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A density-functional-theory study of biradicals from benzene to hexacene

Hyun-Jung Kim^a, Xingyong Wang^b, Jing Ma^{b,*}, Jun-Hyung Cho^{a,**}

^a Department of Physics and Research Institute for Natural Sciences, Hanyang University, 17 Haengdang-Dong, Seongdong-Ku, Seoul 133-791, Republic of Korea

^b School of Chemistry and Chemical Engineering, Institute of Theoretical and Computational Chemistry, Key Laboratory of Mesoscopic Chemistry of MOE, Nanjing University, Nanjing, Jiangsu 210093, People's Republic of China

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ABSTRACT

The singlet–triplet energy gap of biradicals created in benzene and polyacenes is investigated by density-functional-theory calculations. For the biradicals in benzene, naphthalene, anthracene, tetracene, penta-cene, and hexacene, we find that the singlet state is energetically favored over the triplet state by 189, 191, 184, 199, 218, and 244 meV, respectively. The monotonous increase of the singlet–triplet energy gap from anthracene to hexacene is attributed to the enhanced stability of the singlet state for longer polyacenes. Our analysis shows that the spin density of the singlet state is delocalized over all benzene rings, but such a spin delocalization is not present for the triplet state.

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1. Introduction

Organic radicals have attracted intensive attention because of their wide occurrence in organic reactions and biological processes [1,2] as well as for their potential technological applications such as organic magnets [3], electronic devices [4], and organic batteries [5]. Most organic radicals exist only as transient intermediates in a number of thermal and photochemical reactions [6,7]. Therefore, it is difficult to experimentally trace and handle such organic radicals with short lifetimes. Despite their fleeting existence, several biradicals with a singlet ground state have been successfully synthesized and characterized [8–10].

A biradical in organic chemistry is a molecular species with two unpaired electrons that act independently of each other [11,12]. Here, the spins of the two unpaired electrons can be either antiparallel or parallel, corresponding to the singlet or triplet state. The energy preference of the two states is determined by the exchange-coupling constant (J) within the Heisenberg Hamiltonian $\hat{H} = -J\hat{S}_1 \cdot \hat{S}_2$, where $\hat{S}_i$ is the spin operator of unpaired electron at each radical site. The negative (positive) sign of J indicates the preference of an antiferromagnetic (ferromagnetic) interaction between two unpaired electrons, leading to a singlet (triplet) ground state. Thus, the sign and magnitude of J reflect the nature of spin–spin interactions between two radical centers.

There are a number of theoretical studies [13–22] for the biradicals created in simple aromatic molecules such as benzene and naphthalene termed *para*-benzyne (Figure 1a) and 1,4-didehydronaphthalene (Figure 1b), respectively. All the theories predicted the preference of the singlet state over the triplet state, in

accordance with the experimental observation of the singlet ground state [10]. Such a singlet ground state may be expected for the biradicals created in longer polyacenes. This underlying antiferromagnetic correlation between two radicals in polyacenes is analogous to the antiferromagnetic order in graphene nanoribbons with zigzag edges [23,24]. Recently, it was also proposed that the two sp^3 -type defects (created by adsorbed atomic H) on graphene, which have a magnetic moment of $1 \mu_B$ localized on the π orbitals surrounding each H atom, interact ferromagnetically or antiferromagnetically, depending on whether their adsorption sublattices (usually labeled A and B) are the same or not [25–27]. Indeed, the fact that polyacenes can be viewed as the extreme cases of nanographenes implies that the microscopic physics in both systems would be quite similar to each other.

