

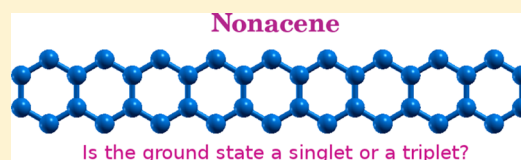
Pariser–Parr–Pople Model Based Investigation of Ground and Low-Lying Excited States of Long Acenes

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S Supporting Information

ABSTRACT: Several years ago, Angliker et al. [*Chem. Phys. Lett.* **1982**, 87, 208] predicted nonacene to be the first linear acene with the triplet state 1^3B_{2u} as the ground state, instead of the singlet 1^1A_g state. However, contrary to that prediction, in a recent experimental work, Tönshoff and Bettinger [*Angew. Chem. Int. Ed.* **2010**, 49, 4125] demonstrated that nonacene has a singlet ground state. Motivated by this experimental



finding, we decided to perform a systematic theoretical investigation of the nature of the ground and the low-lying excited states of long acenes, with an emphasis on the singlet–triplet gap, starting from naphthalene, all the way up to decacene. The methodology adopted in our work is based upon the Pariser–Parr–Pople model (PPP) Hamiltonian, along with the large-scale multireference singles–doubles configuration interaction (MRSDCI) approach. Our results predict that even though the singlet–triplet gap decreases with the increasing conjugation length, nevertheless, it remains finite till decacene, thus providing no evidence of the predicted singlet–triplet crossover. We also analyze the nature of many-particle wave function of the correlated singlet ground state and find that the longer acenes exhibit a tendency toward an open-shell singlet ground state. Moreover, when we compare the experimental absorption spectra of octacene and nonacene with their calculated singlet and triplet absorption spectra, we observe excellent agreement for the singlet case. Hence, the optical absorption results also confirm the singlet nature of the ground state for longer acenes. Calculated triplet absorption spectra of acenes predict two well-separated intense long-axis polarized absorptions, against one such peak observed for the singlet case. This is an important prediction regarding the triplet optics of acenes, which can be tested in future experiments on oriented samples.

■ INTRODUCTION

Polyacenes, which can be seen as linearly fused benzene rings, are known for their well-defined structures and crystalline forms.^{1–6} Because of their small band gaps and high charge-carrier mobilities, they find potential applications in novel optoelectronic devices such as light-emitting diodes, field effect transistors, etc., which make them experimentally and theoretically a very important class of materials.^{7,8} In spite of a long tradition of research,⁹ the field of acenes has experienced a resurgence of interest in recent years because they are also perceived as the building blocks for organic electronic materials such as graphene nanoribbons.^{7,10}

Although pentacene has excellent optical and transport properties, it is conceivable that the longer acenes could have even more attractive properties, with possible applications in the field of nanotechnology.¹⁰ As the size of the longer acenes approaches the nanometer scale, their reactivity also increases, and therefore, it has been difficult to synthesize them from heptacene onward.¹¹ Recently, many efforts have been made to synthesize the longer acenes; e.g., heptacene and its functionalized derivatives have been synthesized by several workers.^{12–16} By using a cryogenic matrix-isolation technique and a protection group strategy, Tönshoff and Bettinger¹⁷ synthesized octacene and nonacene and Kaur et al.¹⁸ prepared functionalized nonacene.

Although all the known oligoacenes ranging from naphthalene to hexacene have a singlet ground state, some years ago

Angliker et al.¹⁹ predicted nonacene to be the first linear acene with the triplet state (1^3B_{2u}) as the ground state, instead of the singlet one (1^1A_g). Their prediction was based upon (a) an extrapolation of the available experimental values of the singlet–triplet gap of the shorter acenes and (b) theoretical calculations of the triplet states (1^3B_{2u}) of acenes using the singles configuration interaction (SCI) method and the Pariser–Parr–Pople (PPP) model Hamiltonian.¹⁹ This was an interesting prediction because, if true, it could open the possibilities of magnetic applications of longer acenes. The singlet–triplet crossover in long acenes, predicted in this early work of Angliker et al.,¹⁹ was also verified by Houk et al.²⁰ on the basis of first-principles density-functional-theory (DFT) based calculations. However, subsequent theoretical investigations have predicted long acenes to have singlet ground states. They include PPP model based density-matrix renormalization group (DMRG) calculations of Raghu et al.,²¹ valence-bond theory based work of Gao et al.,²² first-principles DFT calculations of Bendikov et al.,²³ ab initio DMRG calculations of Hachmann et al.,²⁴ DFT based work of Jiang and Dai,²⁵ and first-principles coupled-cluster calculations of Hajgató et al.²⁶ Recently, on the basis of optical absorption experiments, Tönshoff and Bettinger¹⁷ demonstrated that

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nonacene has a singlet ground state, thus contradicting the prediction of Angliker et al.¹⁹ empirically. Motivated by this experimental finding, we decided to perform a systematic theoretical investigation of the electronic structure of the ground and low-lying excited states of longer acenes, with an emphasis on the singlet–triplet gap and their optical properties. To realize the possible potential of longer acenes in nanotechnology, a deep theoretical understanding of their electronic structure is very important. For our calculations, we adopt a methodology based upon the PPP model Hamiltonian, along with large-scale multireference singles–doubles configuration interaction (MRSDCI) approach.

First we benchmark our PPP-MRSDCI methodology by performing calculations of the singlet–triplet gaps of acenes ranging from naphthalene to decacene and obtain results in very good quantitative agreement with those obtained by other wave function based approaches.^{21,24,26} Next, with the aim of understanding the experiments of Tönshoff and Bettinger,¹⁷ we compute the optical absorption spectra of octacene, nonacene, and decacene, both for the singlet and for the triplet manifolds. We discover that the results of our singlet optical absorption calculations are in excellent agreement with the experimental results for octacene and nonacene,¹⁷ leading us to conclude that the ground state in nonacene is of singlet multiplicity, against the predictions of Angliker et al.¹⁹ Although the experimental results for decacene do not exist as of now, on the basis of the excellent quantitative agreement we obtain with the measured absorption spectra of octacene and nonacene; we predict that the ground state of decacene is also a singlet. Our computed optical absorption spectra for the triplet manifolds of octacene, nonacene, and decacene predict two major well-separated peaks polarized along the long axis, which can be tested in future experiments on longer acenes.

