# Oligoacenes: Theoretical Prediction of Open-Shell Singlet Diradical Ground States

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Polyacenes (**1**) are polycyclic aromatic hydrocarbons consisting of linearly fused benzene rings. These long-known substances have attracted wide interest from both theoretical and experimental scientists.[1] Despite considerable interest, homologues higher than hexacene remain to be fully characterized, and the thorough understanding of electronic properties in large oligoacenes ends with pentacene ($n = 5$).[1a] Pentacene has received much attention as the active semiconducting material in field-effect transistors because of its unusually high charge-carrier mobility.[2]
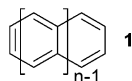
The electronic properties of large oligoacenes have been examined theoretically by many groups. Despite large strides in sophistication of theoretical treatments over the last 30 years, the electronic structure, stability, aromaticity, and most importantly the band gap and HOMO−LUMO gap of an oligoacene or polyacene are still subjects of controversy.[3−7] Large polyacenes were predicted to behave as one-dimensional organic conductors with a zero band gap.[3c,7] Recently, it was proposed that linear polyacenes would behave as two polyacetylene chains with a triplet ground state and a vanishing band gap.[5] Octacene ($n = 8$) was predicted to exhibit a triplet ground state on the basis of extrapolation from the singlet−triplet difference of benzene through hexacene,[8] but whether the ground state is a triplet state has not been determined.

In conjunction with experimental efforts to synthesize larger oligoacenes, we were interested in the prediction of their electronic properties.[2c] We have discovered that at the RB3LYP/6-31G(d) level of theory,[9] the wave function for as small an oligoacene as hexacene (and all longer oligoacenes) becomes unstable.[10] Re-optimization, using the unrestricted broken symmetry B3LYP method (UB3LYP), leads to a singlet state with large amounts of diradical character. This conclusion is supported by a preliminary CASSCF investigation.[9,11] In contrast to the common view that acenes are closed-shell systems or have triplet ground states,[3c,5,8] we predict that the ground states of oligoacenes are singlets, as a result of their disjoint diradical nature. As such, these substances have partially filled orbitals that contribute to their important electronic properties.

For hexacene, at the B3LYP level of theory, the singlet−triplet gap is found to be 10.3 kcal/mol (triplet above singlet), while the closed-shell RB3LYP solution is 0.8 kcal/mol above the open-shell singlet diradical state (Table 1). Here, the spin contamination for singlet is small ($\langle S^2 \rangle = 0.26$). The singlet−triplet gap decreases from hexacene to heptacene and octacene, and then it becomes constant at 5−6 kcal/mol (0.26 eV). With the increase of the number of benzenoid units, the RB3LYP solution becomes higher in energy relative to the open-shell singlet diradical state. For decacene, the calculated ΔE(OS − CS) is −10.4 kcal/mol, and the spin contamination for the open-shell singlet becomes very large ($\langle S^2 \rangle$

Table 1. Energies (kcal/mol) for the Singlet−Triplet Gaps, Spin Contamination for the Open-Shell Singlet ($\langle S^2 \rangle$), Differences between Open-Shell Broken-Symmetry Singlet and Closed-Shell RB3LYP Solution (ΔE(OS − CS) and for Optimized Triplet States Relative to RB3LYP Solution (ΔE(T − CS))

molecule	ΔE(T − OS)[a]	$\langle S^2 \rangle$	ΔE(OS − CS)[b]	ΔE(T − CS)[c]
hexacene	10.3[d]	0.26[d]	−0.8[d]	9.5[d]
heptacene	7.1[d]	0.80[d]	−2.7[d]	4.4[d]
	5.1[e]	0.13[e]	−0.4[e]	4.7[e]
	5.1[f]	0.21[f]	−0.5[f]	4.6[f]
octacene	5.8[d]	1.08[d]	−5.2[d]	0.6[d]
	2.9[g]	0.67[g]	−1.3[g]	1.6[g]
nonacene	5.5[d]	1.26[d]	−7.9[d]	−2.4[d]
	1.8[g]	0.98[g]	−2.9[g]	−1.1[g]
decacene	5.7[d]	1.42[d]	−10.4[d]	−4.7[d]
	1.5[g]	1.10[g]	−6.4[g]	−4.9[g]

[a] Triplet energy minus open-shell singlet energy. [b] Open-shell singlet energy minus RB3LYP singlet energy. [c] Triplet energy minus RB3LYP singlet energy. [d] B3LYP/6-31G(d). [e] PW91/PW91/6-31G(d). [f] BPW91/6-31G(d). [g] BLYP/6-31G(d).

