

Electronic offprint
for author's personal use

JSCSEN 75(9)1167–1313(2010)

UDC 54:66

ISSN 0352–5139

Journal of the Serbian Chemical Society

Electronic version

VOLUME 75

No 9

BELGRADE 2010

Available on line at



www.shd.org.rs/JSCS/

The full search of JSCS
is available through

DOAJ DIRECTORY OF
OPEN ACCESS
JOURNALS
www.doaj.org



J. Serb. Chem. Soc. 75 (9) 1241–1249 (2010)
JSCS–4047

Journal of
the Serbian
Chemical Society

JSCS-info@shd.org.rs • www.shd.org.rs/JSCS

UDC 547.686.004.12:548.12:519.6

Original scientific paper

Diradical character of some fluoranthenes

SVETLANA MARKOVIĆ*, JELENA ĐURĐEVIĆ, SVETLANA JEREMIĆ
and IVAN GUTMAN[#]

*Faculty of Science, University of Kragujevac, 12 Radoja Domanovića,
34000 Kragujevac, Serbia*

(Received 19 April, revised 18 May 2010)

Abstract: It is shown that some Kekuléan fluoranthenes are diradicals and that their ground state is a triplet. In the energetically less favorable singlet state, these hydrocarbons also exhibit pronounced diradical character. The diradical character y of the compounds under investigation was estimated using the unrestricted symmetry-broken (y PUHF) and complete active space (y NOON) methods. It was found that the y PUHF values better reproduce the diradical character of the investigated hydrocarbons. It was shown that singly occupied molecular orbital (SOMO) and SOMO-1 of a diradical structure occupy different parts of space with a small shared region, resulting in a spin density distribution over the entire molecule. The spatial diradical distribution in the singlet diradical structures was examined by inspecting the HOMOs and LUMOs for α and β spin electrons. It was shown that the α -HOMO and the β -LUMO (as well as the β -HOMO and the α -LUMO) occupy practically the same part of space. In this way, there are no unpaired electrons in a singlet diradical structure, yet two of them occupy different parts of space, thus allowing the π -electrons to delocalize.

Keywords: fluoranthenes; diradical; singlet diradical; triplet diradical; unrestricted symmetry-broken method; complete active space calculation.

INTRODUCTION

Density functional theory calculations of large systems sometimes produce energetically quasi-degenerate 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 symmetry-broken method, which allows a spin-symmetry breaking and approximates the static correlation correction by splitting α and β electrons into two different orbitals. In

* Corresponding author. E-mail: mark@kg.ac.rs

[#] Serbian Chemical Society member.

doi: 10.2298/JSC100419080M



