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## 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*

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**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  $\gamma$  of the compounds under investigation was estimated using the unrestricted symmetry-broken ( $\gamma$ PUHF) and complete active space ( $\gamma$ NOON) methods. It was found that the  $\gamma$ 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  $\alpha$  and  $\beta$  spin electrons. It was shown that the  $\alpha$ -HOMO and the  $\beta$ -LUMO (as well as the  $\beta$ -HOMO and the  $\alpha$ -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  $\pi$ -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  $\alpha$  and  $\beta$  electrons into two different orbitals. In

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

# Serbian Chemical Society member.

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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 electrons paired, but a pair of these electrons occupies different parts of space with a small shared 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. We are interested in the usual case when this diradical is in a triplet ground state. In this paper, we are concerned with Kekuléan diradical hydrocarbons, *i.e.*, hydrocarbons for which at least one Kekulé structural formula can be written.

The electronic structure of singlet diradicals with Kekulé structures has attracted much attention.<sup>1–14</sup> Experimental and theoretical methods were used to investigate the diradical character of Chichibabin's hydrocarbon,<sup>1</sup> substituted fluoranthenes,<sup>3</sup> linear polyacenes,<sup>4,7,9,14</sup> phenalenyl-based hydrocarbons,<sup>5,6,8,11–13</sup> and zethrenes.<sup>10</sup> 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 cyclohepta[*def*]fluorene<sup>15</sup> and nonacene and higher linear polyacenes<sup>16–18</sup> being proposed 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,<sup>4</sup> 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 a 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.<sup>9</sup> Furthermore, the assumptions that anthracene-2,3-dimethylene,<sup>19</sup> cyclopenta[*a*]cyclopenta[*i*]anthracene,<sup>20</sup> as well as pleiadene and benzopleiadene<sup>21–24</sup> are triplet Kekuléan hydrocarbons have never been confirmed.

The only Kekuléan hydrocarbon the triplet state of which has been confirmed experimentally is 2,2-dimethyl-2*H*-dibenzo[*cd,k*]fluoranthene (**6** in Fig. 1).<sup>3,25</sup> The compound was generated photochemically and examined spectroscopically in a 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 of **6** was estimated to be 3.3–5.4 kJ/mol in favor of the triplet. It is worth mentioning that the DFT calculation was actually performed on a relative of **6** (the compound in which – for the sake of computational feasibility – the methyl groups of **6** were replaced with H atoms).

In a series of recent papers,<sup>26–35</sup> we studied various  $\pi$ -electron properties of fluoranthenes were studied including also their Kekulé structures.<sup>33,34</sup> Based on the observations made in,<sup>33,34</sup> some triplet-ground-state Kekuléan fluoranthenes were recognized.<sup>35</sup>

Fluoranthenes are polycyclic conjugated hydrocarbons consisting of two benzenoid units joined through a five-membered ring.<sup>26</sup> Interest in nonalternant polycyclic compounds of this kind has recently greatly increased, after the discovery that these compounds are formed from benzenoid hydrocarbons in flash vacuum pyrolysis experiments.<sup>36,37</sup> As fluoranthenes are Kekuléan hydrocarbons, one would expect a singlet ground state for them. Surprisingly, DFT calculations revealed that some fluoranthenes are diradicals, implying that their triplet ground state is energetically more favorable in comparison to the singlet state. In addition, their singlet ground state possesses a significant amount of diradical character. This phenomenon was explained by the tendency of the investigated molecules to delocalize their  $\pi$ -electrons. This leads to aromatic stabilization, which is stronger than the destabilization caused by the unpaired electrons.

In this work, some additional fluoranthene diradicals are reported. The triplet hydrocarbon **6** and the well-defined singlet fluorantheno[8,9-*b*]triphenylene (**7** in Fig. 1) were included in the investigation. The diradical character of the fluoranthenes under investigation is discussed in detail.

#### COMPUTATIONAL METHODS

All calculations were performed with the Gaussian 03W, version 6.1, program package,<sup>38</sup> at the B3LYP/6-311G(d,p) level of theory.<sup>39,40</sup> The frequency calculations showed that the examined structures have no imaginary vibrational frequencies. The hydrocarbons were calculated in their singlet and triplet states using the restricted and unrestricted schemes for closed-shell and open-shell calculations, respectively.

