-pentalene (COP) (g).

The ground and low-lying excited states of these conjugated systems were calculated within the model Pariser−Parr−Pople (PPP) Hamiltonian. As the CP-PAHs are composed of a maximum of 14 carbon atoms, one can express the model Hamiltonian in full CI basis in both singlet and triplet subspaces within the PPP Hamiltonian. We employed the inherent symmetries of these molecules to target the desired excited states in the singlet and triplet subspaces. The symmetry point group is C2v for the molecule acenapthylene (a) and DCPCO isomers (e, f). The C4 axis is in the plane of those molecules. The isomer of pyracylene called cycloocta-pentalene (c) and the DCPCO isomer, cycloocta-pentalene (g), possess C3v symmetry. Only the pyracylene (b) and DCPCO (d) molecules belong to the D2h point group. The model PPP Hamiltonian that describes these molecules includes a kinetic energy contribution due to the hopping of electrons from one atomic site to another and an explicit electron−electron correlation in terms of the long-range Coulombic potential. The electron−phonon interaction was not included in the Hamiltonian. However, such electron−phonon interactions may play a very important role in dictating the energy ordering of excited states. Perturbations like steric hindrance and the electric field driven distortion mechanism in such aromatic molecules have been studied earlier. Vibrational instability may cause a distortion and later on effect the energy ordering however this is beyond the scope of the present study. We assumed undistorted optimized gs geometries of the above molecules in our calculation.

We also investigated the D and A substitution effect on the S1−T1 energy gap for these molecules. In the next section, we discuss the ground and excited state energy ordering followed by the effect of substitution at suitable positions in the molecules. In Section 3, we summarize and conclude the study.
2. RESULTS AND DISCUSSION

Although spin is conserved in all of these molecules, $D_{3h}$ symmetry is present only in two systems, pyracylene (b) and DCPCO (d). For these two systems (b and d) in Figure 1, the gs lies in the A subspace and spin parity is even ‘A’. The state strongly dipole coupled to the gs also lies in even parity subspace ‘B’ termed as the one-photon state. The dipole-forbidden two-photon state is in the even parity ‘2A’ subspace. However, the triplet states lie in the odd parity (o) subspace. The presence of $D_{3h}$ symmetry reduces the dimensionality of the subspaces and helps to target the energy states in A and B in both the singlet and triplet subspaces. However, for molecules without $D_{3h}$ symmetry (a, c, e, f, g in Figure 1), we carried out the full CI calculation in the singlet and triplet subspaces. Obviously, we had to deal with the higher dimensionality of the subspaces for those molecules.

We first discuss the results of the low-lying excited states of pyracylene (b) and DCPCO (d). The gs is singlet $1^1A_g$ ($S_0$) in both cases. The lowest dipole allowed singlet excited state is $1^1B_u (S_1)$. The dipole-forbidden two-photon state is labeled as $2^2A_g$. Finally, we calculated the lowest triplet state ($T_1$) and reported the spin gap $E_{ST} = E(T_1) − E(S_0)$, three singlet gaps $E_1 = E(1^1B_u) − E(S_0), E_2 = E(2^1B_u) − E(S_0), E_3 = E(3^1B_u) − E(S_0)$, and the lowest singlet ($S_0$) to lowest triplet ($T_1$) energy gap $Δ_{ST} = E(S_0) − E(T_1)$. We tabulated the results in Table 1. The energy ordering of the two-photon ($2^1A_g$) and one-photon ($1^1B_u$) state is very important. According to Kasha’s rule, a conjugated system is fluorescent in nature if the lowest dipole allowed singlet state ($1^1B_u$) is energetically below the dipole-forbidden two-photon state ($2^2A_g$). Let us first consider the case of pyracylene molecule (b). The lowest triplet state ($T_1$) with respect to gs is at 1.12 eV. The three excited singlet are listed in Table 1. The one-photon state $S_1 (1^1B_u)$ is at 2.61 eV, and the rest of the higher singlet states are at 3.20, 3.45, 3.60, and 4.21 eV. $T_1$ is below $S_0$, which is, in general, common in conjugated systems. The two-photon dipole-forbidden state ($2^2A_u$) is at 1.75 eV from gs, which is lower than the one-photon state $S_1$. This indicates that pyracylene is not fluorescent. The calculated $Δ_{ST}$ for pyracylene is 1.49 eV. It is also interesting to report that for pyracylene (b), $E(S_1) = 2.61$ eV is greater than $2^2E(T_1) = E(S_0)$ (2.24 eV). However, $E(T_1)$ (2.15 eV) is nearly 0.1 eV lower than $2^2E(T_1)$ (2.24 eV). So, pyracylene may support the idea of a singlet fission process, where a pair of correlated triplet excitons is formed from one singlet excitation on a molecule as $E(S_1)$ is greater than $2^2E(T_1)$.