THEORY

The schematic structures of higher polyacenes studied in this work are shown in Figure 1. The molecule is assumed to lie in the *xy*-plane, with the conjugation direction taken to be along the *x*-axis. The carbon–carbon bond length has been fixed at 1.4 Å, and all bond angles have been taken to be 120°. It can be noted that these structures can also be seen as two polyene chains of suitable lengths, coupled together along the *y*-

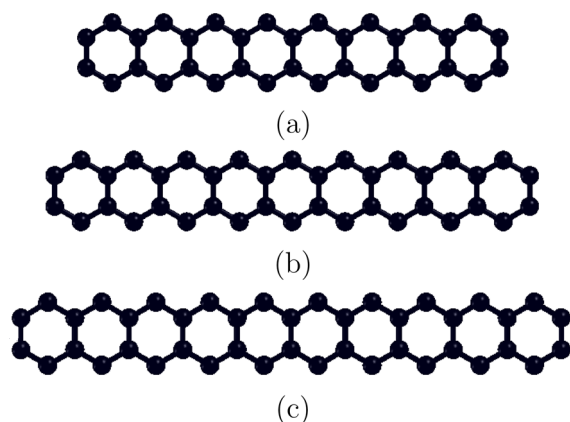


Figure 1. Schematic drawings of long acenes considered in this work: (a) octacene, (b) nonacene, and (c) decacene. The *x* axis is assumed along the conjugation direction, and the *y* axis is perpendicular to it, in the plane of the figure.

direction. The reason for choosing this symmetric geometry, against various other possibilities has already been discussed in our earlier paper.^{27,28} However, in the Supporting Information, we do consider an alternate geometry with nonuniform bond lengths²³ and demonstrate that it leads to small quantitative changes in the optical absorption spectrum, compared to the results obtained using the uniform bond length. Thus, we conclude that small differences in the ground state geometry lead to insignificant changes in the optical absorption spectra of oligo acenes.

The correlated calculations are performed using the PPP model Hamiltonian, which can be written as

$$H = H_{C_1} + H_{C_2} + H_{C_1C_2} + H_{ee}$$

where H_{C_1} and H_{C_2} are the one-electron Hamiltonians for the carbon atoms located on the upper and the lower polyene like chains, respectively. $H_{C_1C_2}$ is the one-electron hopping between the two chains, and H_{ee} depicts the electron–electron repulsion. The individual terms can now be written as

$$H_{C_1} = -t_0 \sum_{\langle k,k' \rangle} B_{k,k'}$$

$$H_{C_2} = -t_0 \sum_{\langle \mu,\nu \rangle} B_{\mu,\nu}$$

$$H_{C_1C_2} = -t_{\perp} \sum_{\langle k,\mu \rangle} B_{k,\mu}$$

$$H_{ee} = U \sum_i n_{i\uparrow} n_{i\downarrow} + \frac{1}{2} \sum_{i \neq j} V_{ij} (n_i - 1)(n_j - 1)$$

In the equation above, k and k' are carbon atoms on the upper polyene chain, μ and ν are carbon atoms located on the lower polyene chain, and i and j represent all the atoms of the oligomer. Symbol $\langle \dots \rangle$ implies nearest neighbors, and $B_{ij} = \sum_{\sigma} (c_{i\sigma}^{\dagger} c_{j\sigma} + \text{h.c.})$, where $c_{i\sigma}^{\dagger} (c_{i\sigma})$ denotes the creation (annihilation) operator for a π orbital of spin σ , located on the i th carbon atom. Matrix elements t_0 and t_{\perp} depict one-electron hops. As far as the values of the hopping matrix elements are concerned, we took $t_0 = 2.4$ eV for all nearest neighbor hopping with $t_{\perp} = t_0$, consistent with the undimerized ground state for polyacene argued by Raghu et al.²⁹

The Coulomb interactions are parametrized according to the Ohno relationship,³⁰

$$V_{ij} = U / \kappa_{ij} (1 + 0.6117 R_{ij}^{-2})^{1/2}$$

where κ_{ij} depicts the dielectric constant of the system which can simulate the effects of screening, U is the on-site repulsion term, and R_{ij} is the distance in Å between the i th and the j th carbon atoms. In the present work, we have performed calculations using “standard parameters”³⁰ with $U = 11.13$ eV and $\kappa_{ij} = 1.0$, as well as “screened parameters”³¹ with $U = 8.0$ eV and $\kappa_{ij} = 2.0$ ($i \neq j$) and $\kappa_{ii} = 1.0$. The screened parameters employed here were devised by Chandross and Mazumdar³¹ with the aim of accounting for the interchain screening effects in phenylene based polymers. However, in the present case, we compare our results of singlet and triplet absorption spectra of octacene and nonacene with the experimental spectra measured by Bettinger and co-workers,¹⁷ with the oligomers located inside the argon matrix. Therefore, here the purpose of screened parameters is to physically model the screening due to the argon matrix.

The starting point of the correlated calculations for the molecules is the restricted Hartree–Fock (RHF) calculations, employing the PPP Hamiltonian, using a code developed in our

group.³² All the resultant HF molecular orbitals are treated as active orbitals. The single-reference CI calculations such as the full/quadruple configuration interaction (FCI/QCI) were employed for shorter acenes, whereas the multireference singles doubles configuration interaction (MRSDCI) method was used for the longer ones. In particular, the FCI method was used for naphthalene and anthracene, the QCI method was employed for the 1^1A_g and 1^3B_{2u} symmetries of tetracene and pentacene, whereas for all other cases MRSDCI calculations were performed. The MRSDCI method is a well-established approach for including electron-correlation effects beyond the mean field both for the ground and for the excited states of molecular systems.^{33,34} We have used this approach extensively within the PPP model to study the optical properties of a number of conjugated polymers,^{35–38} and it can be briefly summarized as follows. After the RHF calculations of the ground state 1^1A_g , the CI calculations of the ground state 1^1A_g and the excited states of symmetries 1^3B_{2u} and 1^3B_{3u} are performed by taking the lowest energy configuration of the corresponding symmetry. They are $H \rightarrow L$ for B_{2u} and $H \rightarrow L+m$ and $H-m \rightarrow L$ (where $m > 0$ is an integer whose value depends on the length of the oligomer) for B_{3u} where H and L correspond to Highest Occupied Molecular Orbital (HOMO) and Lowest Unoccupied Molecular Orbital (LUMO), respectively. A similar approach is adopted for the triplet states as well, except that one has to ensure that the spin multiplicity of the wave functions is triplet. From the CI calculations, we obtain the eigenfunctions and eigenvalues corresponding to the correlated ground and excited states of the examined molecules. Using these eigenfunctions, the dipole matrix elements between the ground state and various excited states are computed. For the triplet states, the matrix elements are calculated with respect to the lowest triplet state 1^3B_{2u} . These dipole matrix elements, along with the energies of the excited states are, in turn, utilized to calculate the linear (or triplet) optical absorption spectrum. Important excited states contributing to various peaks of the spectrum are identified, and a new set of MRSDCI calculations are performed with an increased number of reference configurations contributed both to the ground state and to the excited states, leading to a new absorption spectrum. This procedure is iterated until the computed spectrum converges satisfactorily.

