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Open-Shell Ground State of Polyacenes: A Valence Bond Study

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Applying the density matrix renormalization group (DRMG) method to a nonempirical valence bond (VB) model Hamiltonian, we studied polyacene oligomers of different lengths in the strong electron correlation limit. Geometrical optimizations were performed for the lowest singlet and triplet states of oligomers up to [40]-acene, and a convergence of the bond lengths toward the polymer limit is observed in the interior of the oligomer. For large oligomers, as well as for the polymer, the ground state can be reasonably determined to be a singlet. Furthermore, a high similarity between the singlet geometries and triplet geometries suggests an open-shell character for the singlet ground state. A reasonable speculation of the soliton−antisoliton pair character of the singlet ground state was supported by a spin distribution analysis of the triplet state wave function of large oligomers, with each of the two solitons being broadly delocalized over the upper or bottom edge of the oligomers, respectively.

Introduction

Polyacene oligomers, which are one-dimensional molecules composed of fused benzene rings, are a unique series of conjugated hydrocarbons. Over the past two decades, they have attracted considerable interest from theoretical and experimental scientists due to their fascinating electronic properties originated from their extended π conjugation through out the entire carbon backbone.[1−15] Rather unfortunately, these molecules become less chemically stable with increasing oligomer length, and for many years experimental studies had been limited to oligomers up to pentacene. It was only very recently that functionalized hexacene and heptacene got successfully synthesized and crystallized, which allowed for a deeper insight into their electronic structure as well as physical and chemical properties.[16] To the best of our knowledge, synthesis of even larger oligomers has not been reported. In this sense, polyacene can be considered to be a hypothetically infinite system.[17]

Polyacene poses a great challenge to theoretical scientists. The extended π electron conjugation leads to significant long-range electron correlations, which must be dealt with very carefully to acquire a reasonable description of the electronic structure as well as many physical and chemical properties. Within the theoretical chemistry community, there has been a controversy over their geometries. Early theoretical studies at the level of Hückel molecular orbital (HMO) theory as well as some recent theoretical investigations using nonempirical valence bond (VB) method or density functional theories (DFT) methods suggested that Peierls distortion might take place to remove the HOMO−LUMO degeneration at polymer limit.[15,18−31] In contrast, other investigations showed that electron correlation effect could introduce an energy gap between the ground and the lowest excited states, that is large enough to make the Peierls distortion essentially unnecessary.[11,12,32−35]

Besides molecular geometries, there have also been controversies surrounding the spin of their ground state. Small oligomers are indisputably believed to have a closed-shell (nonferromagnetic) ground state. Large oligomers, however, had been supposed at one time to have a ferromagnetic (FM) triplet ground state[11] (or have an even higher-spin ground state)[31] with unpaired electrons occupying two or more nearly degenerate frontier π orbitals. However, more recent studies claimed that large oligomers have an open-shell singlet (antiferromagnetic, AFM) ground state with diradical or even polyradical characters,[12,36,37] and the transition from a closed-shell nonferromagnetic ground state to an antiferromagnetic ground statee takes place around octacene.

A related point of interest to theoretical chemists is the singlet−triplet energy gap. This energy gap at the polymer limit could usually be extrapolated from results for a series of finite oligomers. Our previous study using a semiempirical valence bond (VB) model suggested a gap of about 0.45 eV.[38] Another investigation using the semiempirical Pariser−Parr−Pople (PPP) model resulted in a value of 0.53 eV.[39] More recent DFT calculations on small oligomers predicted much smaller energy gaps and a more rapidly narrowing of the energy gap with the oligomer size,[12,37] while DFT calculations on even larger oligomers produced a surprising widening of the energy gap, making the overall extrapolation strategy questionable.[36,37] A recent ab initio densiy matrix renormaliztion group (DMRG) calculations on oligomers up to dodecane at the level of the complete-active-space self-consistent-field (CASSCF) presented smaller energy gaps of about 0.14−0.33 eV.[37] In the face of these discrepancies, it would be desirable to further investigate this energy gap with higher accuracy.