In this Letter, using first-principles density-functional calculations [28] within the generalized-gradient approximation [29], we investigate the singlet–triplet (ST) energy gap of biradicals created in benzene as well as polyacenes from naphthalene to hexacene (see Figure 1). Here, each biradical involves the two radical centers which are oppositely located on the two sides of the central benzene ring. For all the biradicals considered, we find that the singlet state is energetically favored over the triplet state. Especially, as the number (n) of benzene rings increases from 3 to 6, the ST energy gap monotonically increases. This result for longer polyacenes can be associated with a drastic difference of spin delocalization between the singlet and triplet states. It is found that the singlet state exhibits a spin delocalization over all benzene rings, whereas the triplet state has the spin density localized on the benzene ring containing the two radicals. Therefore, these different features of spin delocalization between the singlet and triplet states give rise to an enhanced relative stability of the singlet state compared to the triplet state with increasing n .

* Corresponding author. Fax: +82 2 2295 6868.

** Principal corresponding author.

E-mail addresses: majing@nju.edu.cn (J. Ma), chojh@hanyang.ac.kr (J.-H. Cho).

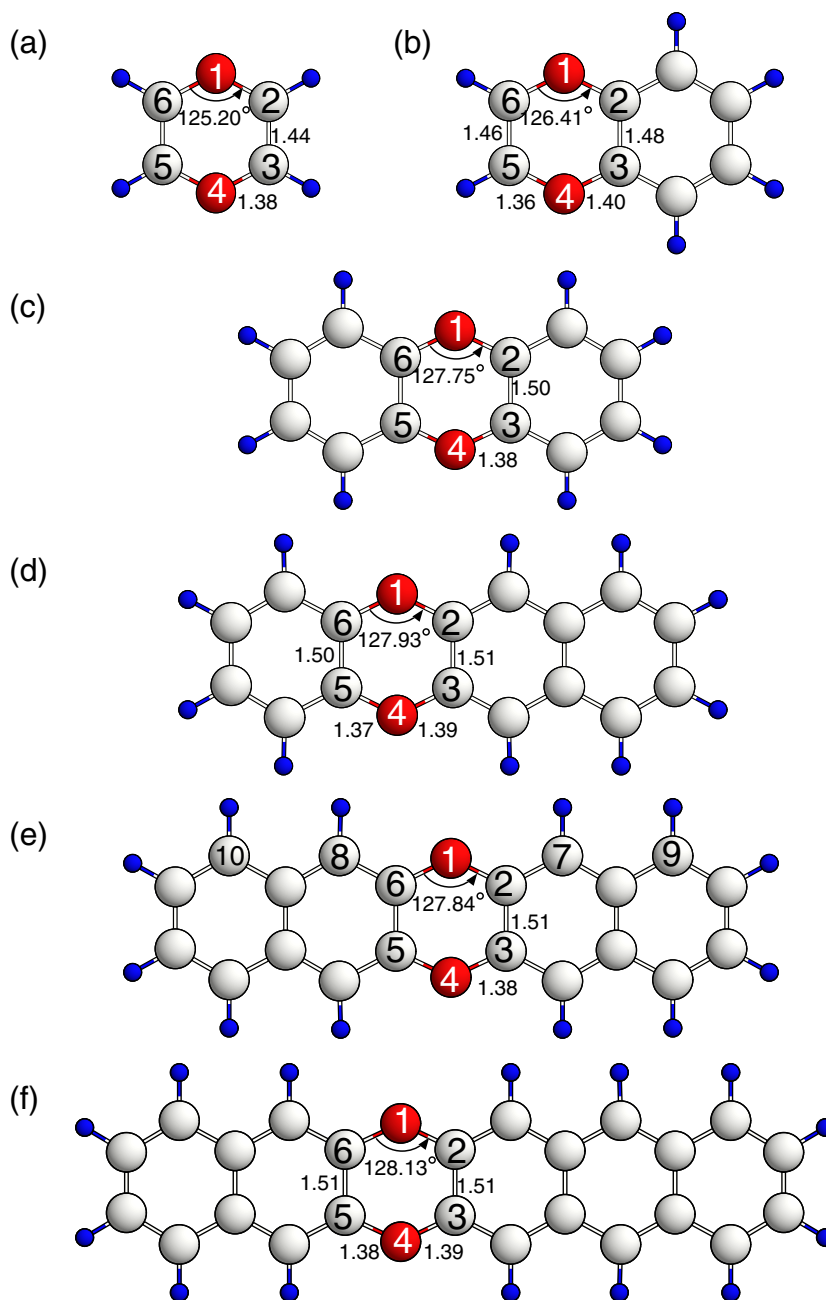


Figure 1. Optimized structure of the singlet state for the biradicals created in (a) benzene, (b) naphthalene, (c) anthracene, (d) tetracene, (e) pentacene, and (f) hexacene. The large and small circles represent C and H atoms, respectively. For distinction, two radical C atoms are represented with dark circles. The numbers denote the C–C bond length (in Å) and angle (in degree).

2. Computational methods

The total-energy and force calculations were performed by using spin-polarized density-functional theory [28] within the generalized-gradient approximation (GGA). We used the exchange–correlation functional of Perdew, Burke, and Ernzerhof (PBE) for the GGA [29]. The norm-conserving pseudopotential of H atom was constructed by the scheme of Troullier and Martins [30,31]. For C atom whose 2s and 2p valence orbitals are strongly localized, we used the Vanderbilt ultrasoft pseudopotential [32]. All the calculations were performed using $12.38 \times 17.15 \times 2.48$ ($n+5$) Å³ supercells with one **k**-point, where the length along the long axis of polyacenes varies with respect to n . The electronic wave functions were expanded in a plane-wave basis set using a

