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Communication: A dramatic transition from nonferromagnet to ferromagnet in finite fused-azulene chain

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One-dimensional fused-azulene oligomers ($n = 2 - 6$) are studied with the effective valence bond as well as density functional theory methods. A nonferromagnetic (closed-shell singlet) to ferromagnetic (triplet) ground state transformation is witnessed with increasing length of oligomers. The computational results are interpreted in terms of spin coupling between the unpaired electrons of two nonbonding molecular orbitals localized, respectively, on the top and bottom chains of the oligomers. The present study provides a theoretical suggestion for understanding the ferromagnetic spin polarizations that has been observed very recently in graphene nanoribbons. © 2011 American Institute of Physics. [doi:10.1063/1.3533363]

I. INTRODUCTION

Azulene is prone to thermally isomerize to naphthalene due to its weaker aromaticity.¹⁻⁴ As illustrated in Fig. 1, topological structure of a fused-azulene chain is like a ladder composed of one cis-polyene chain and one trans-polyene chain, which are combined together by interchain C–C connections. Bending of the chain in the real structure is anticipated to take place due to the unbalanced strains between the top and bottom chains of the straight line structure. While there were few reports on fused-azulene chain,^{5,6} small oligomers of polyacene have been successfully synthesized and gained extensive applications in molecular electronics.⁷⁻⁹ Theoretical studies in recent years have also indicated closed-shell (nonferromagnetic) to open-shell singlet (antiferromagnetic) transformation of the ground state electronic structure along with the increasing length of polyacene chain.¹⁰⁻¹⁴ Meanwhile, we know very little about the electronic structure of fused-azulene chain.

However, recent works from Koskinen's group might bring about some change in the circumstances. Theoretical and experimental studies revealed that fused-azulene structure, which is very probably transformed from polyacene structure, should be a more stable edge morphology in graphene.¹⁵⁻¹⁷ More importantly, the process of edge structure isomerization may take place at room temperatures. Further theoretical studies have been published thereafter, which mainly focused on the stability of fused-azulene edge structure.¹⁸⁻²⁰ However, effects on the electronic behaviors, such as magnetism, charge transportation, etc., introduced by the novel edge structure still remain to be investigated.

In this short communication, valence bond (VB) as well as spin-unrestricted density functional theory (UDFT) calculations are performed to study the ground state electronic

structure of fused-azulene chain, which are intended for further understanding of the edge effect of graphene nanoribbons. Nonempirical valence bond (EVB) model,^{21,22} which is a geometry-dependant Heisenberg Hamiltonian, has proved to be a predictive tool for the study of the low-lying states of conjugated hydrocarbons and in particular for studying spin coupling in radical conjugated hydrocarbons.^{23,24} Our very recent studies on high-spin polyaromatic hydrocarbon molecules showed satisfactory agreements between EVB calculations and high level *ab initio* methods, such as difference-dedicated configuration interaction and complete active space with second order perturbation theory.²⁵ Recently, we employed it to study the open-shell singlet ground state of polyacene,²⁶ by solving the model Hamiltonian with the density matrix renormalization group method (DMRG),²⁷⁻²⁹ and the results agreed with DMRG on the complete-active-space-self-consistent-field (CASSCF) or the active-space variational two-electron reduced-density-matrix-CASSCF.^{11,13,26,30,31}

II. RESULTS AND DISCUSSION

Although it has been well accepted that there existed a closed-shell to open-shell singlet ground state transformation in polyacene with increasing length of the chain, it is still to our surprise to find that all of the computation results listed in Table I indicate a similar transformation also takes place in fused-azulene homologues, but in a different way. The geometries have been optimized for both values of S_z , so that the energy differences are adiabatic. According to EVB calculation, when $n \geq 6$ (smaller n observed in UDFT calculations), the ground state of fused-azulene chains changes to triplet (ferromagnetic), though the singlet–triplet energy gaps (triplet energy minus singlet energy) are very small, which implies that mixed features of both singlet and triplet states might be expected to be observed experimentally at room temperatures. Table I also reports the mean values of the S^2