Previous studies revealed that the nonempirical VB method can give a reasonable description of carbon−carbon bond lengths in conjugated hydrocarbons.[30,40−42] However, the computations were limited to small to medium-sized molecules due to the exponential increase of VB structures along with the system size. Building on our experience on the DMRG method, which has been proven to be a very powerful tool to study strong electron correlation in one-dimensional systems,[43−45] in this work we propose a DMRG method for solving the nonempirical VB model for polyacene oligomers with as many as hundreds

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of carbon atoms. Molecular geometries as well as the electronic structures of the lowest singlet and triplet states will be reinvestigated from the view of strong electron correlation. The ground state will be determined, and the evolution of the lowest energy gap to the polymer limit will be presented and compared against those obtained with other semiempirical and ab initio method. Molecular geometries of the two electronic states will be optimized and compared with each other. Combined with the geometrical analysis, the spin distribution in the triplet state will be analyzed in an effort to look into the soliton character of the ground state.

Methodology

Nonempirical Valence Bond Model. The nonempirical VB model was proposed by Malrieu and his co-workers in 1984.[40] The effective VB Hamitonian had been originally written as

$$H = \sum_{i-j} [R_{ij} + g_{ij}(a_i^+ a_{\bar{j}}^+ a_j^- a_{\bar{i}}^- + a_{\bar{i}}^+ a_j^+ a_{\bar{j}}^- a_i^- - a_i^+ a_{\bar{j}}^+ a_{\bar{j}}^- a_i^- - a_{\bar{i}}^+ a_j^+ a_j^- a_{\bar{i}}^-)] \quad (1)$$

where R_{ij} is a parameter dependent on bonding atoms i and j and g_{ij} accounts for the effective exchange coupling between bonded atoms i and j. The interatomic distance r_{ij} and the torsion angle θ_{ij} dependence of R_{ij} and g_{ij} could be found in the original paper of Said et al.[40] A simpler form of Hamiltonian that is easier to handle could be reformulated by use of spin operators,[30]

$$H = \sum_{i-j} \left[R_{ij} + g_{ij}\left(2\mathbf{S}_i \cdot \mathbf{S}_j - \frac{1}{2}\right)\right] \quad (2)$$

Geometry optimization can be carried out by minimizing the total energy.[40] This model has been proved to give reliable predictions on the low-lying states of conjugated hydrocarbons as well as conjugated diradical or polyradical systems at a comparatively low expense for systems composed of less than 30 electrons.[41,42] However, for even larger molecules, the dimension of configuration spaces becomes prohibitively large. Then it becomes computationally too costly to diagonalize the Hamiltonian matrix, even when large sparse matrix diagonalization techniques, such as Lanczos or Davidson methods, are employed. In such cases, DMRG method supplies a valuable alternative that is both numerically accurate and computationally feasible (at least for one-dimensional systems).

Density Matrix Renormalization Group Method. The density matrix renormalization group method, which was first developed by White in 1992,[43,44] is an extremely effective way to deal with strongly correlated Hamiltonians in the real active space. It has been used very successfully in the study of large conjugated hydrocarbons. A detailed and well organized review of the DMRG algorithm could be found in a recent publication of Schollwöck.[45] Here we shall give a brief description of the technique.

In DMRG, the interaction between different fragments is taken into account with the use of a "superblock" **AB**, which is composed of one "system block" **A** and one "environment block" **B**. For a specific state of the superblock, the importance of each basis function in the system block (toward this superblock state) can be defined by the reduced density matrix ρ of the system block,

$$\rho_{ii'} = \sum_j \psi_{ij}\psi_{i'j} \quad (3)$$

where ψ_{ij} is the contribution of the direct product of basis $|i\rangle$ in the system block and $|j\rangle$ in the environment block to the specific superblock state of interest. In general, the target state is denoted as

$$\Psi = \sum_{ij} \psi_{ij}|i\rangle|j\rangle \quad (4)$$

The diagonalization of ρ leads to a set of eigenvalues ω_α and eigenvectors u^α. According to the definition of the density matrix, the states corresponding to larger eigenvalues of density matrix ρ are the more probable configurations of the system block. Accordingly, the m largest eigenstates are retained, spanning a truncated space for the system block. All the operators (e.g., **H**) are transformed into this representation with lower dimension (m).