$= 1.42$); the ground state of the species has become diradical in character. Qualitatively similar results were obtained with BLYP, PW91, and BPW91 functionals (Table 1). However, using the BLYP method, we find that the transition toward the open-shell singlet ground state starts at octacene, whereas in PW91 and in BPW91 it begins at heptacene, and $\langle S^2 \rangle$ is significantly smaller for these pure DFT methods. Triplet structures are always higher in energy than open-shell singlet structures, but the singlet−triplet gaps become smaller for pure DFT methods. Hence, our calculations predict that oligoacenes will maintain a ground-state singlet even above octacene, although the triplet state is only several kcal/mol above the singlet state and should be thermally accessible.

Preliminary (10,10) CASSCF calculations (see Supporting Information) are in agreement with the DFT prediction, in that significant increase in a diradical character is clear from the large change in the orbital occupation, going from heptacene to octacene, which has 0.78 electrons outside closed-shell bonding orbitals in octacene. For hexacene, the singlet−triplet gap is predicted to be 13.3 kcal/mol, and for octacene it is 6.5 kcal/mol by these calculations.

The geometries of decacene for both singlet and triplet states are presented in Figure 1. Both structures have very similar geometries with the maximal bond length differences of 0.008 Å and resembling two polyacetylene chains connected by sp^2−sp^2 single bonds. This pattern has been rationalized previously.[5] It results from the absence of the Peierls distortion of each poly-acetylene ribbon; this is because there is no stabilization resulting from interaction of singly occupied orbitals in the diradical ground state upon bond alternation.[5]

The data presented here predict a singlet diradical ground state for oligoacenes larger than hexacene. The experimental band gap derived from the UV−vis spectrum for hexacene, 1.84 eV,[8] is close
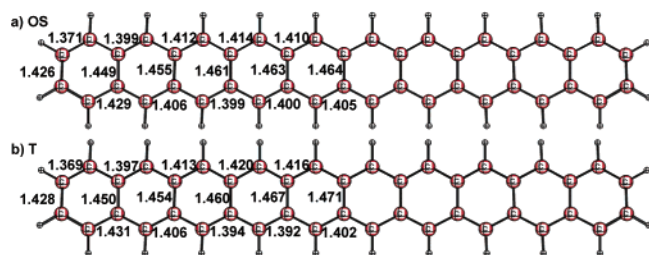
Figure 1. Calculated (B3LYP/6-31G(d)) geometries of (a) open-shell singlet decacene and (b) triplet decacene.
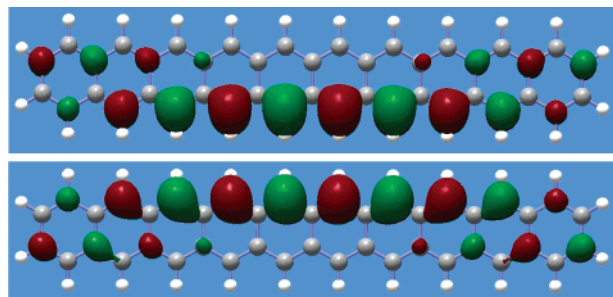

Figure 2. Singly occupied orbitals of decacene (UB3LYP/6-31G(d)).

to the calculated HOMO−LUMO value of 1.80 eV. Beyond this molecule, the ground state becomes an open-shell singlet with partially occupied orbitals, and the lowest excited state is likely to become the state with considerable ionic character resulting from transfer of an electron from one ribbon to the other, in analogy to the very similar electronic structure of tetramethylenebenzene.[13c]

Investigation of frontier molecular orbitals gives more insight into the nature of the open-shell ground state in oligoacenes. The two singly occupied orbitals of decacene are shown in Figure 2. They are essentially localized on the two ribbons. Such a species is a classic disjoint diradical as analyzed elegantly by Borden and others.[13] Disjoint diradicals are species such as cyclobutadiene, tetramethyleneethane, and 1,2,4,5-tetramethylenebenzene, which can be written as diradicals with two NBMOs sharing no common atoms. Indeed, because of the nature of the NBMOs of polyacenes, all of these species become disjoint diradicals when greater than hexacene, and the singlet state is the ground state in all of these oligoacenes.[13]

In conclusion, we have shown computationally that oligoacenes and probably a variety of polyacene derivatives and analogues should exhibit a nonzero band gap. We have found that larger oligoacenes possess an open-shell singlet ground state, where the triplet lies above singlet, a consequence of the disjoint nature of the diradical ground states. Finally, the calculational instabilities found for heptacene−octacene appear to indicate that they are the "connector" between band theory[14] and molecular orbital theory. Molecular design directed to address these predictions is under investigation in our laboratory.

Note Added after ASAP Posting. After this paper was posted ASAP on 05/14/2004, the order of the authors was changed, and the ΔE(OS − CS) reported for decacene in the fourth paragraph was corrected to the negative value. The corrected version was posted 05/26/2004.

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