cutoff of 25 Ry. All the atoms were allowed to relax along the calculated Hellmann-Feynman forces until all the residual force components were less than 1 mRy/bohr. Our plane-wave-basis pseudopotential scheme has been successfully applied for various C-based materials [33].

3. Results and discussion

We begin to study the singlet and triplet states of the biradicals created in benzene and several polyacenes (i.e., naphthalene, anthracene, tetracene, pentacene, and hexacene) by means of the broken symmetry approach [34,35] based on density functional theory. Here, the energetics of the singlet and triplet states can be determined by performing spin-polarized geometry

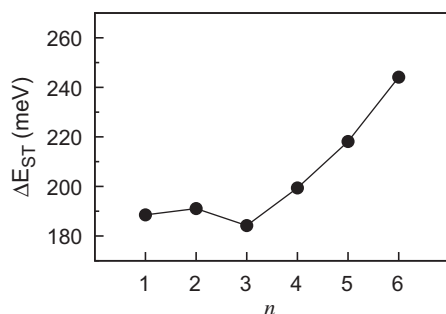


Figure 2. Calculated singlet-triplet energy gap of the biradicals created in benzene ($n = 1$) and polyacenes from naphthalene ($n = 2$) to hexacene ($n = 6$).

optimizations within the antiferromagnetic (AFM) and ferromagnetic (FM) configurations. We note that, although the AFM state obtained from the broken symmetry approach is not an eigenvector of S^2 (therefore it is not a pure state of the real system), the calculated ST gap has been successful in various magnetic systems [35]. For all the biradicals considered, we find that the AFM configuration has the lower energy compared to the FM configuration, resulting in the singlet ground state. The calculated ST energy gap, estimated as the energy difference ($\Delta E_{ST} = E_{FM} - E_{AFM}$) between the FM and AFM configurations [34,35], is plotted in Figure 2. The ST gaps for $n = 1, 2, 3, 4, 5$, and 6 are found to be 189, 191, 184, 199, 218, and 244 meV, respectively. It is interesting to note that the ST gap monotonically increases as n increases from 3 to 6.

To understand the variation of ΔE_{ST} with respect to n , we calculate the spin densities of the AFM and FM configurations from $n = 1$ to 6. The results are displayed in Figure 3. It is clearly seen that the spin density of the AFM configuration is delocalized over all benzene rings composing polyacenes, while that of the FM configuration is localized on the benzene ring containing the two radicals. Since more spin delocalization reduces electron–electron interaction energies, the AFM configuration can be more relatively stabilized compared to the FM configuration with increasing n .