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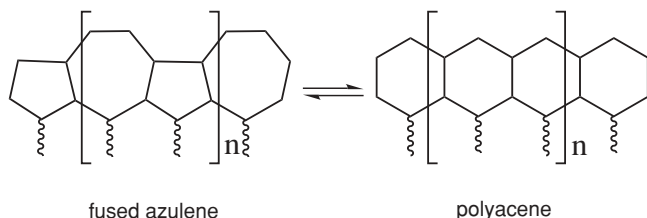


FIG. 1. Topological structure of fused azulene (denoted as [n]-azulene) and polyacene.

operator for the UDFT calculations, showing that the $S_z = 0$ solution becomes a half and half mixture of singlet and triplet states. Adiabatic singlet–triplet energy gaps after spin decontamination are also given.

For [6]-azulene, B3LYP predicted a negligible 0.2 kcal/mol energy gap between the triplet ground state and lowest singlet just above it. EVB calculations using structures either optimized by B3LYP or by EVB itself give slightly larger energy gaps. However, significant difference is observed between results of EVB calculations on [6]-azulene when different geometries are employed. Using EVB optimized structure, the EVB calculations show a sudden dropping of S-T gap after [6]-azulene, which is not surprising as far as non-vertical energy differences are concerned.³⁴ In contrast, using UDFT optimized structure, the S-T gap drops gradually from positive value in small oligomers to negative value in large oligomers. Encouragingly, for large oligomers, when the end effects are comparatively much smaller, the results from both methods are coincident with each other.

The nature of ferromagnetic ground state in longer oligomers can be understood clearly by inspecting the fron-

TABLE I. Adiabatic singlet–triplet energy gaps ΔE (kcal/mol) calculated with EVB and UDFT methods.

n	EVB model		UDFT		
	ΔE^a	ΔE^b	ΔE_{BS}^c	$\langle S^2 \rangle^d$	ΔE^e
1	22.6	19.8	18.1 ^f 17.2 ^g 16.9 ^h		
2	17.1	14.5	6.1 ^f 5.0 ^g 4.6 ^h		
3	12.9	12.2	-0.8 ^f -0.5 ^g 0.8 ^h	0.60 ^f 0.74 ^g 0.79 ^h	-0.04 ^f -0.3 ^g 0.9 ^h
4	8.1	11.3	-1.9 ^f -0.6 ^g -0.5 ^h	1.01 ^f 0.83 ^g 0.81 ^h	-3.2 ^f -0.8 ^g -0.7 ^h
5	1.1	10.4	-1.5 ^f -0.2 ^f	1.00 ^f 0.98 ^f	-2.4 ^f -0.05 ^f
6	-1.0	-0.5			

^aEVB/B3LYP/6-31G(d).

^bEVB/EVB.

^cTriplet energy minus open-shell broken symmetry singlet (BS) state energy.

^dSpin contamination for the open-shell singlet ($\langle S^2 \rangle$).

^eTriplet and singlet energy gaps removed of the spin contamination, $\Delta E_{BS}(\langle S^2 \rangle_T / (\langle S^2 \rangle_T - \langle S^2 \rangle_{BS}))$, following suggestions in Refs.32 and 33.

^fB3LYP/6-31G(d).

^gBLYP/6-31G(d).

^hPW91PW91/6-31G(d).