Finally, we discuss the computational approach for modeling these conjugated systems.

Table 1. Low-Lying Excited States of Pyracylene (b) and DCPCO (d) Molecules

| molecule     | model | spin gap $E_{ST}$ (eV) | two-photon gap (eV) | $Δ_{ST}$ (eV) | singlet gap (eV) | $μ$ (Debye)/f | DOI: 10.1021/acsomega.7b00278 | ACS Omega 2017, 2, 1793–1803 |
|--------------|-------|------------------------|---------------------|--------------|------------------|---------------|------------------------------|------------------------------|
| pyracylene (b) | PPP   | 1.12                   | 1.75                | 1.48         | 2.61             | 0.26          |                              |                              |
|              |       |                        |                     |              | 3.20             | 1.95          |                              |                              |
|              |       |                        |                     |              | 3.45             | 2.95          |                              |                              |
|              |       |                        |                     |              | 3.60             | 2.38          |                              |                              |
|              | TDDFT | 1.56                   | 0.43                | 2.0          | 0.0              |               |                              |                              |
|              |       |                        |                     |              | 3.19             | 0.02          |                              |                              |
|              |       |                        |                     |              | 3.59             | 0.14          |                              |                              |
|              |       |                        |                     |              | 4.15             | 0.14          |                              |                              |
| DCPCO (d)    | PPP   | 0.58                   | 1.57                | 0.09         | 0.48             | 1.26          |                              |                              |
|              |       |                        |                     |              | 2.44             | 0.10          |                              |                              |
|              |       |                        |                     |              | 3.11             | 1.21          |                              |                              |
|              |       |                        |                     |              | 3.32             | 0.50          |                              |                              |
|              | TDDFT | 1.27                   | 0.24                | 1.03         | 0.0              |               |                              |                              |
|              |       |                        |                     |              | 2.57             | 0.0           |                              |                              |
|              |       |                        |                     |              | 2.74             | 0.0           |                              |                              |
|              |       |                        |                     |              | 4.05             | 1.74          |                              |                              |
lying singlet states for these systems, along with a transition dipole moment. The lowest triplet excited state \((T_1)\) energies and \(\Delta_{ST} = E(S_1) - E(T_1)\) are summarized in Table 2. We first discuss the results obtained for acenaphtylene (a). The spin gap is 1.88 eV and the lowest dipole allowed singlet excited state \((S_1)\) is 2.69 eV higher relative to the gs singlet. The higher \(\Delta_{ST}\) is 1.88 eV and the lowest dipole allowed singlet excited state discuss the results obtained for acenaphtylene (crucial) \(\Delta\) (eV) below \(S_0\), indicating the triplet state \((T_1)\) is the gs, which is compare the calculated singlet excited state values with the value obtained in the model Hamiltonian method. We later \(\Delta\) (eV) (spin gap) is nearly 0.63 eV. So, the magnitude of \(\Delta_{ST}\) is very low, nearly 0.01 eV, for the case of DCPCO isomer (f). The calculated \(\Delta_{ST}\) (0.01 eV) is the lowest amongst the isomers of DCPCO. The singlet excitations based on TDDFT give comparatively higher absorption values at 1.197, 2.52, and 2.66 eV. The spin gap is at 1.196 eV and the important \(\Delta_{ST}\) is nearly zero, which is similar to what obtained through the model Hamiltonian calculation. Both the model Hamiltonian and TDDFT results indicate \(\Delta_{ST}\) to be very small for DCPCO isomer (f). Thus, DCPCO isomer (f) could be useful in electroluminescent device applications. Finally, we concentrate on the case of cycloocta-pentalene (g), shown in Figure 1. The calculated lowest three singlet absorptions are at 0.43, 1.22, and 1.81 eV, and the spin gap is at 0.52 eV. So, \(\Delta_{ST}\) for cycloocta-pentalene molecule (g) is nearly 0.09 eV. The calculation based on TDDFT shows singlet absorption values at 1.16, 2.49, and 2.65 eV with the spin gap at 1.18 eV, and \(\Delta_{ST}\) is very low at 0.01 eV. Both the model Hamiltonian and the TDDFT approach show very small \(\Delta_{ST}\) values. Cycloocta-pentalene could also be regarded as an isomer of DCPCO. So, we conclude that all of the isomers of DCPCO exhibit very small \(\Delta_{ST}\), and among them, DCPCO isomer (f) showed the lowest.