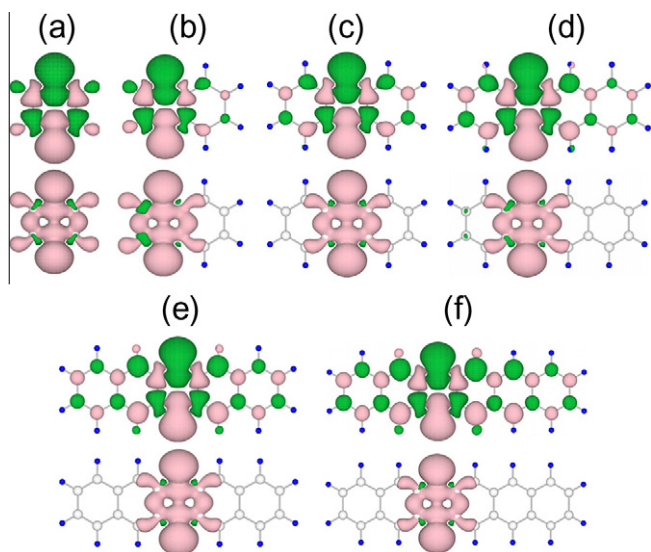


Figure 3. Calculated spin densities of the AFM (upper side) and FM (lower side) configurations for the biradicals created in (a) benzene, (b) naphthalene, (c) anthracene, (d) tetracene, (e) pentacene, and (f) hexacene. Here, the spin density is defined by the difference of charge densities $\rho_{up} - \rho_{down}$ between spin-up and spin-down electrons. The positive (negative) spin density is displayed in bright (dark) color with an isosurface of 0.01 (−0.01) electrons/Å³. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Table 1

Calculated ST energy gap for the biradicals created in benzene and polyacenes from $n = 2$ to 6, in comparison with those obtained using the FHI-aims code (Ref. [38]).

n	PBE	PBE (aims)	PBE0 (aims)
1	189	172	85
2	191	178	86
3	184	171	84
4	199	183	104
5	218	196	161
6	244	213	255

As a matter of fact, ΔE_{ST} monotonically increases with increasing n from 3 to 6 (see Figure 2). It is, however, seen that in $n = 1$ and 2, ΔE_{ST} deviates from its monotonous increase between $n = 3$ and 6. Note that ΔE_{ST} for $n = 1$ and 2 are slightly larger than that for $n = 3$ by 4 and 6 meV, respectively. This deviation of ΔE_{ST} for $n = 1$ and 2 represents the small-size effect that the AFM configuration has a minimal energy gain arising from spin delocalization while the FM configuration has an increased electron–electron repulsion due to a confinement within the small size of $n = 1$ and 2. Thus, the variation of the ST gap as a function of n is likely to be associated with the different features of spin densities between the AFM and FM configurations.

It is known that the GGA tends to give the delocalization (or self-interaction) error [36]. To see the effect of the correction of the self-interaction error on the ST gap, we performed spin-polarized calculations using the PBE0 functional [37] which includes 25% of Fock-exchange instead of the same amount of exchange in the PBE functional. For these PBE and PBE0 calculations, we used the FHI-aims code [38] to obtain the ST gap for $n = 1, 2, 3, 4, 5$, and 6. The results are listed in Table 1. We find that PBE gives the ST gaps for $n = 1, 2, 3, 4, 5$, and 6 as 172, 178, 171, 183, 196, 213 meV, respectively, in good agreement with the PBE results obtained by our pseudopotential plane-wave-basis code [33], while the corresponding PBE0 values are 85, 86, 84, 104, 161, and 255 meV, respectively. The general trend of the ST gap with the singlet ground state is preserved in both the PBE0 and PBE calculations. However, the PBE0 calculation shows a wide variation of the ST gap with respect to the length of polyacenes. Especially, for benzene and shorter polyacenes (i.e., $n = 2$ and 3), the partial use of Fock-exchange is found to significantly reduce the ST gap.

