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Open-Shell Singlet Character of Stable Derivatives of Nonacene, Hexacene and Teranthene

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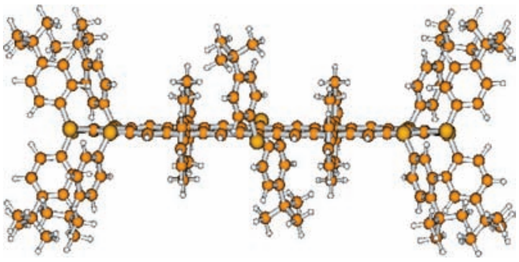
ABSTRACT



The electronic ground states of the recently synthesized stable nonacene derivatives (*J. Am. Chem. Soc.* 2010, *132*, 1261) are open-shell singlets with a polyradical nature instead of closed-shell singlets as originally assumed, according to the unrestricted broken spin-symmetry density functional theory (UBS-DFT) computations (at B3LYP/6-31G*). It is the bulky protecting groups, not the transfer from the open-shell singlet to closed-shell singlet ground state, that stabilizes these longest characterized acenes. Similar analyses also confirmed the open-shell singlet character of the hexacene and teranthene derivatives.

Carbon conjugated compounds formed by the linear annelation of benzene rings are called acenes (**1**, $n \geq 3$).[1] Tetracene (**1**, $n = 4$) and pentacene (**1**, $n = 5$) are among the best organic semiconductors and have been extensively applied in organic electronics and photoelectronics.[2] Higher acenes (**1**, $n \geq 6$) are inherently more interesting owing to the smaller HOMO−LUMO gaps and possible larger charge-carrier mobilities.[3]

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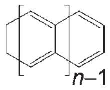
However, these tantalizing molecules are short-lived toward oxidation, falling short of the required stability for application.[4] This is mainly due to the free radical character expected for higher acenes.[5−7] Thus, synthesizing the parent higher acenes is a daunting challenge. Decades' efforts only realized a few higher acenes. For example, Mondal et al.[8] obtained heptacene at room temperature in a poly(methyl methacrylate) matrix, while Bettinger and his co-workers achieved heptacene, octacene, and nonacene in the solid inert gas matrices at cryogenic temperatures.[9] Thus, stabilizing and synthesizing higher acenes and understanding their electronic characters are all challenging but rewarding goals for chemists.



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Employing bulky protecting groups is a widely used strategy to stabilize the higher acenes. Using this approach, several groups successfully synthesized heptacene derivatives with improved stability.[10] Miller and co-workers' joint experimental and computational studies on a large series of pentacene derivatives revealed that a combination of steric resistance, electronic effects, and the positional location of each substituent can effectively control the photooxidative resistance and HOMO−LUMO gap.[11] Migrating these strategies to even higher acenes, Miller's team recently synthesized persistent nonacene (**1**, $n = 9$) derivatives, **2** and **3** (Figure 1), stabilized by the arylthio substituents.[12] Using unrestricted broken spin-symmetry B3LYP (UB3LYP) method, the authors computationally studied the electronic structures for a series of nonacene models−hypothetic nonacene derivatives with phenylthio (SPh) or methylthio (SCH_3) groups placed at different positions of the nonacene skeletons, and found that models with the substituents on the terminal rings have a vanished spin-squared expectation value ($<S^2> = 0$).[12] It was inferred that the terminal substituents should have similar electronic effects on **2** and **3** and result in closed-shell singlet (CS) ground states for them.[12] Note that the CS states considered for **2** and **3** are in sharp contrast to the parent nonacene, which was calculated to be an open-shell singlet (OS) polyradical at ground state.[5−7]