RESULTS AND DISCUSSIONS

In this section we present the results of our CI calculations on polyacenes ranging from naphthalene to decacene examining their singlet–triplet gaps, with the aim of determining the spin-multiplicity of their ground state. Furthermore, we also present MRSDCI calculations on the optical absorption of the long acenes, namely, octacene to decacene, from their lowest triplet states (1^3B_{2u}) and the lowest-singlet state (1^1A_g) and compare the results with the experimental ones, where available.

Singlet–Triplet Gap. We performed the first set of calculations to explore the singlet–triplet (1^1A_g – 1^3B_{2u}) gap in oligoacenes using the singles-configuration-interaction (SCI) method. The values of the singlet–triplet gap $\Delta E_{ST} = E(1^3B_{2u}) - E(1^1A_g)$ obtained from these calculations for oligoacenes up to acene-15 (acene- n denotes an oligomer with n benzene rings) are presented in Table 1. Examining the values of the singlet–triplet gap for various oligomers, it is obvious that (a) in the standard-parameter based calculations, the triplet state is never lower than the singlet one, whereas (b) with the screened parameters, the singlet and the triplet states become nearly

Table 1. Singlet–Triplet Gap ($\Delta E_{ST} = E(1^3B_{2u}) - E(1^1A_g)$) of Acene- n , Computed Using the SCI Method and the Standard (std) and Screened (scr) Coulomb Parameters

n	ΔE_{ST} (eV)	
	std	scr
2	2.66	2.07
3	1.63	1.16
4	1.04	0.63
5	0.68	0.32
6	0.42	0.12
7	0.34	0.00
8	0.26	−0.06
9	0.23	−0.10
10	0.24	−0.11
11	0.26	−0.12
15	0.41	−0.06

degenerate for acene-7, and the crossover takes place starting with acene-8. In both sets of calculations, ΔE_{ST} first decreases with increasing n and, subsequently, begins to increase, suggesting the inadequacy of the SCI method for longer acenes. Nevertheless, our screened-parameter based SCI results appear to confirm the essential prediction of Anglikier et al.¹⁹ that the singlet–triplet crossover will take place in oligoacenes with increasing lengths, although they differ in detail because Anglikier et al.¹⁹ predicted the crossover from acene-9 onward. Although Anglikier et al.¹⁹ also used the PPP-SCI approach for their calculations, they used a smaller value of the nearest-neighbor hopping matrix element $t = -2.318$ eV, and a Mataga–Nishimoto³⁹ type Coulomb parametrization $V_{ij} = 1439.5/(132.8 + R_{ij})$, which corresponds to an effective value of $U = 10.84$ eV. It is obvious that the results of our SCI-PPP calculations differ from those of Anglikier et al.¹⁹ because of different values of parameters employed. Furthermore, another calculation, performed by Houk et al.,²⁰ also predicted the singlet–triplet crossover in oligoacenes. However, ab initio DFT²⁰ can be unreliable for treating multireference correlation effects, which are important in the excited states of conjugated systems. On the basis of past calculations performed on other polymers such as *trans*-polyacetylene,⁴⁰ it is a well-known fact that to be able to predict the correct excited state orderings in conjugated polymers, it is very important to account for the electron-correlation effects in an accurate manner. Therefore, we decided to go beyond the SCI approach and performed large-scale CI calculations to explore the singlet–triplet ordering in polyacenes. Before we present and discuss our results, we give a flavor to the reader as to the size of the CI calculations performed. Table 2 presents the number of reference states used in the MRSDCI calculations, and the total size of the resultant CI matrix. As mentioned in the previous section, the number of references (N_{ref}) used in various MRSDCI calculations was increased until acceptable convergence was achieved. For example, the convergence of the excitation energies of $1^1B_{2u}^+$ and $1^3B_{2u}^+$ states of nonacene with respect to N_{ref} computed using the screened parameters, has been demonstrated explicitly in the Supporting Information.

The calculated values of the singlet–triplet gap are presented in Table 3, using both the standard and the screened parameters, for the oligoacenes ranging from naphthalene to decacene. The variation of the calculated values of the singlet–triplet gap and their comparison with the experimental and other theoretical calculations, for the oligoacenes ranging from

Table 2. Number of Reference Configurations (N_{ref}) and the Total Number of Configurations (N_{total}) Involved in the MRSDCI (or FCI or QCI, Where Indicated) Calculations, for Different Symmetry Subspaces of Various Oligoacenes

n	1A_g		$^1B_{2u}$		$^3B_{2u}$	
	N_{ref}	N_{total}	N_{ref}	N_{total}	N_{ref}	N_{total}
2	1 ^a	4936 ^a	1 ^a	4794 ^a	1 ^a	4816 ^a
3	1 ^a	623576 ^a	1 ^a	618478 ^a	1 ^a	620928 ^a
4	1 ^b	193538 ^b	1 ^b	335325 ^b	100 ^c	323063 ^c
					86 ^d	319005 ^d
5	1 ^b	1002597 ^b	1 ^b	1707243 ^b	52 ^{c,d}	581702 ^{c,d}
6	100 ^c	1110147 ^c	100 ^c	1173212 ^c	65 ^c	1461526 ^c
	100 ^d	1177189 ^d	100 ^d	1328252 ^d	63 ^d	1551590 ^d
7	35 ^c	856788 ^c	30 ^c	674925 ^c	33 ^c	1369624 ^c
	22 ^d	615590 ^d	30 ^d	850627 ^d	29 ^d	1300948 ^d
8	18 ^c	768641 ^c	14 ^c	509119 ^c	19 ^c	1066355 ^c
	12 ^d	540651 ^d	4 ^d	145978 ^d	14 ^d	918645 ^d
9	13 ^c	959737 ^c	13 ^c	769387 ^c	18 ^c	1626229 ^c
	12 ^d	871397 ^d	3 ^d	186651 ^d	12 ^d	1152071 ^d
10	11 ^c	1202681 ^c	12 ^c	1192394 ^c	15 ^c	1735352 ^c
	11 ^d	1199887 ^d	3 ^d	270187 ^d	10 ^d	1318156 ^d

^aFCI method with standard as well as screened parameters. ^bQCI method with standard as well as screened parameters. ^cUsing standard parameters. ^dUsing screened parameters.