In the model Hamiltonian approach, except for the case of the pyracylene molecule, the calculated \(\Delta_{ST}\) values for the others vary from 0.01 to 0.48 eV. Among them, the \(\Delta_{ST}\) values of DCPCO isomers (f) and cycloocta-pentalene (g) are 0.01 and 0.09 eV, respectively. The TDDFT method also shows nearly zero \(\Delta_{ST}\) for DCPCO isomer (f) and 0.2 eV for cycloocta-pentalene (g). So, beside pyracylene, the rest of the molecules could support the idea of RISC. The isomers of DCPCO (d, e, f, and cycloocta-pentalene (g)) are very promising in this respect. In addition to that, the PPP calculation also reveals that except for acenaphthylene (a) and pyracylene (b), the lowest singlet absorption ranges from 0.43

### Table 2. Low-Lying Excited States of Small Conjugated Molecules

| molecule | model | spin gap (eV) | \(\Delta_{ST}\) (eV) | singlet gap (eV) | \(\mu\) (Debye)/\(f\) |
|----------|-------|--------------|----------------------|-----------------|---------------------|
| a        | PPP   | 1.88         | 0.81                 | 2.69            | 1.1                 |
|          |       | 3.48         | 1.9                  | 3.60            | 2.3                 |
|          |       | 4.21         | 1.5                  | 4.16            | 1.1                 |
| a        | TDDFT | 1.13         | 1.94                 | 3.08            | 0.0                 |
|          |       | 3.84         | 0.1                  | 4.16            | 1.1                 |
| c        | PPP   | 1.2          | 0.27                 | 1.47            | 0.57                |
|          |       | 2.70         | 1.21                 | 3.08            | 1.46                |
| c        | TDDFT | 1.13         | 0.96                 | 2.1             | 0.0                 |
|          |       | 2.88         | 0.01                 | 3.62            | 0.05                |

### Table 3. Low-Lying Excited States of Small Conjugated Molecules

| molecule | model | spin gap (eV) | \(\Delta_{ST}\) (eV) | singlet gap (eV) | \(\mu\) (Debye)/\(f\) |
|----------|-------|--------------|----------------------|-----------------|---------------------|
| e        | PPP   | 1.29         | 0.12                 | 1.17            | 0.73                |
|          |       | 1.81         | 0.82                 | 2.18            | 0.75                |
| f        | PPP   | 0.63         | 0.01                 | 0.62            | 0.38                |
|          |       | 1.62         | 0.59                 | 1.93            | 0.65                |
| g        | PPP   | 0.52         | 0.09                 | 0.43            | 0.75                |
|          |       | 1.22         | 0.51                 | 1.81            | 0.41                |
| g        | TDDFT | 1.17         | 0.19                 | 1.37            | 0.0                 |
|          |       | 2.05         | 0.0                  | 2.90            | 0.07                |
to 1.47 eV which is suitable for absorbing solar radiation in the NIR region.