A typical real space DMRG computation is divided into two stages. The infinite system algorithm in the first stage where one starts from a small fragment of a targeting system and then enlarges the system block by a few atoms within each iteration until the superblock reaches the size of the targeting system. The second stage adopts the finite system algorithm, where the basis set for the system and environment blocks are optimized to further improve accuracy, while the size of the superblock is kept constant.

Results and Discussion

Geometries. Geometry optimizations for the lowest electronic state in both $S_z = 0$ and $S_z = 1$ subspaces were performed with VB Hamiltonian on polyacene homologues up to [40]-acene. At this length, a convergence of the lowest energy gap as well as the terminal carbon−carbon bond lengths was observed. Bond lengths from both VB and DFT calculations are tabulated in the Supporting Information. The ground state is always found to be a singlet (S_0) with all oligomers (of different lengths) under our investigation, while the triplet (T_1) state is higher in energy. For singlet S_0 states of long oligomers, our results agree very well with results from a previous VB calculation on infinite polyacene by Garcia-Bach et al.[30] In the central region of the oligomer chain, our DMRG calculation yielded transannular bond lengths that converged to 1.428 Å, which is comparable to the value of 1.43 Å from direct computation of the polymer with transfer matrix technique. In our calculation, the carbon−carbon bond lengths on the upper (or bottom) zigzag edges are found to converge to 1.406 Å in our work, again within an agreement with the literature value of 1.40 Å. Such consistencies suggest that the electronic structure in the central part of long oligomers under our investigation is already very similar to that of a polymer chain.

For a clear comparison with the previously reported results from DFT calculations, the change in transannular bond lengths along the chain of decacene is illustrated in Figure 1, and a plot for the bonds on the upper zigzag edge is shown in Figure 2. The bonds displayed in both figures go from one end to the other. Since our VB calculations indicate no symmetry distortion in all oligomers under investigation, i.e., the molecules always retain their D_{2h} symmetry, we chose to display bonds along the upper edge in Figure 2. In addition, there is no difference in going from left to right, or in reversed direction. Compared with the VB method, the DFT method tends to yield longer lengths

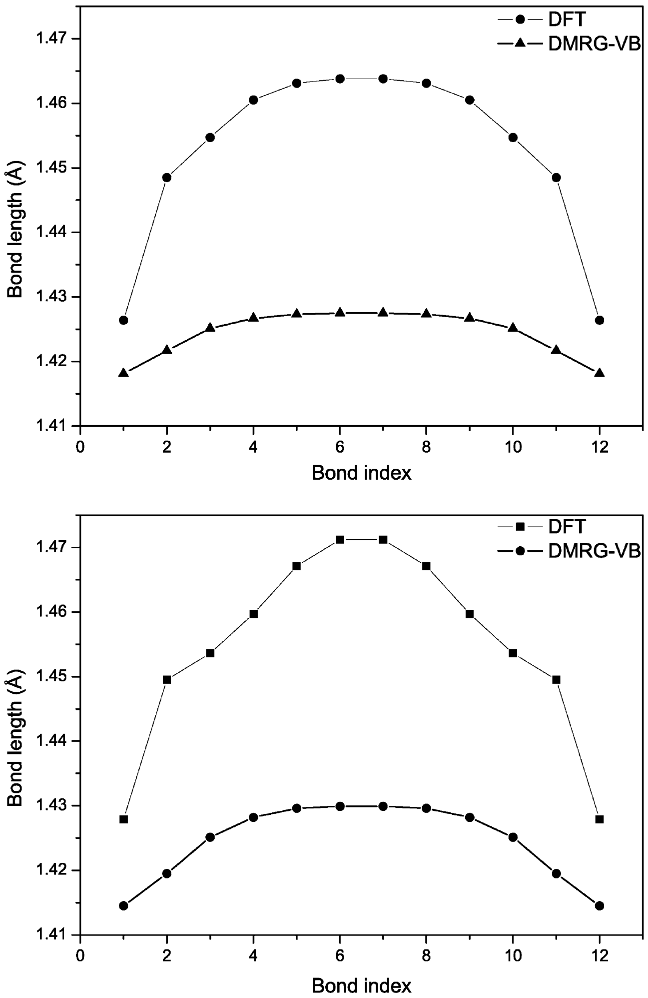

Figure 1. Ttransannular bond lengths of the singlet and the triplet states in decacene.