Table 3. For Various Oligomers, the Singlet–Triplet Gaps ($\Delta E_{\text{ST}} = E(^1B_{2u}) - E(^1A_g)$) Obtained from Large-Scale CI Calculations (cf. Table 2), Employing the PPP Model Hamiltonian and the Standard (std) and Screened (scr) Parameters

n	ΔE_{ST} (eV)	
	std	scr
2	2.53	2.11
3	1.73	1.48
4	1.25	1.11
5	0.99	0.93
6	0.87	0.85
7	0.73	0.69
8	0.68	0.58
9	0.60	0.56
10	0.57	0.54

naphthalene to decacene, as a function of the oligomer length is presented in Figure 2. It is obvious from the figure that the excitation energy of the $^1B_{2u}$ state decreases as the oligomer length increases. Nevertheless, even for decacene the singlet–triplet gap is nonvanishing and appears to saturate as a function of the increasing chain length. As far as comparison with the work of other authors is concerned, we observe the following trends in Figure 2: (a) Our standard-parameter results are in good quantitative agreement with most other works, (b) in particular, our standard-parameter results are in excellent agreement with the PPP-DMRG results of Raghu et al.,²¹ and also in very good agreement with the ab initio DMRG results of Hachmann et al.,²⁴ further vindicating our MRSDCI approach, and (c) our screened-parameter results predict smaller values of the singlet–triplet gap as compared to other wave function based approaches for the shorter acenes, but for longer ones, they are also in good agreement with other results. However, DFT based UB3LYP calculations performed by Bendikov et al.²³ agree with other works for shorter acenes, but for longer

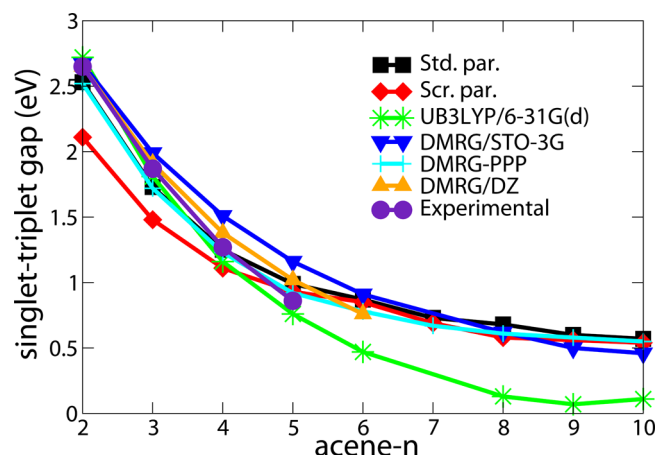


Figure 2. Singlet–triplet energy gap as a function of the acene lengths.

ones, they predict much smaller singlet–triplet gaps. We believe that these smaller gaps obtained in the work of Bendikov et al.,²³ could be attributed to the well-known tendency of DFT to underestimate the energy gaps. Therefore, on the basis of the fact that for decacene our calculations predict a singlet–triplet gap >0.5 eV, we conclude that even for longer acenes, the singlet state 1A_g will be the ground state, and thus no singlet–triplet crossover of the kind predicted by Anglikar et al.,¹⁹ occurs as per our calculations, and in agreement with all other works except that of Houk et al.²⁰ Recently, Hajgato et al.²⁶ performed first principles coupled cluster CCSD(T) calculations on the singlet–triplet gaps of acenes ranging from octacene to undecacene (acene-11), and their reported value of 0.58 eV for octacene is in almost perfect agreement with our PPP-MRSDCI results (cf. Table 3). However, for nonacene and decacene their reported values 0.46 and 0.35 eV,²⁶ respectively, are smaller than both our standard and screened-parameter values (cf. Table 3). Regarding the singlet–triplet gap in the polyacene limit ($n \rightarrow \infty$), DMRG-PPP work of Raghu et al.²¹ predicted it to be 0.53 eV, whereas Gao et al.,²² using a spin Hamiltonian, estimated it to be 0.446 eV, both of which are reasonably close to our standard/screened-parameters values of 0.57/0.54 eV, computed for decacene.

Bendikov et al.²³ noted that the restricted singlet density functional ground state of higher acenes would become unstable due to its open-shell nature, with two unpaired electrons (a singlet diradical⁴¹) for acenes longer than hexacene. On the basis of ab initio DMRG calculations on acenes in the range $n = 2$ –12, Hachmann et al.²⁴ concluded that the ground state wave functions for longer acenes were of the type of polyradical singlets. In another DFT work, Jiang and Dai²⁵ predicted the ground state of octacene and higher acenes to be antiferromagnetic (in other words, open-shell singlet), but not necessarily a diradical. Unlike the DFT calculations, in our approach, the many-body wave functions of the ground state and the excited states of the studied oligomers were available. Therefore, we decided to probe the nature of the ground state of longer acenes to ascertain whether they exhibit a polyradical character. The character of the many-body wave functions of the 1A_g ground state, obtained in our best CI calculations on oligomers ranging from naphthalene to decacene are presented in Table 4, for both the standard and the screened parameters. From the results it is obvious that the singlet ground state of longer acenes begins to exhibit significant configuration mixing.

Table 4. Magnitudes of the Coefficients of the Closed Shell (CS) Doubly Excited Virtual Configuration $|H \rightarrow L; H \rightarrow L\rangle$ and the Open Shell (OS) Doubly Excited Virtual Configuration $|H \rightarrow L; H - 1 \rightarrow L + 1\rangle$ to the Singlet 1^1A_g Ground State CI Wave Functions of Acene- n , Obtained Using the Standard (std) and the Screened (scr) Parameters in the PPP Model^a

n	CS		OS	
	std	scr	std	scr
2	0.114	0.143	0.145	0.126
3	0.148	0.168	0.132	0.109
4	0.173	0.179	0.119	0.134
5	0.191	0.186	0.134	0.140
6	0.198	0.184	0.144	0.142
7	0.234	0.269	0.168	0.188
8	0.246	0.289	0.186	0.202
9	0.263	0.294	0.194	0.211
10	0.266	0.297	0.203	0.218

^aH stands for the highest occupied molecular orbital (HOMO), and L stands for lowest unoccupied molecular orbital (LUMO).