In Table 2, we compare the present results of ΔE_{ST} for $n = 1$ and 2 (i.e., *para*-benzynes and 1,4-didehydronaphthalene) with those obtained by previous [13–16] calculations. It is seen that the ST gap for *para*-benzynes (1,4-didehydronaphthalene) shows a wide variation ranging from 143 to 251 (from 199 to 243) meV depending on the employed calculation schemes such as CAS-BCC4 [13], CASPT2 [14], MCSCF+MP2 [15], and UBLYP/6-31G* [16]. Despite this wide variation of ΔE_{ST} for *para*-benzynes and 1,4-didehydronaphthalene, all the theories agree with each other, supporting the singlet ground state. The present value of $\Delta E_{ST} = 189$ meV for *para*-benzynes is within the range of previously calculated values, in good agreement with an experimental value of 165 meV measured by negative-ion photoelectron spectroscopy [10].

Figure 1 shows the optimized structures of the singlet ground state for the biradicals from $n = 1$ to 6, together with the C–C bond lengths ($d_{C_1-C_2}$) and angle (θ) in the central benzene ring. Note that the structures of odd (even) numbered $n = 1, 3, 5$ (2, 4, 6) are symmetric (asymmetric) under reflection through the line connecting the two radicals. We find that the values of $d_{C_1-C_2}$, $d_{C_2-C_3}$, and θ are saturated to be ~ 1.38 Å, ~ 1.51 Å and $\sim 128^\circ$ for the biradicals above $n = 3$. In Table 1, our results of $d_{C_1-C_2}$ and θ for $n = 1$ and 2 are compared with those obtained by previous [13–16] calculations, showing a good agreement with each other.

To examine the electronic properties of the biradicals within the AFM and FM configurations, we calculate the electronic energy

Table 2
Calculated ST energy gap and geometrical parameters for the biradicals created in benzene and naphthalene, in comparison with those obtained by previous calculations and experiment.

	This	CAS-BCC4 ^a	CASPT2 ^b	MCSCF+MP2 ^c	UBLYP/6-31G* ^d	Expt. ^e
<i>n</i> = 1						
ΔE_{ST} (meV)	189	143	251	208	178	165
$d_{\text{C1-C2}}$ (Å)	1.38	1.39		1.38	1.38	
$d_{\text{C2-C3}}$ (Å)	1.44	1.43		1.41	1.45	
$\angle \text{C}_6\text{-C}_1\text{-C}_2$ (°)	125.20	125.11		124.06	124.90	
$\angle \text{C}_1\text{-C}_2\text{-C}_3$ (°)	117.37	117.44		117.97	117.55	
<i>n</i> = 1						
ΔE_{ST} (meV)	191		243	221	199	
$d_{\text{C1-C2}}$ (Å)	1.40		1.42	1.41	1.40	
$d_{\text{C2-C3}}$ (Å)	1.48			1.43	1.50	
$d_{\text{C4-C5}}$ (Å)	1.36		1.36	1.36	1.36	
$d_{\text{C5-C6}}$ (Å)	1.46		1.44	1.44	1.47	
$\angle \text{C}_6\text{-C}_1\text{-C}_2$ (°)	126.41		124.9	124.91	126.22	
$\angle \text{C}_1\text{-C}_2\text{-C}_3$ (°)	116.10		117.0	117.05	116.11	
$\angle \text{C}_4\text{-C}_5\text{-C}_6$ (°)	117.48		118.0	118.05	117.66	

^a CAS-BCC4 taken from Ref. [13].

^b CASPT2 taken from Ref. [14].

^c MCSCF+MP2 taken from Ref. [15].

^d UBLYP/6-31G* taken from Ref. [16].

^e Experimental value taken from Ref. [10].