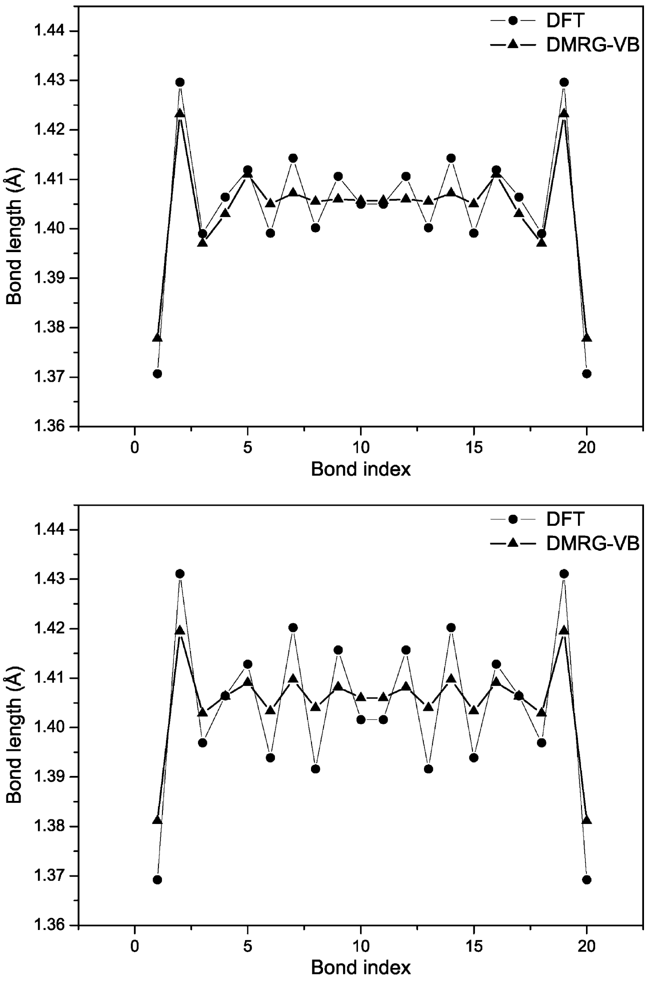

Figure 2. Zigzag edge bond lengths of the singlet and the triplet states in decacene.

for the transannular carbon−carbon bonds in both the S_0 and the T_1 states of acene oligomers.[11,12,36,46] For the [40]-mer, the interior transannular bonds in the S_0 state converge to 1.461 Å within the spin-polarized GGA density functional theory using a planewave basis set.[36] B3LYP calculation using the 6-31G(d) basis set resulted in a slightly larger value of 1.463 Å for decacene. Similar differences were also observed for acene polymer; i.e., the DFT method predicted a longer transannular carbon−carbon bond in the inner region of the polymer chain. However, a small difference between spin-polarized DFT method and the B3LYP method does exist, with a transannular bond length of 1.459 Å with spin-polarized DFT,[36] and 1.466 Å with B3LYP.[31] Since DFT provides more accurate transannular bond lengths for small oligomers,[11] DFT methods are believed to provide more accurate transannular bond lengths than VB method. However, at the very least, VB method does produce qualitatively correct results, such as displaying a rapid convergence of transannular carbon−carbon bond length in the inner region of oligomer chain.