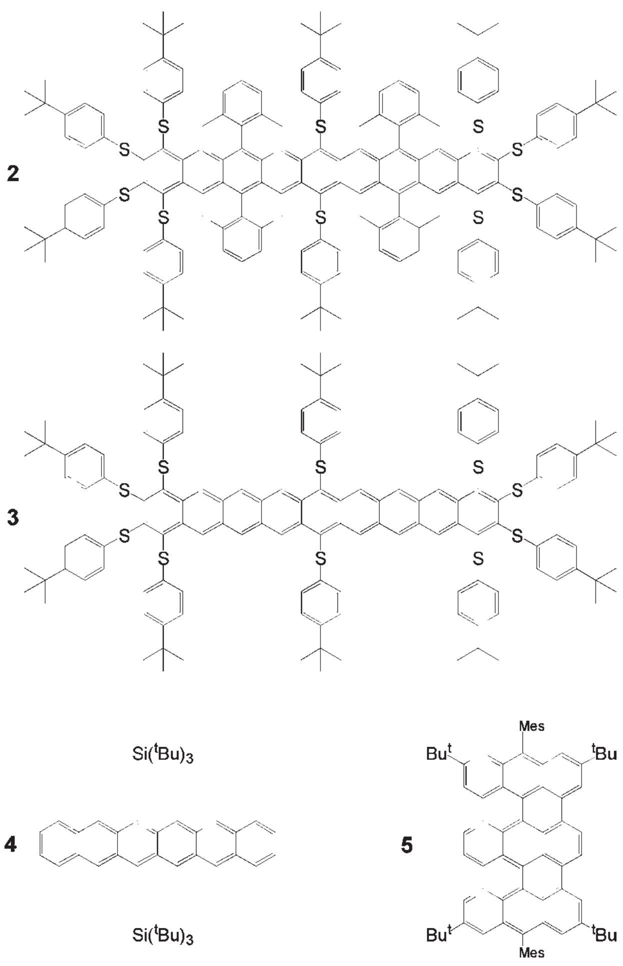

Figure 1. Derivatives of nonacene (**2** and **3**), hexacene (**4**), and teranthene (**5**).

Also employing bulky protecting groups, Anthony and co-workers recently synthesized the bis-triisopropylsilylethynyl (TIPS)-substituted hexacene derivative **4**,[13] while Konishi and co-workers synthesized teranthene derivative **5**.[14] The ground-state electronic structure of **4** has not been characterized yet,[13] whereas the CASSCF calculation and experimentally measured HOMO−LUMO gap, ^1H NMR, and SQUID consistently indicated that **5** is a singlet diradical (i.e., OS) at the ground state.[14]

Here we examine the electronic structures for **2**, **3**, **4**, **5**, and a series of bis(methylthio)nonacenes with methylthio groups attached at different positions. Our study correctly reproduces the OS ground state for **5**; however, all the other species, including **2** and **3**, are also calculated to have OS ground states rather than CS, irrespective of the positions the substituents are placed.

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The structures of **2**−**5** together with noncene were first fully optimized at B3LYP/STO-3G and characterized as local minima by frequency analysis, then optimized at B3LYP/6-31G*; the unrestricted broken spin-symmetry density functional theory (UBS-DFT) was used to get the OS and triplet state.[15] To reduce the spin contamination effect, an approximate spin projection (AP) technique[16] was applied to correct the OS energies, using the equations shown here

$$J = \frac{E_{\mathrm{OS}} - E_{\mathrm{T}}}{\langle S^2 \rangle_{\mathrm{T}} - \langle S^2 \rangle_{\mathrm{OS}}} \qquad (1)$$

$$E_{\mathrm{AP-OS}} = E_{\mathrm{OS}} + J \cdot \langle S^2 \rangle_{\mathrm{OS}} \qquad (2)$$

where E_{OS} and $< S^2 >_{\mathrm{OS}}$ are the calculated total energies and $< S^2 >$ for the OS wave function, E_{T} and $< S^2 >_{\mathrm{T}}$ are those for the triplet, and $E_{\mathrm{AP\text{-}OS}}$ is the AP-corrected energy for the OS. Although it can be considered a “poor man’s multi-configuration” method that simulates a multideterminantal character within a single determinant framework, the unrestricted broken spin-symmetry method has been successfully used to predict the radical character of higher acenes yielding similar results as the more complicated methods including density matrix renormalization group algorithm,[7aa,bb] restricted active space spin-flip configuration interaction approach,[7c7c] and active-space two-electron reduced-density-matrix method.[7d7d]

All computations were performed with the GAUSSIAN 03 program.[17]

In the calculated ground-state geometries for **2** and **3**, the arylthio groups are arranged above and below the nonacene skeleton, staggered to minimize the intersubstituent steric hindrance (see Figure S-1, Supporting Information). Both of these structures show C_i symmetry. Similarly, **4** and **5** also possess bulky substitutients (Figure 1). The calculated ground-state geometries of TIPS-substituted hexacene derivative **4** shows C_1 symmetry due to the unsymmetric substitution pattern of the substituents, while the teranthene derivative **5** displays C_{2h} symmetry, with the mesityl susbtituents arranged perpendicularly to the acene skeleton.