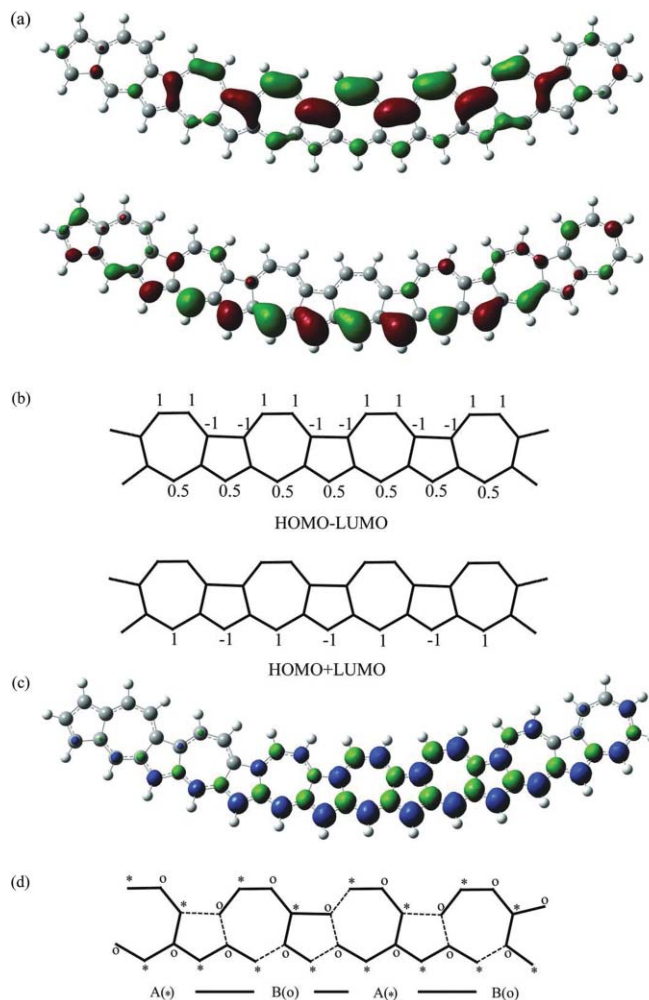


FIG. 2. (a) Two near-degenerate FMOs calculated with UB3LYP/6-31G(d). (b) Comparative contribution of each atomic orbital in the two FMOs determined by molecular graph theoretical methods. Ground state spin distribution of [6]-azulene calculated with EVB, and (d) mapping of fused azulene into a spin 1/2 chain.

tier molecular orbitals (FMOs), which are nearly degenerate for large oligomers. The two nearly degenerate FMOs of [6]-azulene showed in Fig. 2(a), which are calculated with UDFT method, indicated obviously nonbonding characters. Looking at the central part of the chain, one of the FMOs is distributed predominantly on the bottom chain, with alternating signs on succeeding carbon atoms, which is similar to the case of polyacene.¹⁰ The other FMO locates mainly on the top chain, but with a small portion of distributions on the carbon atoms indirectly connected with the top chain, while the coefficients of atomic orbitals are signed alternatively on pentagons and heptagons. The above results can be rationalized by a simple molecular graphical analysis on the Hückel nonbonding molecular orbitals (MOs) in periodical fused-azulene chain unit presented in Fig. 2(b). In the case of polyacene, the open-shell character of the ground state could be explained by the electron correlation of the electrons singly occupying the nonbonding FMOs.^{10,35,36} These MOs may be localized in the upper and lower side atoms, respectively. Let us call singly occupied molecular orbital a and b , respectively, these localized nonbonding MOs. Since they have zero amplitudes on

the central atoms, their exchange integral, K_{ab} , which would favor a ferromagnetic coupling, is negligible. The spin polarization of the closed-shell MOs results in an antiferromagnetic ground state.¹⁰ In contrast, in the case of fused azulene, the direct exchange ferromagnetic contribution, K_{ab} , is nonzero, as easily seen when calculating it from a Hubbard Hamiltonian, since the upper side SOMO a has amplitudes on the atoms bearing the lower side SOMO b , making the parallel spin (ferromagnetic) state preferable. In small oligomers, closed-shell ground state is due to strong ends effect leading to large energy separation of the two FMOs, which are either doubly occupied or unoccupied. In large oligomers with open-shell ground state, our calculations indicated that the partially occupied FMOs are largely populated in the central part of the chain, which explains the trend of the geometries evolution of the terminal rings to an azulene monomer, as shown in supplementary material.³⁷ Despite the observations, a simple extrapolation to infinite length fused azulene is dangerous, due to that more natural MOs will become partially occupied, so that one must consider the spin polarization of more closed-shell MOs as in the case of polyacene, which will make the problem more complicated.

