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Electronic structure study of the triplet azulene-like molecules

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ABSTRACT

In this Letter a detailed electronic structure study of singlet and triplet states of a series of azulene-like molecules was performed using several DFT and complete active space (CAS) methods. According to the results obtained at the B3LYP level of theory using the unrestricted symmetry-broken method, the singlet–triplet splitting for the members of the series with three and more hexagons is quite small, and in addition, four members of the series were found to be triplet diradicals. The CASSCF calculations revealed that higher members of the series of the azulene-like molecules with six and more hexagons are triplet diradicals.

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1. Introduction

Azulene is an important representative of the nonalternant conjugated hydrocarbons family. Although azulene and naphthalene are isoelectronic, azulene is blue while naphthalene is colorless. The characteristic electronic spectrum and electronic excitations of the azulene molecule have been used as a test model for several quantum chemical methods, starting from the early post-Hückel theories [1] to the more sophisticated *ab initio* approaches [2–4]. In addition, the aromaticity of azulene has been the subject of numerous studies [5–7].

In the present Letter we are concerned with a series of azulene-like molecules (Figure 1). Azulene-like molecules are important in several contexts. They are the members of polycyclic aromatic compounds (PAHs). PAHs have been the subject of interest of chemists for more than a century, because of their importance in many diverse fields, such as materials and nanoscience [8,9], theoretical organic chemistry [10–12] and astrochemistry [13]. Many of these compounds are extremely hazardous environmental pollutants generated during incomplete combustion of hydrocarbon-containing fuel sources [14,15]. On the other hand, it has been found that some of azulene derivatives are responsible for biological activity of some plant extracts and have important pharmaceutical applications [16]. In a recent work, Zhou et al. [17] have performed a DFT study showing that the azulene-like molecules can be used as molecular rectifiers.

The structural similarity between the azulene-like molecules (Figure 1) and linear polyacenes is evident. The nature of the electronic ground state for the higher homologues of the polyacene series has been examined in a number of papers [18–23]. Some research groups have proposed that longer acenes may possess an unusual electronic ground state that is not a simple closed-shell

singlet, but the open-shell singlet state with large amount of diradical character [18–20]. In addition, Reyne et al. have shown that the broad range of popular DFT methods predict a triplet as the ground state of higher polyacenes [21]. On the other hand, Hajgato et al. [22,23] have performed high-level quantum chemical studies, which strongly suggest that all linear polyacenes have a closed-shell singlet ground state. Their singlet–triplet energy gap approaches to zero with the increasing polyacenes size, but is never negative.

The electronic structure of open-shell singlet molecules with Kekulé structures has been much examined in the recent past [24–33]. Experimental and theoretical methods have been used to investigate the diradical character of Chichibabin's hydrocarbon [24], substituted fluoranthenes [25], phenalenyl-based hydrocarbons [26–31], polyacenequinododimethides [32], zethrenes [33,34] and multi-zinc-expanded oligoacenes [35]. The question whether Kekulé system can exist in a triplet ground state is another interesting problem. The only experimentally characterized Kekulé triplet diradical is 2,2-dimethyl-2H-dibenzo[cd,k]fluoranthene [25,36]. In our recent works [37,38], the DFT calculations showed that some fluoranthenes are triplet diradicals, implying that their ground state is a triplet. It was observed that the molecules which exhibit diradical character have very small number of Kekulé structures, i.e. very large number of fixed single and double bonds. These fixed single and double bonds disable the π -electron delocalization, and invoke energetic destabilization. For this reason, such molecules rather exist as singlet or triplet diradicals, whose electronic structure enables the π -electron delocalization, and thus, aromatic stabilization. In addition, all known triplet diradicals are large molecules [25,37,38], as large molecules enable two unpaired electrons to avoid each other as much as possible.

Already in 1975, Aihara supposed that some azulene-like molecules may have triplet ground state [5], but this assumption has never been confirmed. In addition, all azulene-like molecules have exactly two valence Kekulé structures. Provoked by the Aihara's

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