Table 1 summarizes the relative energies of OS, CS, and triplet states for **2**−**5**. For comparison, the corresponding values of nonacene are also given.

The OS state of **5** is 5.3 kcal/mol lower in energy than the CS and triplet states (Table 1), thus is the ground state. The calculated singlet−triplet energy gap ($\Delta E_{\mathrm{S-T}}$, 5.3 kcal/mol) is very close to the value estimated by SQUID measurement (3.8 kcal/mol),[14] and the predicted OS ground state for **5** is the same with the characterization by CASSCF(2,2)/6-31G computations and experiments.[14] Including the zero-point energy correction (evaluated at B3LYP/STO-3G) only slightly changes the relative energies (see Table S2, Supporting Information). This suggests that the UBS-DFT approach can correctly predict the ground-state electronic structure for singlet diradicals, which agrees with the previous reports.[7]

Table 1. Energies (kcal/mol) Relative to OS Calculated with R(U)/B3LYP/6-31G(d) [a]

species	OS	CS	triplet
nonacene	0.0 (1.26[b])	15.2 (0.00[b])	13.9 (2.04[b])
2	0.0 (1.24[b])	13.5 (0.00[b])	12.5 (2.04[b])
3	0.0 (1.22[b])	13.1 (0.00[b])	12.2 (2.04[b])
4	0.0 (0.44[b])	2.8 (0.00[b])	11.0 (2.03[b])
5	0.0 (0.92[b])	5.3 (0.00[b])	5.3 (2.07[b])

[a] The B3LYP energies of the OS are corrected with the AP technique. [b] The value of $< S^2 >$.

The OS state of **2** is 13.5 and 12.5 kcal/mol lower in energy, respectively, than the CS and triplet states (Table 1). For **3**, these energy differences are almost identical, at 13.1 and 12.2 kcal/mol. For **4**, the energy difference between OS and CS markedly reduces to 2.8 kcal/mol, whereas the energy difference between OS and triplet is 11.0 kcal/mol. For nonacene, both energy differences increase to 15.2 and 13.9 kcal/mol. The OS state of all the species in Table 1 is lower in energy than the CS and triplet states. Thus, just as for **5**, nonacene and its derivatives **2** and **3**, as well as hexancene derivative **4**, are all singlet diradicals in their ground states. The characterization of an OS ground state for nonacene is in agreement with previous studies.[5−7]

Figure 2 portrays the spin density distribution of **2** in the OS ground state. The spin-up and spin down electrons are located along the two zigzag edges of the nonacene skeleton, oppositely. Such a distribution pattern is in good agreement with the previous finding about higher order acenes,[5−7] zigzag-edged nanographenes,[18,19] and nanotubes.[20]

Our computations demonstrate that the fully optimized geometries of the OS and triplet states of **2-5** and noncene are very close to those of the relevant CS states. We computed their OS and triplet singlet-point energies on the basis of the CS geometries at B3LYP/6-31G*. This computational procedure leads to the same OS ground state, and only gives a slightly different stability ordering between CS and triplet states (S-Table 1, Supporting Information). Since the characterizations of ground states are most important in this work, we used this simplied approach to study the six bis(methylthio)nonacenes.

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(15) Mixing the HOMO and LUMO of initial guess is the commonly used approach to obtain an OS wave function. With Gaussian 03 program, this can be done by provoking keyword “GUESS = MIX”. However, this approach did not result in OS states for **2** and **3**, instead the CS states ($< S^2 > = 0$) with internal instabilities. Further optimization of the CS wave functions using “STABLE = OPT” keyword healed the instabilities and converged to stable OS wave functions.

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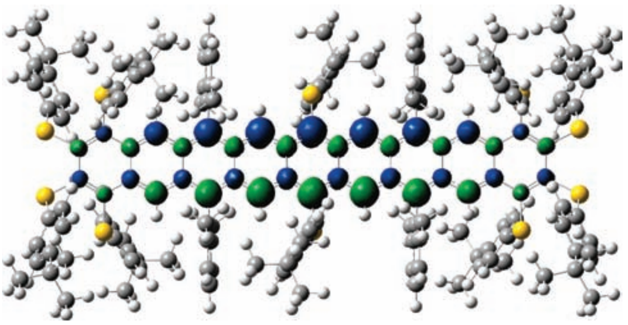

Figure 2. Calculated spin density distribution of **2** (UB3LYP/6-31G*). Green and blue colors represent different spin electrons.