As mentioned earlier, in both S_0 and T_1 states of long oligomers, VB calculations predict a length of 1.406 Å for bonds in the middle of either zigzag edge, which is very close to the value at the polymer limit. Spin-polarized DFT calculations also predict a converged length of 1.406 Å for the same bonds in the open-shell singlet ground states of polyacene.[36] On the other hand, B3LYP calculations on a relatively smaller [10]-acene resulted in slightly longer bonds, 1.410 Å in the open-shell S_0 state, and 1.416 Å in the triplet, respectively.[12] In short oligomers like [10]-acene, bond length alternation is still quite noticeable, so a convergence of the bond length (for bonds in the middle of the zigzag edges) to the polymer limit definitely has not been reached. However, in larger oligomers, one witnesses a clear bond-length equalization for most bonds except for those at both ends of the molecules due to terminal effects. Such bond length equalization indicates an absence of the Peierls distortion, which usually takes place to remove the degeneracy between HOMO and LUMO orbitals in infinite systems with degenerate ground states.[36] In previous studies, one or more solitions were found to form on each zigzag edge when each edge contains an odd number of carbon atoms and the bond-length equalization is reached. Therefore, large acene oligomers were believed to have the diradical or even polyradical type of ground state S_0.[11,12,36,37] While VB and DFT calculations displayed the same trends for the bond lengths to vary along the oligomer chain (see Figure 2), the differences between them are remarkable. On one hand, VB calculations predict a much smaller bond length alternation in the central region of smaller oligomers, both for S_0 and for T_1; on the other hand, by inspecting longer oligomers, it is found that spin-polarized DFT calculations resulted in a wider region of bond length alternation, which reflects much stronger terminal effects than that from VB calculations.[36] Further comparisons are expected to confirm the different behavior of these two methods. A lot of previous research revealed that the present-generation density functionals has a problematic description of long-range π electron correlations in conjugated systems.[49,50]

As for the acene oligomers, spin-polarized DFT calculations yielded a (questionable) value of 1.398 Å for the bond lengths in the inner region of [40]-acene, which is even shorter than the polymer limit. It is rather unphysical for these bonds to shorten gradually from small to moderately sized oligomers, and to lengthen thereafter to the polymer limit.

The geometrical differences and similarities between T_1 and S_0 states is also worth further attention. VB and DFT calculations led to very similar geometries for both states. For oligomers as large as [18]-acene, both states have essentially equal bond lengths along the zigzag edges, with the largest error being less than 0.001 Å. The differences in the transannular bond length are slightly larger, but only up to 0.004 Å. Such similarity was noted by Bendikov et al., whose DFT calculations on a series of smaller oligomer up to decacene yield a bond length difference of only up to 0.008 Å between two states.[12] Our calculations in this work on even longer oligomers led to even smaller differences in bond lengths as the size of oligomer grows further. Such geometrical similarity suggests to us that these two states also have similar electronic structures. In the next subsection, we will further analyze the spin distributions of the T_1 state, and we will suggest that the T_1 state is most likely a weakly coupled soliton pair with the two solitons being spatially well-separated, i.e., one on each zigzag edge. On the other hand, the longer cross-ring bond lengths in the triplet state could be rationalized by following the elegant interpretation of Borden et al. on the geometrical similarities and differences between the ^1A_g and ^3B_u states of tetramethylenebenzene.[47] Essentially, the electron spin polarizations are the same on the upper and bottom edges in the triplet state, whereas in the open-shell singlet they are opposite, giving rise to an additional π bonding between the upper and bottom edges that leads to shorter cross-ring bonds.

Spin Density of the Triplet State. Even though spin unrestricted DFT method can provide qualitatively correct geometries for the T_1 of polyene oligomers,[48] it has been shown to be unable to reproduce the spin density distribution pattern of neutral solitons in polyene.[49,50] In contrast, a qualitatively correct picture can always be achieved with the semiempirical PPP method, whose applicability can be significantly improved with the DMRG technique.[50] In this work, our focus is the use of the VB method rather than PPP, because the VB model is computationally less expensive, which would allow us to handle much larger oligomers composed of hundreds of atoms. In our earlier work,[51] we showed that VB method can also lead to a qualitatively correct description of spin distribution in diradical or even polyradical systems.

A spin distribution pattern for the triplet state T_1 of [40]-acene is illustrated in Figure 3, which shows how the spin densities vary along the zigzag edge. It could be inferred from the geometrical symmetry of polyacene that the triplet state should be composed of two longitudinally distributed weakly interacting solitons on the upper and bottom edges, respectively. Very interestingly, the spin distribution pattern of each soliton is very similar to that of a neutral soliton in polyene except for the following three aspects.