For a better understanding of the energy ordering of all of these molecules discussed above, we summarize the energy states in the singlet and triplet subspaces obtained from the model PPP Hamiltonian in Figures 2 and 3.

2.1. D–A Substituted Systems. The optical absorption of these small CP-PAH molecules can be further modulated with proper D–A substitution at suitable atomic positions in experiments. Theoretically, we also calculated the low-lying excitations of the above-described systems with D–A substitution and the effect of D and A group is simulated by introducing an atomic site or orbital energies at the atomic positions at which these groups substitute the hydrogen atom. A negative site energy (ε) simulates the A group, whereas a positive value induces the effect of a D group. The low-lying singlet excitations are sensitive to the effect of D–A substitution in conjugated systems. The atomic positions of the D–A substitutions are depicted in Figure 1 for all of the molecules discussed above. A nonzero value of ε provides the strength of substitution. First, we plotted the variation of optical gap and ΔST for acenaphthylene as a function of |ε| in Figure 4.

In the case of acenaphthylene, D–A substitution does not show any effect on the ΔST value up to maximum |ε| = 5 eV, however.

Figure 2. Low-lying energy ordering obtained using the PPP model Hamiltonian method in the singlet and triplet subspaces of acenaphthylene (a), pyracylene (b), and cyclopenta-acenapthylene (c), respectively.
a slight increase in the value of the optical gap was noticed. We next concentrate on comparing the optical excitations in pyracylene (b) and its isomer, cyclopenta-acenapthylene (c). The suitable positions for substitution are depicted in Figure 1. We summarized the results in a plot wherein the variation in optical gap is shown as a function of the magnitude of D–A strength in Figure 5. Comparing the low-lying excitations in pyracylene (b) and cyclopenta-acenapthylene (c), we found that the optical gap in these systems is sensitive to D–A substitution. The effect of D–A strength (|\(\epsilon|\)) in reducing the optical gap is more pronounced in pyracylene (a) than in its isomer cyclopenta-acenapthylene (c). The optical gap of 2.6 eV can be reduced to 1.4 eV for an |\(\epsilon|\) value up to 5 eV, whereas for cyclopenta-acenapthylene (c), the gap is reduced from 1.4 to 1.2 eV only. It should also be noted that \(\Delta_{ST}\) is nearly same over the entire range of D–A substitution (0.5–0.3 eV) for both molecules.

In the case of DCPCO and its isomers (d–g in Figure 1), the effect of D–A substitution on the optical and \(\Delta_{ST}\) energy gap is summarized in Figure 6. We found that the value of optical gap is smaller when |\(\epsilon|\) = 0, and with increasing D–A strength, the value of optical gap increases as a function of |\(\epsilon|\), except for the DCPCO (e) isomer. In the case of the DCPCO isomer (e), we see a decrease in the gap with an increase in |\(\epsilon|\) from 1.17 to

Figure 3. Low-lying energy ordering obtained using the PPP model Hamiltonian method in the singlet and triplet subspaces of isomers of dicyclopentacyclo-octenes (DCPCO) (d), (e), (f), and cycloocta-pentalene (COP) (g), respectively.
0.84 eV. So, the modulation of optical gap as function of D–A strength is possible for these isomers. The calculated lowest singlet–triplet ($\Delta_{ST}$) energy gap is very interesting in these isomers. Figure 6 shows that the initial $\Delta_{ST}$ is nearly 0.1 eV for $|\epsilon| = 0$ for the DCPCO isomers (d, e, f), except it is 0.01 eV for cycloocta-pentalene (g). The $\Delta_{ST}$ values of the DCPCO isomers d, e, f can be modulated with $|\epsilon|$ strength and almost vanish (0.03 eV for e, f and 0.003 eV for d) at $|\epsilon| = 4$ eV. So, the model Hamiltonian calculation shows that the DCPCO isomers are very good candidates for RISC. In the case of cycloocta-pentalene (g), we found a small increment (0.01–0.18 eV) of $\Delta_{ST}$ with an $|\epsilon|$ strength up to 5 eV.