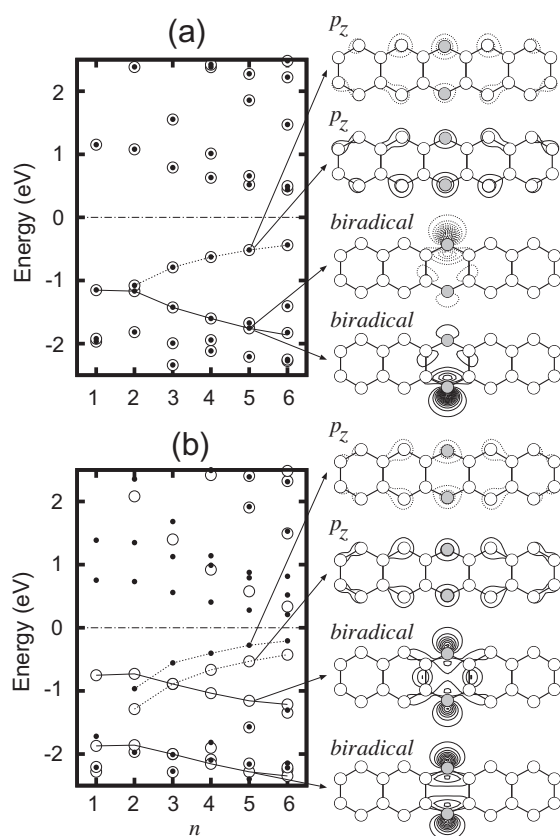


Figure 4. Calculated electronic energy levels and charge densities of eigenstates for (a) the AFM configuration and (b) the FM configuration as a function of the number of benzene rings. Open circles represent spin-up levels and small dots represent spin-down levels. The charge densities of the occupied spin-up (spin-down) states originating from p_z orbitals and biradical are drawn in solid (dotted) lines. In the contour plots, the first line is at 0.01 electrons/Å³ with spacings of 0.02 electrons/Å³.

levels and the spin characters of the two occupied eigenstates originating from p_z orbitals and biradical. The results are displayed in Figure 4. We find that as n increases, the energies of the occupied

states originating from p_z orbitals move upward, while those originating from biradical move downward. In Figure 4, for the AFM configuration the gap $\Delta E_{\text{HOMO-LUMO}}$ between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) is 2.31, 2.15, 1.58, 1.26, 1.04, and 0.87 eV from $n = 1$ to 6. Similarly, for the FM configuration the corresponding values are 1.46, 1.45, 1.12, 0.81, 0.56, 0.41 eV from $n = 1$ to 6. This decrease of $\Delta E_{\text{HOMO-LUMO}}$ with increasing n is analogous to the cases of polyacenes where $\Delta E_{\text{HOMO-LUMO}}$ decreases upon going from naphthalene to heptacene [39]. As shown in Figure 4a, the charge densities of eigenstates for the AFM configuration of $n = 5$ obviously represent a biradical character, excluding a possibility of the symmetric singlet state with a closed shell. It is noteworthy that spin characters of the occupied states originating from p_z orbitals show a drastic difference between the AFM and FM configurations. As shown in Figure 4, the spin-up and -down p_z orbitals in the AFM configuration are not equal to each other, leading to a spin delocalization over all benzene rings. On the other hand, for the FM configuration such a spin polarization of p_z orbitals is absent, remaining the radical spin densities localized on the benzene ring containing the two C-radical atoms.

Finally, we perform spin-polarized PBE calculations for several biradicals positioned on one side of pentacene as shown in Figure 5. We find that such biradicals termed 1,7-pentacene, 7,8-pentacene, 8,9-pentacene, and 9,10-pentacene favor energetically the FM configuration over the AFM configuration, yielding a triplet ground state. The calculated ST gaps for 1,7-pentacene, 7,8-pentacene, 8,9-pentacene, and 9,10-pentacene are −20, −21, −8, and −3 meV, respectively (see Figure 5a). Thus, we can say that the sign of the exchange coupling (antiferromagnetic or ferromagnetic) in biradicals considered in the present study is similar to that in the zigzag graphene nanoribbons, where the edge states are ferromagnetically ordered but the two ferromagnetic edges are antiferromagnetically coupled with each other. Figure 5b shows the spin densities of the AFM and FM configurations for various pentacene biradicals. It is seen that the spin density of the FM configuration is more delocalized compared to that of the AFM configuration, contrasting with the above-mentioned biradical cases. Especially, for the FM configuration, the spin delocalization of 1,7-pentacene and 7,8-pentacene is greater than that of 8,9-pentacene and 9,10-pentacene, thereby giving rise to the relatively larger magnitude of the ST gap.