First, the spin density, which spreads almost over the entire oligomer except for several terminal atoms, is distributed much more broadly than that of neutral solitons in polyene. In other words, π electrons are more delocalized in polyacene than in polyene. This broader spin distribution is, to a certain degree, consistent with the rapid bond-length equalization in both S_0 and T_1 states when going from two ends to the central part of the oligomer. A detailed analysis based on the molecular orbital model was previously offered to rationalize the absence of Peierls distortion in polyacene.[11] However, the two singly occupied molecular orbitals (SOMOs) would, in their canonical form, overlap strongly with each other, and cannot be pictured very easily. In a more recent work, two SOMOs are transformed into localized MOs, which only overlap marginally at the transannular bonds.[12] It is believed that a weak coupling between these two solitons would not only remove the degeneracy of the ground state (and thus make a Peierls distortion unnecessary) but also allow for an open-shell singlet ground state.[52]

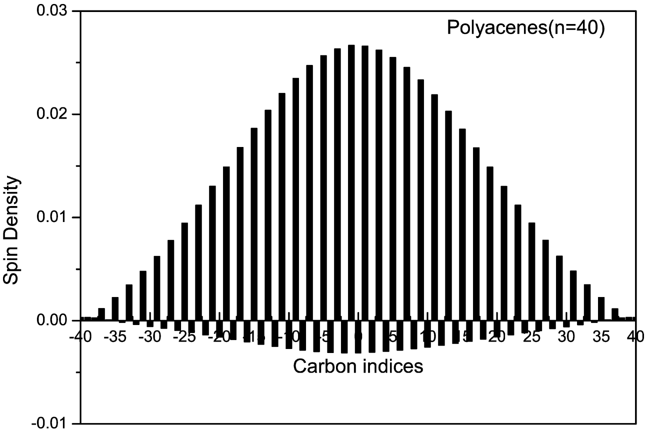

Figure 3. T_1 state spin density distribution along one zigzag edge of [40]-acene.

Second, while in most parts along the edge the spin distribution resembles a neutral soliton, there is a small but non-negligible spin fluctuation on several terminal atoms, which contrasts with the case of a neutral soliton where spin polarization diminishes gradually to zero away from the soliton center. This nonzero spin density at the terminal atoms can potentially be interpreted via the polyradical character of large acene oligomers.[36,37] For instance, the second highest occupied orbital (HOMO−1) and the second lowest unoccupied orbital (LUMO+1) are largely distributed at the two ends instead of the center of the oligomer. Configurations involving the excitation from HOMO−1 to LUMO+1 could account for the small spin fluctuation near the ends of oligoacene. Unfortunately, due to its single-occupation presumption, the VB theory cannot be used to evaluate the polyradical character of oligomers.

Third, the spin polarizations are almost 1 order of magnitude smaller than those of the neutral solitons on polyene. This is very likely related to the interchain coupling of the two solitons through the transannular bonds. Such interchain coupling also suppressed the negative spin polarization at the interedge connecting atoms, which leads to much greater averaged ρ_+/ρ_- ratio than that of the neutral solitons in polyene.[50]

Singlet−Triplet Energy Gap. Based on the above analysis of the interior bond-length equalization in long acene oligomers, and based on the very broad spin-distribution over the entire oligomer chain, it is very natural to picture the ground state S_0 and the lowest triplet state T_1, both of strong radical characters, as two weakly interacting solitons, with each soliton distributed mainly on one zigzag edge of polyacene. These two solitons have opposite spin in an open-shell singlet state S_0, and the extra bonding between them can potentially lead to a lower energy for this singlet state, which can largely account for the singlet−triplet energy gap. At the polymer limit, the energy gap is expected to converge to a limited but nonzero value, because these two solitons are spatially incompletely avoided.