With the increasing oligomer lengths, the contributions of several doubly excited configurations to the ground state wave function increase. Thus, on the basis of these results, we conclude that the longer acenes studied in this work exhibit a tendency toward a singlet ground state, with a significant diradical open-shell character.

Singlet Linear Optical Absorption Calculations. In an earlier work in our group, we had reported the calculations of linear optical absorption spectra of oligoacenes ranging from naphthalene to heptacene.²⁷ In this work, we extend our calculations to longer acenes, and present the calculations of linear optical absorption in octacene, nonacene and decacene. In Figures 4–6, we present the singlet linear absorption spectra

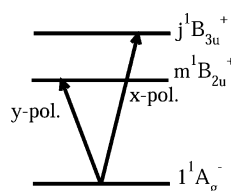


Figure 3. Diagram of the essential states involved in the singlet linear optical absorption in oligoacenes and their polarization characteristics. The arrows connecting two states imply optical absorption, with polarization directions stated next to them. The location of states is not up to scale.

of these oligoacenes from their $1^1A_g^-$ singlet state computed using the standard parameters and the screened parameters. As per dipole selection rules for the D_{2h} symmetry, allowed one-photon transitions from the $1^1A_g^-$ state occur to $1^1B_{2u}^+$ ($1^1B_{3u}^+$) type states via short-axis (long-axis) polarized photons, where we assume that the short (long) axis corresponds to the y (x) direction. The essential states contributing to the linear absorption spectra of various acenes are depicted in Figure 3. The many-particle wave functions of the excited states contributing to various peaks in the spectra are presented in Tables 1–6 of the Supporting Information. While plotting the absorption spectra, we have restricted ourselves to states which lie below 6 eV, the estimated value of the ionization potentials of the long acenes.⁴²

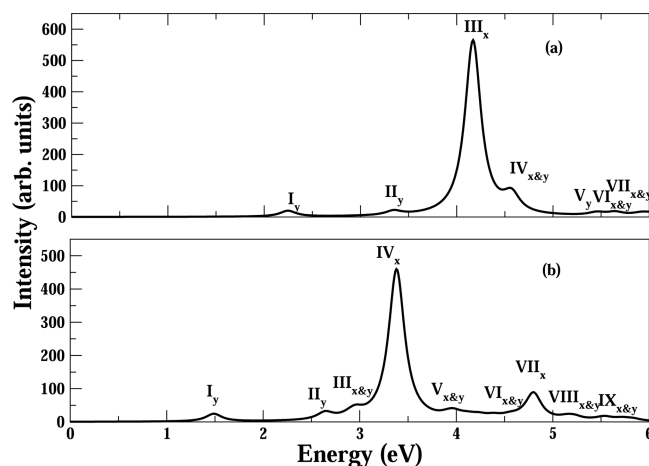


Figure 4. Singlet linear absorption spectra of octacene computed using (a) standard parameters and (b) screened parameters. A uniform line width of 0.1 eV was assumed while plotting the spectra. The subscripts attached to the peak labels indicate the polarization directions x and y .

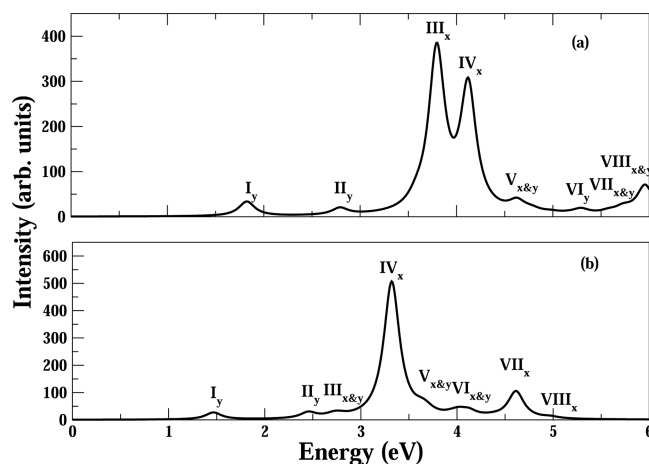


Figure 5. Singlet linear absorption spectra of nonacene computed using (a) standard parameters and (b) screened parameters. The rest of the information is the same as in the caption of Figure 4.

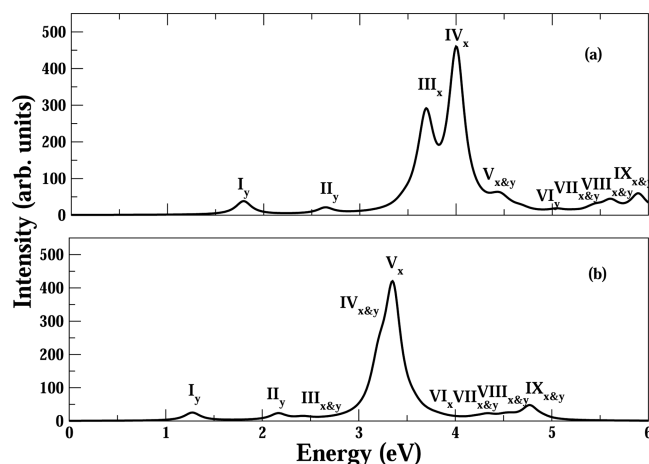


Figure 6. Singlet linear absorption spectra of decacene computed using (a) standard parameters and (b) screened parameters. The rest of the information is the same as in the caption of Figure 4.

A peak-by-peak detailed description of the computed singlet absorption spectra is provided in the Supporting Information.

Here we list the salient features of the calculated linear optical absorption of octacene, nonacene, and decacene:

1. Quantitatively speaking, screened-parameter spectra are red-shifted as compared to the standard-parameter ones.
2. Most of the intensity is concentrated in the x -polarized (long-axis polarized) spectra originating from the absorption into the $1^1B_{3u}^+$ type of states, whereas the y -polarized (short-axis polarized) absorption into the $1^1B_{2u}^+$ type states is comparatively weak. However, a closer examination reveals that most of the intensity in the x -polarized spectrum is derived from the single transition to an $n^1B_{3u}^+$ state (or states that split away from it). If we ignore this transition, then the short- and long-axis polarized spectra are of comparable intensity. This aspect of the singlet linear absorption spectrum of long acenes is consistent with what is also observed in the shorter acenes.²⁷
3. The first peak corresponds to the y -polarized transition, to the $1^1B_{2u}^+$ excited state of the system. The most important configuration contributing to the many-particle wave function of the state corresponds to $|H \rightarrow L\rangle$ excitation, irrespective of the choice of the Coulomb parameters employed in the PPP model.
4. We have observed that the most intense absorption for the oligoacenes is through an x -polarized photon to a $1^1B_{3u}^+$ state, irrespective of the Coulomb parameters employed in the calculations. For acene- n , the many-particle wave function of this state exhibits the following general features: (a) for the standard-parameter case, single excitations $|H \rightarrow L + n/2 - 1\rangle + c.c.$, for $n \equiv \text{even}$, and $|H \rightarrow L + (n - 1)/2\rangle + c.c.$, for $n \equiv \text{odd}$, dominate the wave function, whereas (b) with screened parameters the dominant configurations are single excitations $|H \rightarrow L + n/2\rangle + c.c.$ for $n \equiv \text{even}$, and $|H \rightarrow L + (n - 1)/2\rangle + c.c.$ for $n \equiv \text{odd}$. The aforesaid difference between the standard and the screened parameters is because of different energetic ordering of the symmetries of the molecular orbitals for the standard and screened parameters.