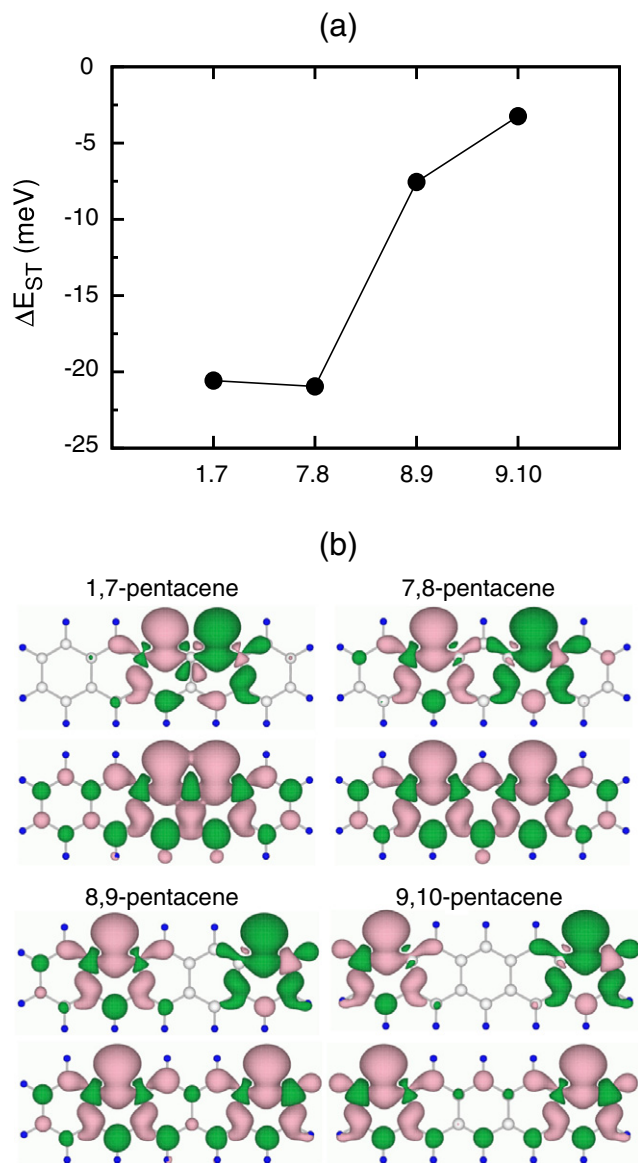


Figure 5. Calculated (a) singlet–triplet energy gap and (b) spin densities of various biradicals created in pentacene. The upper and lower sides in (b) represent the spin densities of the AFM and FM configurations, respectively. For numbering of C atoms, see Figure 1e. The positive (negative) spin density is displayed in bright (dark) color with an isosurface of 0.01 (–0.01) electrons/Å³. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

4. Summary

We have investigated the ST energy gap of biradicals created in benzene as well as polyacenes from naphthalene to hexacene using first-principles density-functional calculations within the generalized-gradient approximation. For all the biradicals considered, the singlet state is found to be energetically favored over the triplet state. Especially, the ST energy gap shows a monotonous increase from anthracene to hexacene, caused by the increased spin delocalization of the singlet state for longer polyacenes. It was re-

vealed that the spin delocalization of the singlet state is mediated by a spin polarization of p_z orbitals, contrasting with the triplet state where p_z orbitals are not polarized.

Acknowledgments

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