Knowledge of spin distribution is helpful for understanding the nature of the spin polarization in radical systems; however, it is often overestimated by UDFT calculations due to spin contamination from higher spin states. Encouragingly, the EVB method is free from such defects. The results are illustrated in Fig. 2(c) for the triplet state of [6]-azulene. Obviously, the larger spin densities on central atoms indicates stronger radical character in central region of the fused-azulene chain. It is found that on both the top and bottom chains, the sign of spin changes alternatively on succeeding atoms, which inevitably resulted in alternative antiferromagnetic and ferromagnetic spin couplings on crossing bonds (indicated by either the same or opposite sign of spin on the two bonding atoms), which is very different from polyacene, in which all of the spin couplings at the cross chains are ferromagnetic in the triplet state.²⁶ It may be interesting to further explore the VB wavefunctions for polyazulene and polyacene, following the definition of “local-spin” as well as “local-spin coupling” suggested by Davidson and Clark.^{38–40} Local spin coupling between top and bottom chains, which is defined as $\langle S_{\text{top}} S_{\text{bottom}} \rangle$ are calculated for [6]-azulene and [12]-acene. In [6]-azulene, the triplet state has a slightly stronger coupling (−1.8) than the singlet state (−1.7). As shown in Fig. 2(c), VB results disclosed that the triplet state could have been stabilized by the nonnegligible antiferromagnetic coupling at the right side terminal crossing bond, which should have been ferromagnetic following the alternative spin-coupling mode along the chain. Since the coupling patterns are similar in central region of the fused-azulene chain for both singlet and triplet states, we may tentatively ascribe the unusual transition mostly to the end effects. In contrast, for [12]-acene, it is found that $\langle S_{\text{top}} S_{\text{bottom}} \rangle$ is −3.4 and −2.9 in the open-shell singlet and triplet states, respectively, stronger spin coupling between the top and bottom chains in the singlet state indicates antiferromagnetic ground state.

If we use Ovchinnikov’s rule,⁴¹ which is also known as Lieb’s theorem in solid state physics for a Hubbard

Hamiltonian,⁴² to predict the spin multiplicity of the ground state in infinite length conjugated molecules, it is easy to find that there is no difference in the spin distribution pattern in the singlet and triplet states, which will predict a zero energy gap between both states. However, both works are explicitly restricted to alternant systems, and the ground states are not necessarily given in nonalternant systems (such as fused azulene) by less frustrated spin distribution.⁴³ On the other hand, as one of the authors suggested recently,^{44–46} infinite fused azulene can be mapped into dimerized spin 1/2 chains, which may be considered as built from A and B blocks of 7 and 9 sites with different values J_1 , J_2 between the A - B and B - A blocks, according to Fig. 2(d). As a well-known result, dimerized $S = 1/2$ AB chain has suggested a singlet ground state with a finite gap. It is still difficult to judge which result is correct, more EVB calculation is still underwork to obtain the asymptotic gap in very large oligomers.

III. CONCLUSION

In summary, energy computation, electron spin distribution analysis as well as the strength of spin coupling between the top and the bottom edges of fused-azulene chain presented above support a transformation from a nonmagnetic ground state to a ferromagnetic ground state, with the increased length of fused-azulene chain. Further study of fused-azulene morphology edge in graphene nanoribbons has also been initiated in our group. Preliminary calculations have confirmed the existence of ferromagnetic ground state, at even shorter ribbon lengths.⁴⁷ One of the recent hot spot in “graphene rush” in material science community, which involves the disputes of the existence and origin of magnetic polarization in graphene nanoribbons, might be explained by the existence of the azulene-like edges, which can be generated from zigzag edge reorganization. In this respect, the present work does not only supply an explanation of the electronic structure of [n]-azulene, it also offers a theoretical track for the understanding of the electronic properties of graphene nanoribbons.

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