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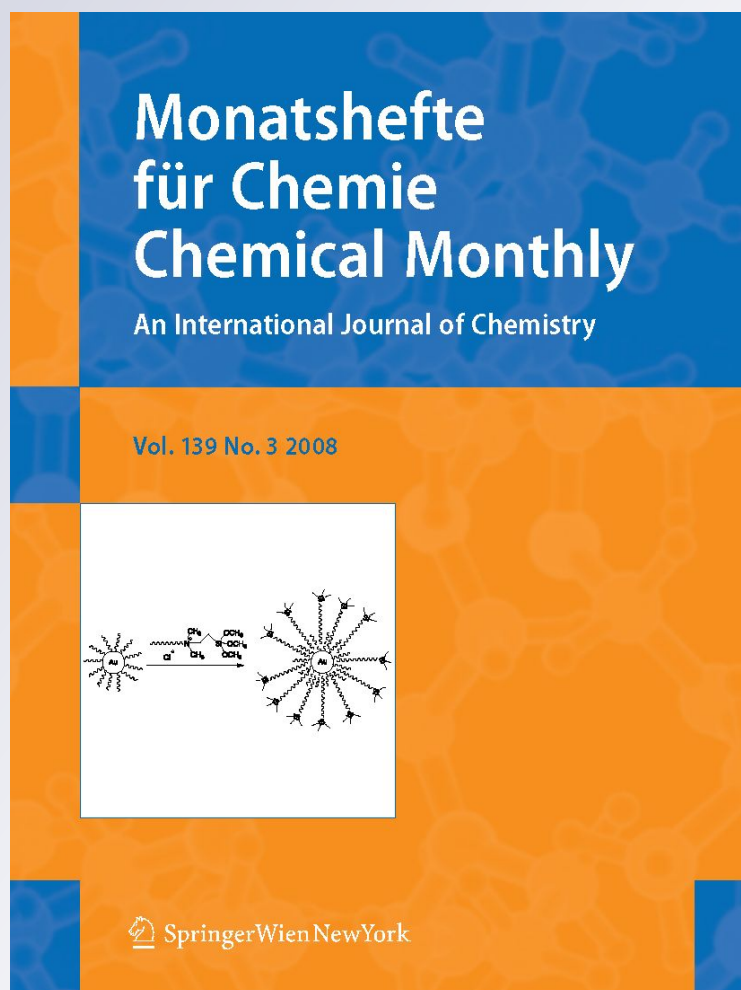
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The diradical character of polyacenequinododimethides

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Abstract An electronic structure study of singlet and triplet states of two series of polyacenequinododimethides was performed using the B3LYP method. It was found that the ground state of all examined polyacenequinododimethides is a singlet with significant diradical character. The diradical character of the compounds under investigation was estimated using the unrestricted symmetry-broken and complete active space methods. It was shown that polyacene-2,3-quinododimethides have more pronounced diradical character than polyacene-2,*x*-quinododimethides. The diradical character of polyacene-2,*x*-quinododimethides monotonically increases with their increasing molecular size. Within the series of polyacene-2,3-quinododimethides the diradical character is not a monotonic function of the number of hexagons. It was found that pentacene-2,3-quinododimethide has the most pronounced diradical character in this series. It can be predicted on the basis of the singlet–triplet gap values that even higher polyacenequinododimethides will be singlet, but not triplet molecules.

Keywords Polycyclic aromatic hydrocarbons · Singlet–triplet gap · Density functional theory · Electronic structure · Diradicals · Singlet diradicals

Introduction

Polyacenequinododimethides are a class of polycyclic aromatic hydrocarbons (PAHs), compounds that have

continuously attracted scientists' attention for almost a century [1–5]. Research in PAH chemistry has experienced a surge during the last decades, as these hydrocarbons are of importance in many diverse fields, such as materials and nanoscience, theoretical organic chemistry, and astrochemistry [2–5]. On the other hand, PAHs constitute an important group of environmental pollutants generated during incomplete combustion of hydrocarbon-containing fuel sources [6–8].

It has been widely accepted that polyacenequinododimethides are olefinic in nature [9] because only one classical resonance structure having no conjugated circuits [10] can be written for them. These hydrocarbons possessing exocyclic methylene groups have been used as polyene-like reference structures in homodesmotic reactions [11, 12]. In recent work [13], Aihara et al. showed that polyacenequinododimethides are moderately aromatic and that the conjugated circuit model cannot be applied to these molecules.

The presence of two methylene groups in molecules depicted in Fig. 1 causes these molecules to exist in a single Kekulé structure. This distinctive feature of these polycyclic molecules was the reason to suspect that molecules from this class can be triplet Kekuléan hydrocarbons [14]. In the present work, the B3LYP method was used to examine the electronic structure of series of polyacene-2,*x*-quinododimethides (2,*x*-dimethylene-2,*x*-dihydropolyacenes) and polyacene-2,3-quinododimethides (2,3-dimethylene-2,3-dihydropolyacenes).

It is known that density functional theory calculations of large systems sometimes produce energetically quasidegenerate orbitals that cause a static correlation effect. Although computationally demanding, the complete active space (CAS) method is a straightforward way to include a correction of the static correlation. One of the alternatives to decrease the computational costs is the unrestricted

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