In Figure 4 we present the singlet−triplet energy gaps calculated with the DMRG-VB method for acene oligomers with

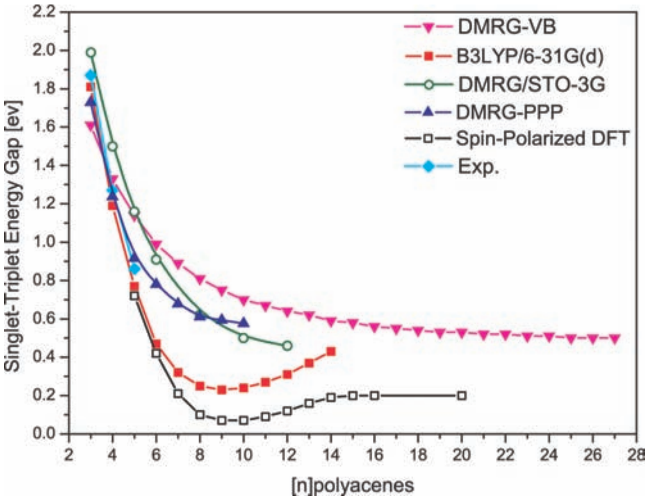

Figure 4. Singlet−triplet energy gap of acene oligomers calculated with different methods.

up to $n = 27$, as well as other previously published experimental and theoretical results. Experimental data are available only up to pentacene, due to the high instabilities of large oligomers.[53−55] Published results of DMRG-CASSCF calculations were available for oligomers as large as dodecacene.[37] DMRG-PPP model calculations were performed on oligomers as large as decacene with all of the carbon−carbon bonds being fixed at 1.397 Å. Spin-unrestricted B3LYP methods were employed first by Bendikov et al. to study oligomers as large as decacene,[12] it was later extended to dodecacene by Hachmann et al.[37] and is further extended to tetradecacene in this work. Spin-unrestricted calculations on even longer oligomers is very difficult due to serious spin-contamination. On the other hand, spin-polarized DFT calculations can be used to handle longer oligomers.

From VB, PPP, and CASSCF calculations, one can see a similar trend of the energy gap decreasing and approaching the polymer limit. With VB, we can extrapolate the energy gap for long oligomers to around 0.47 eV for the polymer limit, which is comparable to an estimated value of 0.53 eV with the PPP method.[39] Both VB and PPP values, however, are significantly higher than CASSCF results presented in Figure 4, where CASSCF calculations predict this energy gap to be ca. 8.69 kcal/mol (0.38 eV), or an even narrower gap of 3.33 kcal/mol (0.14 eV) with DZ basis set. But the extrapolation done with CASSCF could be less accurate due to insufficient data points. In Figure 4, we also observe that DMRG-VB and DMRG-CASSCF gaps around pentacene, with DMRG-VB predicting smaller energy gaps for shorter oligomers, and larger gaps for longer oligomers.

For short oligomers, results from the spin-unrestricted DFT calculations are found to be in the best agreement with experimental observations, which demonstrates the strength of DFT method in computing small to moderate size molecules near equilibrium geometry. However, as noted by Hachmann et al.,[37] spin-unrestricted DFT calculations results in a questionable evolution of the singlet−triplet energy gap beyond octacene, with the gap hitting a lowest value first and going up unexpectedly again. We have yet to see how the energy gap converges with DFT for longer oligomers. Spin-polarized DFT displayed a similarly strange evolution behavior, and it is our guess that these unphysical pictures is ultimately caused by spin-contamination and other spin-related defects embedded in the present generation of exchange functionals.

Conclusion

By virtue of the DMRG technique, the nonempirical VB method is applied to very large polyacene oligomers, which allows for a systematic study on the electronic structures of the lowest singlet and triplet states. Our calculations produced very minor geometrical differences between these two states, except for the slightly shorter transannular carbon−carbon bonds in the singlet state. This suggests that these two states have similar electronic structures. A direct analysis of the spin distributions in the T_1 state of long oligomers reveals an essentially two-soliton character, with one soliton on each zigzag edge of the molecule. On the basis of this analysis, we suggest that the lowest singlet state S_0 has a similar soliton−antisoliton open-shell character. The antiparallel spins of the two solitons would allow for an extra bonding between them, which explains why state S_0 is lower in energy than state T_1.

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Supporting Information Available: From [4]-acene to [40]-acene, the calculated carbon−carbon bond lengths for the ground (S_0) and the lowest triplet state (T_1) are listed. This material is available free of charge via the Internet at http://pubs.acs.org.

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