



Research paper

Theoretical investigation of structures and electromagnetic properties of double-electron oxidized ring-expanded base pairs

Mei Wang^{a,*}, Laibin Zhang^a, Yunxian Liu^a, Fufang Su^a, Jing Zhao^b, Mengmeng Zheng^a, Jing Li^a^aSchool of Physics and Physical Engineering, Qufu Normal University, Qufu 273165, China^bShandong Collegial Key Laboratory of Biotechnology and Utilization of Biological Resources, College of Life Science, Dezhou University, Dezhou 253023, China

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ABSTRACT

This work presents that the x-bases and xx-bases can be combined with their counterparts to form stable Watson-Crick ring-expanded base pairs. For double-electron oxidation Watson-Crick ring-expanded base pairs, they possess open-shell broken symmetry singlet states except for $[\text{xxGC}]^{2+}$. Some complexes exhibit a significantly large amount of diradical character and some of diradical base pairs also possess excellent magnetic characteristics. $[\text{xGC}]^{2+}$, $[\text{xAT}]^{2+}$ and $[\text{xxAT}]^{2+}$ show more and more strong AFM with the size expansion of guanine and adenine. The magnetic interactions get relatively weaker and weaker with the size expansion of cytosine and thymine. $[\text{xxTA}]^{2+}$ even manifests a weak FM character.

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1. Introduction

It is known that DNA bases can form stable base-pair through hydrogen bonds, and these base pairs can make up DNA helical structures through π -stacking in the one-dimensional direction. More specifically, DNA bases are π -aromatic, which improves electron conduction [1,2]. In the past decades, the study of their derivatives has attracted great interest as potential building blocks for self-assembled structures and electronic nano-devices [3–7]. To improve the electronic properties of limited native nucleic acids, DNA modification has developed into an important and active field of research [8–15].

Recently, much attention has been paid to design and synthesize un-natural nucleobases, since the Watson–Crick (WC) recognition pattern of DNA could be enlarged in principle by using un-natural nucleobase derivatives, which might expand the genetic alphabet and lead to new DNA duplexes with improved biotechnological properties [16–22]. Thus, several strategies have been adopted, such as using non-natural hydrogen-bonding patterns, metal-mediated pairs, and covalently lined base pairs. In particular, Kool and co-workers have synthesized ring-expanded DNA bases using the ring-expansion strategy, which are characterized by being a fusion between a natural base (A, C, G and T) and a benzene/naphthalene ring, and made outstanding contributions to this field [23–25]. Currently, there are three types of ring-expanded bases, the x-bases (xA, xC, xG and xT;), the y-base (yC and yT;) and the

yy-base (yyC and yyT). Among them, the x-bases and y-bases were obtained by benzo-homologation, while the yy-bases were obtained by naphtho-homologation. These newly synthesized bases have been proved to have more attractive properties than the natural bases for the following reasons. First, the delocalization π -bond is enlarged by the inserted benzene/naphthalene ring. The enhanced π - π coupling leads to stronger stacking interaction and a smaller HOMO (H)–LUMO (L) gap. Second, thanks to the extra benzene/naphthalene ring, these bases are fluorescent, a property making them good candidates for applications in nucleic acid research to study the structures and dynamics as well as the kinetics of interactions between DNA and other molecules. Third, the genetic alphabet has been expanded. These facts imply a potential application in the information storage technology.

High-spin state organic molecules have become the goal of many researchers. In recent decades, many theoretical chemists have been working on predicting the type (antiferromagnetic/ferromagnetic) of spin coupling in π -conjugated molecules. As an ideal matrix, the use of DNA has become a major strategy in biological, supramolecular and materials chemistry. For highly linear energy transfer radiation such as α particles or heavier ion beams, densely ionized orbitals are formed where the neighboring molecules have a much higher probability of ionization associated with radical formation [26–28]. The proximate radicals generated in these orbits are likely to form new molecular species with unique properties. It is expected that the formation of diradicals in the DNA base pair will form and undergo a radical–radical reaction by ionizing radiation with an increased probability as the linear energy transfer of the radiation increases. It is well known that the role of a coupler

* Corresponding author.

E-mail address: qfwmei@163.com (M. Wang).

between two radical centers or groups is extremely crucial for estimating intramolecular magnetic coupling interactions [29–31]. A large number of couplers which connect two radical centers or groups have been intensively investigated both theoretically and experimentally, exhibiting different magnetic coupling properties (ferromagnetic/FM versus antiferromagnetic/AFM couplings) [32,33]. Recently, we have discussed the $[\text{GC}]^{2+}$ [34] and $[\text{AT}]^{2+}$ [35] diradical systems. The results have shown some double-electron oxidized Watson–Crick GC base pairs with strong antiferromagnetic coupling. Most importantly, the energy gap between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) of the obtained x bases is less than the natural ones, indicating that they can expand the genetic alphabet and have potential for charge transfer and magnetic exchange. The resulting structures are expected to be more stable, since the π -conjugations in nucleobases are conducive for spin delocalization. These prompt us to initiate a procedure aimed at elucidating the double-electron oxidative electromagnetic properties of ring-extended WC base pair analogues. As present, xx-bases have not been synthesized experimentally. Therefore, it is necessary and meaningful to investigate the electronic properties of novel base pairs consisting of x-bases/xx-bases and their complementary bases theoretically. Theoretical investigations can be an important counterpart to the experimental investigations.