**2.2. Comparison with Experimental Observations.** The calculated singlet absorption values obtained from the full CI and TDDFT techniques were compared with existing absorption maxima observed experimentally for the above molecules reported in the literature. The calculated lowest singlet absorption for pyracylene (Table 1) at 2.61 eV with a nonzero transition dipole moment (0.26 Debye) obtained through a model Hamiltonian is in very good agreement with the experimental value of 2.56 eV in hexane solution.\(^{25}\) The lowest singlet absorption was calculated to be 2 eV with zero oscillator strength using the TDDFT methodology. We could observe that the full CI results within the PPP model Hamiltonian give better agreement with experiments over the TDDFT results of the lowest singlet optical absorption in the case of pyracylene (b). In the case of acenaphthylene, the absorption at 4.1 eV found experimentally is in very good agreement with the model Hamiltonian value (4.21 eV) and TDDFT-based result (4.16 eV).\(^{30}\) The 2,7-di(tert-butyl) derivative of the DCPCO (d) isomer is shown in Figure 1. It exhibits the longest wavelength absorption maxima ($\lambda = 1375$ (0.9) nm (eV)).\(^{37}\) The calculated optical gap at highest D–A strength ($|\epsilon| = 5$ eV) was found to be 0.7 eV, which is very close to the experimentally found absorption (0.9 eV) reported for the 2,7-di(tert-butyl) derivative of the DCPCO isomer. The TDDFT result of the optical absorption (1.0 eV) of DCPCO (d) is also in good agreement with experiments. The synthesis and optical absorption study of DCPCO isomer (e) was reported by Oda et al.\(^{37}\) The UV/vis spectra of DCPCO isomer (e) shows the longest wavelength at 767 (1.61) nm (eV). The calculated value of optical gap of the above molecule is nearly 1.17 eV (0.73 Debye), whereas the TDDFT results show absorption at a comparatively higher energy of 2.67 eV with nonzero oscillator strength.

**3. CONCLUSIONS**

The low-lying excited states of seven CP-PAHs, namely, acenaphthylene, isomers of pyracylene, cycloocta-pentalene, and dicyclo-pentacyclo-octenes (DCPCO) were studied within a model PPP Hamiltonian as well as using the TDDFT technique. Calculations employed relevant symmetries to target the desired excited states in the model Hamiltonian approach. The calculated optical gap of the above molecules ranges from 0.43 to 1.4 eV, except for pyracylene and acenaphthylene, indicating the possibility of their applicability in harvesting NIR region solar radiation. The calculated lowest singlet ($S_1$) and lowest triplet ($T_1$) excitation energy gap ($\Delta_{ST}$) is comparatively smaller ranging from 0.01 to 0.48 eV, except for pyracylene,
showing that they can be used to improve the efficiency of OLEDs and photovoltaic devices through RISC. The singlet optical absorption of pyracylene and acenaphylene are in very good agreement with experimental observations. The optical excitations in D–A substituted the dicyclo-pentacyclo-octenes (DCPCO) isomers agree well with experiments. Thus, calculation of the low-lying excited states of the above molecules shows that these are very promising for harvesting solar energy at the NIR region and can be useful in enhancing the electroluminescent efficiency in light-emitting devices.

4. COMPUTATIONAL APPROACH

All of the conjugated molecules shown in Figure 1 obey the 4n + 2 (n integer) rule except acenaphylene. Aacenaphylene and pyracylene C60 fragments. For a wide range of π-conjugated molecules and polymers involving sp2 carbon backbone, it has been shown earlier that the PPP model Hamiltonian provides a physically consistent and numerically accurate description. This correlated electron model Hamiltonian for π-conjugated systems restricts the orbital basis to just pπ orbitals. The PPP Hamiltonian includes the explicit long-range electron–electron interactions along with the on-site Hubbard interaction (U)26–29 The model Hamiltonian is written as

$$H_{PPP} = -\sum_{\sigma,q} t_{ij}(\hat{a}_{i\sigma}^\dagger \hat{a}_{j\sigma} + H.c.) + \sum_{i} \hat{n}_{i}\epsilon_{i} + \frac{1}{2} \sum_{ij} U_{ij}(\hat{n}_{i} - 1) + \sum_{ij} V_{ij}(\hat{n}_{i} - z_{i})(\hat{n}_{j} - z_{j})$$

