
STRUCTURE OF MATTER
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DFT Study on Singlet Diradical Character of Zethrenes¹

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Abstract—The diradical character of zethrenes was investigated using a symmetry-broken UB3LYP/6-311G(*d, p*) method. The number of hexagons in the investigated molecules ranges from 6 to 12. It was found that all zethrenes are singlet diradicals, whose diradical character increases with the increasing size of the molecules. A singlet diradical structure provides a possibility for an electron pair to occupy different parts of space, and allows for achieving aromatic stabilization. It can be predicted, on the basis of the singlet–triplet values, that even higher zethrenes will be singlet, but not triplet molecules.

Keywords: zethrenes, singlet diradical character, density functional theory calculations.

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INTRODUCTION

Density functional theory calculations of large systems sometimes produce energetically quasi-degenerate orbitals that cause a static correlation effect. One of the alternatives to include a correction of the static correlation with reasonable computational costs is the unrestricted symmetry-broken method. This method allows a spin-symmetry breaking and approximates the static correlation correction by splitting α and β electrons into two different orbitals. In the symmetry-broken method a singlet spin state with strong static correlation is expressed as a singlet diradical.

A singlet diradical can be defined as a molecular species that has all paired electrons, but a pair of these electrons occupy different parts of space with a small sharing region. The ground state of such species is a singlet, yet they exhibit diradical character. On the other hand, a pure diradical is a molecular species with two electrons occupying two degenerate, or nearly degenerate, molecular orbitals. In this paper we are focused on Kekuléan hydrocarbons, i.e., hydrocarbons for which at least one Kekule structural formula can be written.

The electronic structure of singlet diradicals with Kekule structures has attracted much attention [1–14]. Experimental and theoretical methods were used to investigate the diradical character of Chichibabin's hydrocarbon [1], substituted fluoranthenes [3], linear polyacenes [4, 7, 9, 14], phenalenyl-based hydrocarbons [5, 6, 8, 11–13], and zethrenes [10]. On the other hand, the question whether Kekuléan system can exist

in a triplet ground state has been less thoroughly examined. An assumption that a sufficiently small HOMO–LUMO gap should allow the promotion of an electron to produce a diradical, resulted in proposing cyclohepta[*def*]fluorene [15] and nonacene and higher linear polyacenes [16–18] as possible representatives of triplet Kekuléan hydrocarbons. However, cyclohepta[*def*]fluorene has never been synthesized.

In addition, Bendikov et al. showed that the RB3LYP wave function becomes unstable for polyacenes as small as hexacene, and all higher polyacenes [4], implying that the calculated energies for singlet states are unrealistically high. They performed reoptimization applying the unrestricted symmetry-broken method, and showed that higher polyacenes exist in a singlet state with large amount of diradical character. In agreement with the findings of Bendikov et al., high level *ab initio* calculations showed that the ground state of linear polyacenes is a singlet for all chain lengths from naphthalene to dodecacene [9]. Furthermore, the assumptions that anthracene-2,3-dimethylene [19], cyclopenta[*a*]cyclopenta[*i*]anthracene [20], as well as pleiadene and benzopleiadene [21–24] are triplet Kekuléan hydrocarbons have never been confirmed.

The only Kekuléan hydrocarbon whose triplet state has been confirmed experimentally is 2,2-dimethyl-2*H*-dibenzo[*cd,k*]fluoranthene [3, 25]. The compound was generated photochemically, and examined spectroscopically in cryogenic matrix, and in solution using nanosecond laser flash photolysis. On the basis of spectroscopic measurements, trapping experiments, and DFT calculations, the singlet–triplet gap

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