Here, we extend our research on double-electron oxidized ring-expanded WC base pairs ($[\text{xGC}]^{2+}$, $[\text{xCG}]^{2+}$, $[\text{xTA}]^{2+}$, $[\text{xAT}]^{2+}$, $[\text{xxGC}]^{2+}$, $[\text{xxCG}]^{2+}$, $[\text{xxTA}]^{2+}$, $[\text{xxAT}]^{2+}$, and $[\text{xxGC}]^{2+}$, respectively) by presenting ab initio results on their relevant structural characteristics, electronic and magnetic properties. We also intend to see what happens if the double-electron oxidation forms a diradical for the WC ring-expanded base pairs analogue. Some novel phenomena are found, for example, diradical character and more and more strong antiferromagnetic interaction for $[\text{xGC}]^{2+}$, $[\text{xAT}]^{2+}$ and $[\text{xxAT}]^{2+}$ with the size expansion of guanine and adenine. We hope these studies may provide valuable information not only fundamentally but also for various applications in biological systems.

2. Computational methods

The Gaussian03 suite of programs was used for all calculations [36]. The unrestricted B3LYP (Becke3 parameter exchange, Lee–Yang–Parr correlation) hybrid functional in combination with the 6-311++G** basis set [37] was used to carry out all molecular geometry optimizations. The optimized geometries were further confirmed to be local minima on the potential energy surfaces by vibrational analyses, which show no imaginary frequency. For each double-electron oxidized structure, we compute three states, which are closed-shell singlet (CS), open-shell broken symmetry (BS) singlet (OS), and open-shell triplet (OT) states. It is worth noting that the keyword “guess = mix” was used through the UB3LYP calculations for the BS state. This is because the UB3LYP singlet calculations can only obtain the results very similar to those at the restricted RB3LYP level for the singlet state and do not really reflect the polyradical character and the lowest state energies for the polyradical molecules. Natural bond orbital (NBO) and charge distribution are further analyzed. The same method is also adopted in the relevant electronic property calculations, which include spin densities, binding energies, ionization potentials (IPs), electron affinities (EAs), the gap (H–L gap) between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO), and the magnetic coupling constants (J).

For the magnetic coupling constants (J), their positive and negative values reflect anti-ferromagnetic (AFM) and ferromagnetic (FM) interactions between the two unpaired electrons in the design. In addition, the magnetic interactions for these diradicals

were determined by evaluating the Heisenberg coupling constant J. Therefore, the coupling constant J was calculated using a broken symmetry approach proposed within an unrestricted DFT framework, which has been viewed as the most appropriate one for estimating the magnetic exchange coupling constant of diradicals and was proposed by Yamaguchi and co-workers [38–40]. The formula is given as $J = (E_{\text{BS}} - E_{\text{T}}) / (\langle S^2 \rangle_{\text{T}} - \langle S^2 \rangle_{\text{BS}})$ where E_{BS} and E_{T} refer to the energies of the unrestricted open-shell BS singlet and triplet states, while $\langle S^2 \rangle_{\text{BS}}$ and $\langle S^2 \rangle_{\text{T}}$ are the corresponding average spin square $\langle S^2 \rangle$ values, respectively.

To confirm the diradical character of the base pairs formed by the ring-expanded bases, the orbital occupation number characters of the corresponding base pairs were also calculated directly by using the complete active space self-consistent field (CASSCF) method with 10 orbitals and 10 electrons and 6-31G* basis set level [41]. The CASSCF calculations were carried out only with the 6-31G* basis set to reduce the computational cost and also make the CASSCF calculations possible.

3. Results and discussion

3.1. Optimized geometries

3.1.1. Ring-expanded bases

Schematic diagrams of eight ring-expanded bases (x-bases and xx-bases) are shown in Fig. 1. They are proved stable by the optimization and frequency calculations. It can be seen that the most significant change brought by the introduction of benzene ring is an expansion of molecular size. The B3LYP method reveals that the x-bases have nonplanar geometries, similar to xxG, xxC, and xxA, which is caused by the inherent pyramidalization of amino groups and the nonplanarity of the aromatic rings, while xxT has a planar ground-state geometry because it does not possess external $-\text{NH}_2$ groups. Besides this, the structural character is hardly affected. The bond length differences between ring-expanded bases and the natural ones are no more than 0.02 Å. Table S1 gives the adiabatic and vertical ionization potentials, electron affinities, and HOMO–LUMO gaps of the isolated bases, which are quite important to understand electron transfer processes along the DNA chain. The IPs and EAs are calculated with the formula which is widely used to deal with nucleobases [42]. The adiabatic IPs (AIPs) of four nucleobases are about 7.663–9.288 eV with an order of $\text{G} < \text{A} < \text{C} < \text{T}$. For comparison purposes, we also show HOMO–LUMO gap for the x-bases in previous studies [43]. These data are well consistent with previous theoretical and experimental studies [44,45]. This shows that the theoretical method which has been employed in this work is credible. An inspection of Table S1 reveals that the IP value decreases gradually with the ring-expanded bases, while the AEA/VEA value increases gradually with the ring-expanded bases. Meanwhile, it is noteworthy that the IP order ($\text{xG} < \text{xA} < \text{xC} < \text{xT}$ and $\text{xxG} < \text{xxA} < \text{xxC} < \text{xxT}$) is the same as that of the natural bases. That is, xxG has the lowest IP, suggesting that the benzo homologation would not change the fact that the purine moiety is the most easily oxidized base among DNA nucleobases. Thus, the electron-loss center created in an xx-DNA duplex will be most likely localized on xxG. The adiabatic electron affinity (AEA) values of the natural nucleobases range from -0.351 to 0.016 eV, which are basically consistent with the reported data, too. Both the AEA and VEA values are increased thanks to the addition of benzo/naphtho. That is, x-bases and xx-bases can be easier to capture electrons than the natural bases. The H–L gaps of xx-bases are smaller than those of x-bases. Considering that IPs and H–L gaps are two important indexes of conductivity, the ring-expanded bases are suggested to be candidates for applications in nanowire technology.

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