The six bis(methylthio)nonacenes we studied are 8,19-, 7,20-, 6,21-, 5,22-, 1,4-, and 2,3-bis(methylthio)nonacenes, respectively, each having two methylthio groups placed on a single benzenoid ring of the nonacene skeleton (Figure 3a). In this series, the positions of the substituents vary from the center to the terminal end of the nonacene skeleton.

Figure 3b plots the computed energy difference between CS and OS and triplet and OS. The energies of the OS states are all below the respective CS and triplet states (Figure 3b). The calculated $<S^2>$ at OS are close, ranging only from 1.12 to 1.14, whereas the calculated $<S^2>$ at triplet are 2.04. These results suggest that the substitutions of methylthio groups at different positions do not alter the stability order of OS $<$ CS $<$ triplet and that all the six structures are open-shell singlets at ground state. On the other hand, the energy gap between CS and triplet depends on the position of the methylthio groups: as the positions go from the end (2,3) to the center (8,19) of the nonacene skeleton, the energy gap reduces from 2 to 1.0 kcal/mol (Figure 3b).

In summary, the electronic ground states of nonacene derivatives **2** and **3** are OS, rather than CS, as are hexacene derivative **4** and teranthene derivative **5**. The recent computational finding that arylthio substituents on the terminal rings of the nonacene skeleton eliminate total spin while lowering the HOMO−LUMO gap was not confirmed in our study. Instead, we found a dependence of the energy gap between CS and triplet on the substituent positions for bis(methylthio)nonacenes. It is, therefore, the bulky protecting groups, not the transfer from the open-shell singlet to closed-shell singlet ground state, that stabilize these longest characterized acenes. More deliberate work is still desirable to further search appropriate substituents which can eradicate the spin of higher acenes before we can stabilize these molecules solely by electronic effect.

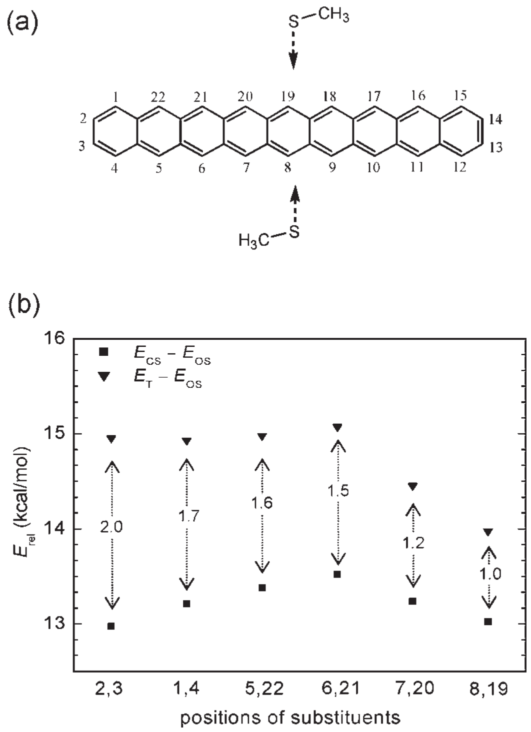

Figure 3. Position effect of bis(methylthio)nonacene. (a) Labeling of positions of substituents. (b) Energy differences between CS and OS ($E_{\mathrm{CS}} - E_{\mathrm{OS}}$) and triplet and OS ($E_{\mathrm{T}} - E_{\mathrm{OS}}$) for bis(methylthio)nonacenes at the R(U)B3LYP/6-31G(d) level of theory. The calculated $<S^2>$ for the OS state range from 1.12 to 1.14; those for the triplet are 2.04. The numbers on the dashed lines are the energy differences between CS and triplet states.

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Supporting Information Available. The optimized structures of nonacene and **2**−**5**, the relative energies of different electronic states using different methods, and the full citation of ref 17.. This material is available free of charge via the Internet at http://pubs.acs.org.