Triplet Optical Absorption Calculations. In optical absorption experiments, one can probe the triplet excited states because frequently the first singlet excited state S_1 ($1^1B_{2u}^+$ in the present case) decays to the first triplet excited state T_1 ($1^3B_{2u}^+$ in the present case) located below S_1 , through nonradiative intersystem crossing (ISC), as shown in Figure 7. Once the system reaches the triplet manifold, normal optical absorption experiments can be performed to probe higher triplet states. In the present work, we restrict ourselves to the triplet one-photon absorption spectra of octacene, nonacene, and decacene from their $1^3B_{2u}^+$ state, computed using the MRSDCI method. For the case of oligoacenes, as per electric-dipole selection rules of the D_{2h} point group, the long-axis (x -axis) polarized photons cause transitions from the $1^3B_{2u}^+$ to $3^1B_{1g}^-$ type of states, whereas the short-axis (y -axis) polarized ones lead to the $3^1A_g^-$ type states (cf. Figure 7). The calculated triplet absorption spectra of these oligoacenes are displayed in Figures 8–10, whereas the wave functions of the excited states contributing to various peaks in the spectra are presented in Tables 7–12 of the Supporting Information. While plotting the triplet absorption spectra, we have been careful to include only those states that lie below 6 eV excitation energy (with respect to the $1^1A_g^-$ state), which is the estimated value of the ionization

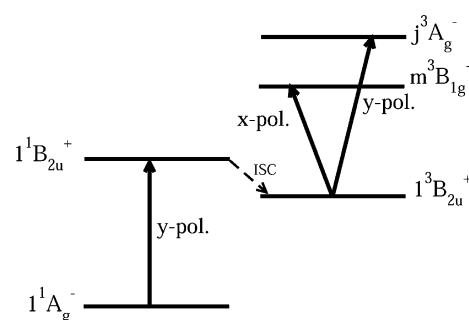


Figure 7. Diagram of the essential states involved in the triplet absorption spectra of oligoacenes and their polarization characteristics. The arrows connecting two states imply optical absorption, with polarization directions stated next to them. The location of states is not up to scale. ISC refers to intersystem crossing.

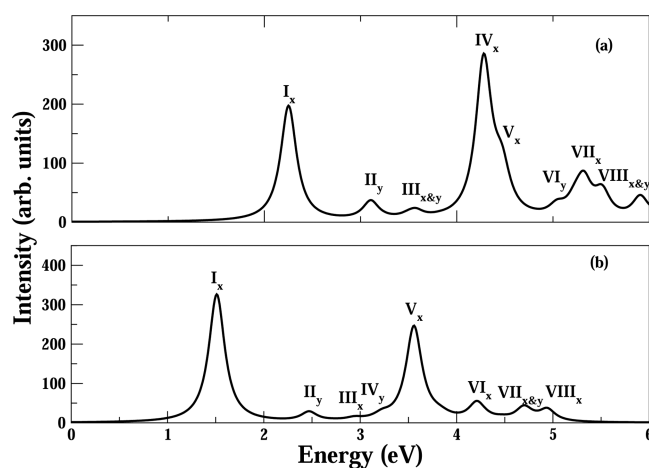


Figure 8. Triplet absorption spectra of octacene from the $1^3B_{2u}^+$ state computed using (a) standard parameters and (b) screened parameters. A uniform line width of 0.1 eV was assumed while plotting the spectra. The subscripts attached to the peak labels indicate the polarization directions x and y .

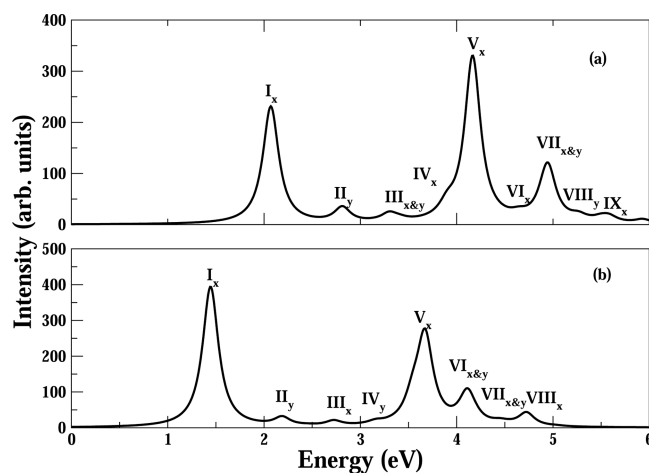


Figure 9. Triplet absorption spectra of nonacene from the $1^3B_{2u}^+$ state computed using (a) standard parameters and (b) screened parameters. The rest of the information is the same as in the caption of Figure 8.

potentials of the long acenes.⁴² A detailed description of the characteristics of various peaks in the calculated triplet absorption spectra of octacene, nonacene, and decacene, is

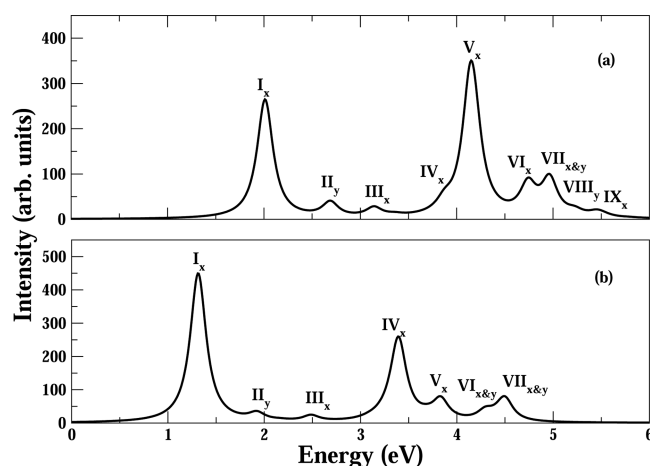


Figure 10. Triplet absorption spectra of decacene from the $1^3B_{2u}^+$ state computed using (a) the standard parameters and (b) the screened parameters. The rest of the information is the same as in the caption of Figure 8.

