

Triplet fluoranthenes: Aromaticity versus unpaired electrons

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Abstract Three fluoranthenes and one substituted fluoranthene, 2,2-dimethyl-2*H*-dibenzo[*cd,k*]fluoranthene, were investigated using the unrestricted symmetry-broken and complete active space methods. It was shown that four Kekuléan hydrocarbons are diradicals, implying that their ground state is a triplet. In the energetically less favorable singlet state these hydrocarbons exhibit pronounced diradical character. This occurrence is explained with the tendency of the investigated molecules to delocalize their π -electrons. This leads to aromatic stabilization which is stronger than destabilization due to unpaired electrons. Our results for 2,2-dimethyl-2*H*-dibenzo[*cd,k*]fluoranthene are in excellent accord with experimental findings of McMaster et al. concerning this compound.

Keywords Complete active space calculation · Diradical · Singlet diradical · Triplet state · Unrestricted symmetry-broken method

Introduction

Fluoranthene is a well-known conjugated hydrocarbon present in large amounts in coal tar [1]. It consists of a benzene and naphthalene unit, joined through a five-

membered ring. Other polycyclic conjugated hydrocarbons consisting of two benzenoid units joined through a five-membered ring are referred to as fluoranthenes [2]. Interest for nonalternant polycyclic compounds of this kind has recently much increased, after the discovery that these are formed from benzenoid hydrocarbons in flash vacuum pyrolysis experiments (see [3, 4] and the references cited therein).

A polycyclic conjugated hydrocarbon is said to be *Kekuléan* if it possesses at least one Kekulé structure, i.e., a resonance formula in which all carbon atoms are pairwise joined by double bonds [5, 6].

While studying π -electron properties of fluoranthenes [7–9], we observed that there is a class of such compounds that possesses unusual Kekulé structures [10]. The Kekulé structures of these fluoranthenes possess a significant number of fixed single and double bonds. Some characteristic representatives of these species are the fluoranthene congeners 1–3, depicted in Fig. 1.

Since the compounds 1–3 are Kekuléan, one would expect a singlet ground state for them. Surprisingly, however, our DFT calculations indicated that 1–3 are diradicals, implying that their triplet ground states are energetically more favorable than the singlet states. In addition, their singlet ground states exhibit a significantly large amount of diradical character.

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 a pronounced diradical character. On the other hand, a diradical is a molecular species with two electrons occupying degenerate, or nearly degenerate, molecular orbitals (resulting in a triplet ground state). In this paper we will focus on Kekuléan diradical hydrocarbons.

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