(1)

where \(a_{i\sigma}^\dagger\) (\(a_{i\sigma}\)) creates (annihilates) a π-electron in the \(p_{\pi}\) orbital on atom site \(i\) with spin \(\sigma\). \(n_{i}\) = \(\sum_{\sigma} a_{i\sigma} a_{i\sigma}^\dagger\) is the total number of electrons on atom \(i\). \(\epsilon_{i}\) is termed the orbital energy or site energy at atomic site \(i\). and \(z_{i}\) are the local chemical potentials, which is 1 for carbon. \(t_{ij}\) is the hopping matrix element or transfer integrals between the bonded pair of atoms \(i\) and \(j\). The Hubbard \(U_{ij}\) is the on-site electron–electron repulsion and \(V_{ij}\) is termed as the intersite Coulomb interaction potential parameterized in Ohno interpolation scheme.30

$$V_{ij} = 14.397 \left(\frac{28.794}{U + U_{ij}} \right)^{2} + r_{ij}^{2}\right)^{-1/2}$$

(2)

The transfer integrals \(t_{ij}\) for the carbon atoms are taken to be 2.4 eV and the on-site Hubbard repulsion is \(U_{C} = 11.26\) eV. The value of orbital or site energy \(\epsilon_{i}\) at atomic site \(i\) is taken to be uniform as all atoms are carbon. We considered \(\epsilon_{i}\) to be zero for carbon atoms and can simulate the effect of D (A) substitution at any atomic position by changing the values to positive (negative) numbers, respectively. The magnitude of the D (A) strength in this model simulates the strength of D (A) substitution. Only the two molecules (b) and (d) in Figure 1 possess inherent \(D_{2h}\) symmetry. However, \(D_{2h}\) symmetry cannot be employed for the rest of the molecules in Figure 1. The PPP model Hamiltonian described above conserves the total spin. So, spin symmetry will reduce the computational effort by partitioning the singlet and triplet states. For systems possessing \(D_{2h}\) symmetry, the ground (A) and lowest dipole allowed excited states (B) are in even spin parity subspace and they are singlet. The dipole-forbidden, two-photon state 2A also has even spin parity. On the other hand, the triplet states lie in the odd parity subspace. In the case of the molecules without \(D_{2h}\) symmetry, we calculated the gs and few low-lying excited states in the singlet and triplet manifold. In any case, spin symmetry can be employed to calculate the ground and low-lying excited states in singlet and triplet subspaces separately. We employed the diagrammatic valence bond (DVB) basis as the spin adapted basis for those systems discussed.38,39 The resultant basis is nonorthogonal but linearly independent. So, the Hamiltonian matrix in this basis will be nonsymmetric. Rettpur's modification to Davidson’s algorithm was implemented to obtain the few low-lying excited states.31,32

The PPP Hamiltonian is expressed in a complete basis, so the results obtained are exact within the PPP model. Such a full CI space grows exponentially with system size. All of those molecules in Figure 1 consist of 14 carbon atoms except acenaphylene, which has 12 carbon atoms. So, it is possible to study the ground and low-lying excited states of these molecules in full CI space. The advantage of using the PPP model Hamiltonian for the above small molecules is that it can be diagonalizable in a complete full CI basis.

The gs geometries of the molecules shown in Figure 1 were optimized based on a DFT method implemented in Gaussian 09 using a B3LYP exchange-correlational functional with a 6-311g+(d,p) basis set.35,36 The optimized geometries of these CP-PAHs were used to carry out full CI calculations using a DVB basis through a model Hamiltonian approach. In addition to the full CI calculations, we also carried out TDDFT calculations to compare results from the two methodologies. The TDDFT calculations were carried out using a 6-311g+(d,p) basis with a B3LYP exchange-correlational functional.

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