presented in the Supporting Information. Below we discuss the salient features of our results:

1. Similar to the case of singlet absorption, screened-parameter spectra are red-shifted as compared to the standard-parameter ones.
2. Most of the intensity is concentrated in the x -polarized (long-axis polarized) spectra corresponding to the absorption into the $^3B_{1g}^-$ type of states, whereas the y -polarized absorption into the $^3A_g^-$ type states is very faint.
3. From Figures 8–10 it is obvious that the triplet absorption spectrum is dominated by two intense x -polarized peaks that are well separated in energy (>2 eV), irrespective of the oligoacene in question, or the Coulomb parameters employed in the calculations. The first of these peaks is peak I in all the cases, whereas the second one is either peak IV or V, depending upon the oligoacene, or the Coulomb parameters employed. In the standard-parameter based calculations, peak I is always the second most intense peak, whereas the second of these peaks (IV or V) is the most intense. In the screened-parameter calculations, the situation is exactly the reverse, with peak I being the most intense and peak IV or V being the second most intense peak of the spectrum. Peak I always corresponds to the $^3B_{1g}^-$ excited state of the system, whose wave function is dominated by the single excitations $|H \rightarrow L + 1\rangle + \text{c.c.}$, irrespective of the oligoacene in question or the choice of Coulomb parameters. The second intense peak (IV or V) corresponds to a higher $^3B_{1g}^-$ type state of acene- n , whose wave function mainly consists of (a) for the standard parameters, double excitations $|H \rightarrow L; H - (n/2 - 1) \rightarrow L\rangle + \text{c.c.}$, for $n \equiv \text{even}$, and $|H \rightarrow L; H - (n - 1)/2 \rightarrow L\rangle + \text{c.c.}$, for $n \equiv \text{odd}$, and (b) for the screened parameters, double excitations $|H \rightarrow L; H - n/2 \rightarrow L\rangle + \text{c.c.}$, for $n \equiv \text{even}$, and $|H \rightarrow L; H - (n - 1)/2 \rightarrow L\rangle + \text{c.c.}$, for $n \equiv \text{odd}$. This difference between the standard and the screened-parameter results is because of the different energetic ordering of the molecular orbital symmetries in longer acenes, for the two sets of Coulomb parameters.
4. Other peaks in the spectrum correspond to either x or y polarized transitions to the higher excited states of the

system, which are described in detail in the Supporting Information.

Comparison of Singlet and Triplet Absorption Calculations of Octacene and Nonacene with the Experimental Results. In Table 5, the results of the

Table 5. Experimental Values of the Energies, Relative Intensities, and Tentative Assignments of the UV/Vis Electronic Absorptions of (a) Octacene and (b) Nonacene¹⁷

	E (eV)	I (rel)	electronic state
(a)	1.54	0.025	S_1
	1.69	0.011	
	1.73	0.016	
	1.86	0.007	
	2.40	0.02	S_2
	2.54	0.05	S_3
	2.72	0.05	
	3.16	0.08	S_4
	3.29	0.49	S_5
	3.33	0.43	
	3.48	0.46	S_6
	3.68	0.90	S_7
	3.78	1.00	
(b)	1.43	0.020	S_1
	1.58	0.006	
	1.62	0.016	
	2.33	0.033	S_3
	2.50	0.023	S_4
	2.67	0.030	S_5
	2.80	0.048	S_6
	2.97	0.19	S_7
	3.14	0.52	
	3.42	0.14	S_8
	3.66	1.00	S_9

experimental absorption of octacene and nonacene, reported by Tönshoff and Bettinger,¹⁷ have been presented, showing the excitation energies, relative intensities, and tentative assignments of the UV/vis electronic absorptions. Next, we compare our computed singlet and triplet absorption results with the experimental ones, in terms of the peak energies (in eV) and relative intensities/oscillator strength. The relative oscillator strength (ROS) in the computed absorption spectra is the ratio of the calculated oscillator strength of a given state, with respect to that of the most intense state. The relative oscillator strengths of the peaks in the calculated absorption spectra are compared with the reported relative intensities (RI) of the corresponding peaks in the experimental spectra.

Octacene. When the experimental values of the energies of the absorption peak of octacene from the Table 5a are compared with our calculated values for the singlet case (Tables 1 and 2, Supporting Information), the lowest state S_1 (1.54–1.86 eV, RI = 0.025 for the 1.54 eV) of the experimental results matches nicely with the first peak at 1.49 eV (ROS = 0.050) obtained in the screened-parameter calculations. We note that the first peak of our standard-parameter calculations is located at 2.24 eV and is thus significantly higher than the experimental value. The second state of the experimental results S_2 (2.40 eV, RI = 0.02) again agrees much better with the screened-parameter result, 2.65 eV (ROS = 0.047) than with the standard-parameter one located at 3.34 eV. The third state of the experimental results, S_3 (2.54 eV, RI = 0.050) has a better

agreement with the third state of the screened-parameter spectrum 2.97 eV (ROS = 0.046), than with corresponding standard-parameter peak at 4.17 eV. The most intense peak in the experimental results, corresponding to S_7 (3.68–3.78 eV, RI = 1.0), lies between the highest peak of the screened and standard-parameter calculations located at 3.38 eV (ROS = 1.0) and 4.17 eV (ROS = 1.0), respectively. We note that with the increasing peak energy, the agreement between the experiments and theory begins to deteriorate. Nevertheless, even in the worst case scenario of the most intense peak (S_7 of the experiments), the disagreement between the screened-parameter results and the experiments is below 10%, as far as the peak location is concerned. This disagreement, which is fairly acceptable from a quantitative aspect, is possibly due to the reduced computational accuracy of our approach because of the high energies of the states involved. As far as the comparison of the experimental results with the triplet absorption calculations (Tables 7 and 8, Supporting Information) is concerned, the first peaks in the computed triplet spectra, 3.04 eV (ROS = 0.839) for the standard parameter and 1.97 eV (ROS = 1.0) for the screened parameters, disagree completely with the location of S_1 , as well as its relative intensity in the experimental spectrum. The same trend holds for the higher excited states as well. Thus, we conclude that the experimental absorption spectrum of octacene is indeed from the $1^1A_g^-$ ground state of the system, confirming yet again that the ground state of octacene has the singlet multiplicity.

We also note that Raghu et al.²¹ predicted a very large optical gap of 2.60 eV for octacene, on the basis of their DMRG calculations, employing the PPP Hamiltonian.

Nonacene. Similarly, when the experimental values of the energies of the absorption peak of nonacene from the Table 5b are compared with our calculated values for the singlet case (Tables 3 and 4, Supporting Information), the lowest state S_1 (1.43–1.62 eV, RI = 0.020 for 1.43 eV) of the experimental results matches better with the first peak of 1.46 eV (ROS = 0.051) obtained in the screened-parameter calculations than with the corresponding one for the standard-parameter case located at 1.82 eV. The second state of the experimental results, S_3 (2.33 eV, RI = 0.033), again agrees much better with the second peak of the screened-parameter result, 2.45 eV (ROS = 0.043), than with the standard-parameter one located at 2.79 eV. The third state of the experimental results, S_4 (2.50 eV, RI = 0.023), has a better agreement with the third state of the screened-parameter spectrum, 2.71 eV (ROS = 0.020), than with the corresponding standard-parameter peak at 3.80 eV. The most intense peak in the experimental results, S_9 (3.66 eV, RI = 1.0), lies between the highest peak of the screened and standard-parameter calculations located at 3.32 eV (ROS = 1.0) and 3.80 eV (ROS = 1.0), respectively. For this most intense peak, the standard-parameter results appear to agree slightly better with the experiments, as compared to the screened ones. But, keeping in mind the lower energy peaks discussed above, overall the screened-parameter based results have a much better agreement with the experiments, just as in case of octacene. Similar to the case with octacene, we again note that with the increasing peak energy, the agreement between the experiments and theory begins to deteriorate, which we again attribute to the reduced computational accuracy for higher energies. As far as the comparison of the experimental results with the triplet absorption calculations (Tables 9 and 10, Supporting Information) is concerned, the first peaks in the computed triplet spectra, 2.56 eV (ROS = 0.785) for the standard

parameter and 1.86 eV (ROS = 1.0) for the screened parameters, disagree completely with the location of S_1 , as well as its relative intensity in the experimental spectrum. The same trend holds for the higher excited states as well. Thus, we conclude that the experimental absorption spectrum of nonacene is indeed from the $1^1A_g^-$ ground state of the system, confirming yet again that the ground state of nonacene has the singlet multiplicity. Again, we note that the DMRG based calculations employing the PPP model, performed by Raghu et al.²¹ predict an unrealistically large optical gap of 2.59 eV for nonacene. Our values of the calculated optical gaps of octacene, nonacene, and decacene are in very good agreement with the estimated optical gap of polyacene 1.18 ± 0.06 eV, reported by Tönshoff and Bettinger.¹⁷

To conclude, the experimentalists are confident that the absorptions which they observed are all from the ground states of octacene and nonacene. Because our singlet absorption spectra (as against the triplet absorption) computed using the screened parameters are in excellent agreement with those experiments, we conclude that the ground states of octacene and nonacene are of singlet multiplicity (1^1A_g), in perfect agreement with our singlet–triplet crossover calculations. Although the experiments have not been performed on acenes longer than nonacene, the trend emerging from our calculations leads us to conclude that the ground state will be of singlet type in those systems as well.

CONCLUSIONS

To summarize, we presented large-scale MRSDCI calculations on the electronic structure and optical properties of oligoacenes, with focus on the longer acenes, namely, octacene, nonacene, and decacene. By performing such calculations on the lowest singlet and triplet states of oligomers ranging from naphthalene up to decacene, we established that the ground state in oligoacenes has singlet multiplicity, with a singlet–triplet gap of approximately 0.5 eV even for decacene. The trends visible from our calculations rule out a singlet–triplet crossover for the ground states of longer oligoacenes as well. This result of ours has thus resolved an old speculation predicting that nonacene onward, the ground state of oligoacenes will be of triplet multiplicity.¹⁹

Moreover, the many-body wave function analysis of the correlated singlet ground state $1^1A_g^-$ reveals increasing contribution of configurations with two open shells, accompanied with the decreasing one from the closed-shell Hartree–Fock reference state, with the increasing chain length. Thus our calculations predict an open-shell diradical character for the singlet ground state of longer acenes.²³

As far as the singlet linear optical absorption is concerned, in all the acenes, the first peak is due to a y -polarized transition to the $1^1B_{2u}^+$ state, corresponding to the HOMO to LUMO transition. The most intense state is the x -polarized transition to a $1^1B_{3u}^+$ state, which is also dominated by single excitations. When we compare our singlet linear absorption spectra of octacene and nonacene with the experimental ones,¹⁷ excellent agreement is obtained on the important peak locations and intensity profiles. Furthermore, the measured absorption spectra of longer acenes show no resemblance with our computed triplet absorption spectra, confirming once again the conclusion that the ground state of the longer acenes is indeed singlet in nature.

Our calculations on the one-photon triplet absorption spectra predict two intense x -polarized absorptions, which are

well separated in energy. Besides these two, there are a number of weaker peaks that are either x - or y -polarized. This is in sharp contrast to the singlet absorption that predicts only one intense peak. The existence of two well-separated x -polarized peaks in the triplet absorption spectrum is one of the most important predictions of this work and can be tested in future experiments on oriented samples of longer acenes.

We also performed singlet and triplet optical absorption calculations on decacene, a molecule that has not been synthesized yet. We are hopeful that in the future, once decacene is synthesized in the laboratory, our theoretical predictions could be tested in experiments.

In this paper we restricted ourselves to the low-lying excited states of longer acenes that contribute to their linear optical properties. However, not many calculations have been performed as far as the nonlinear optical properties of these materials are concerned. In particular, it will be of interest to compute the nonlinear susceptibilities corresponding to two-photon absorption, and third harmonic generation. Both these nonlinear optical processes have the capability to probe the higher excited states of polyacenes, which is essential to obtain a deeper understanding of the optical response of π electrons. At present, studies along these directions are underway in our group.

■ ASSOCIATED CONTENT

■ Supporting Information

Discussion of convergence of excitation energies in MRSDCI calculations (including a figure showing the convergence of excited states of nonacene), influence of the geometry on the optical absorption in long acenes (including a figure showing calculated absorption spectra for nonacene), singlet linear absorption (including tables of excited states contributing to the absorption spectra of long acenes), and triplet absorption (including tables of excited states contributing to the absorption spectra of long acenes). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

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