The singlet diradical character of the investigated hydrocarbons was estimated using two approaches. In the first approach, a CASSCF(6,6) method in the RB3LYP/6-311G(d,p) optimized geometry was used. The diradical index  $\gamma_{\text{NOON}}$  was determined according to the NOON (natural orbital occupation number) analysis,<sup>41</sup> *i.e.*, based on the occupation number ( $n$ ) of the LUMO, resulting from the CAS calculation. In the second approach, a symmetry-broken UB3LYP/6-311G(d,p) method along with geometry optimization was applied. The diradical index  $\gamma_{\text{PUHF}}$ , related to the HOMO and LUMO for singlet states, is defined by the weight of the doubly-excited configuration in the multi-configurational MC-SCF theory, and is formally expressed in the case of the spin-projected UHF (PUHF) theory as:<sup>10,42,43</sup>

$$\gamma_{\text{PUHF}} = 1 - \frac{2T}{1+T^2} \quad (1)$$

where  $T$  is the orbital overlap between the corresponding orbital pairs, and can be calculated using the occupation numbers of UHF natural orbitals:

$$T = \frac{n_{\text{HOMO}} - n_{\text{LUMO}}}{2} \quad (2)$$

The applicability of both approaches was tested based on the results for singlet fluoranthene **7** and compound **6**, the triplet state of which has been confirmed experimentally.<sup>3,25</sup>

### RESULTS AND DISCUSSION

The optimized geometries of the investigated fluoranthenes are presented in Fig. 1. The molecules **4** and **7** are planar, whereas in **6** only the two methyl groups deviate from planarity. The other investigated molecules afford non-planar geometries, due to the repulsion of the hydrogen atoms located on the opposite sides of the bays. The results of this research are summarized in Table I.

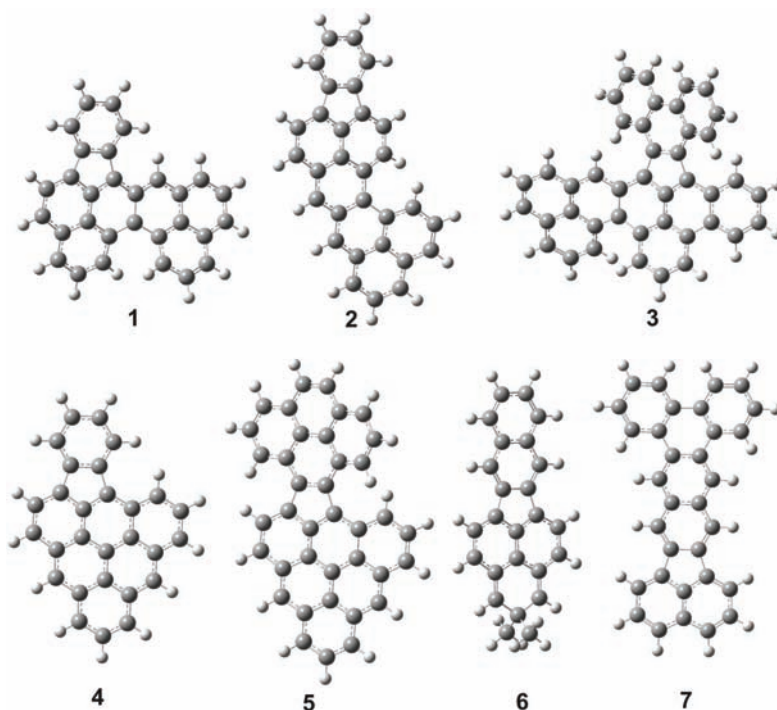


Fig. 1. Optimized geometries of triplet (1–6) and singlet (7) fluoranthenes.

As expected, the application of the symmetry-broken method to the triplet **6** led to a negative singlet–triplet gap, whereby the calculated value perfectly matched the experimental estimation. In the case of **7**, the singlet–triplet gap was positive. In addition, there was no energy lowering ( $\Delta E_{OS-CS} = 0.0$  kJ/mol) or invoked structural changes, in comparison to the closed-shell calculation. These findings are in harmony with the fact that **7** is a singlet Kekuléan hydrocarbon. All these facts confirm the applicability of the unrestricted symmetry-broken method to the hydrocarbons under investigation. According to the values for  $\Delta E_{T-OS}$  and  $\Delta E_{OS-CS}$  in Table I, hydrocarbons **1–6** are pure diradicals, the less favorable

singlet states of which are best described by the unrestricted symmetry-broken method, and show pronounced diradical character.

TABLE I. Difference in the total energy ( $\text{kJ mol}^{-1}$ ) between the open-shell symmetry-broken singlet and the closed-shell RB3LYP solution ( $\Delta E_{\text{OS-CS}}$ ), singlet–triplet gap ( $\Delta E_{\text{T-OS}}$ ),  $n$ LUMO and diradical character  $y$  (%), calculated using the NOON and PUHF approaches, and the orbital overlap  $T$

Compound	$\Delta E_{\text{OS-CS}}^{\text{a}}$	$\Delta E_{\text{T-OS}}^{\text{b}}$	$n$ LUMO (NOON)	$y$ NOON	$n$ LUMO (PUHF)	$T$	$y$ PUHF
<b>1</b>	-37.3 <sup>26</sup>	-16.5 <sup>26</sup>	0.431	43	0.979	0.021	96
<b>2</b>	-36.5 <sup>26</sup>	-16.1 <sup>26</sup>	0.495	50	0.955	0.045	91
<b>3</b>	-12.5	-10.9	0.175	18	0.943	0.057	89
<b>4</b>	-23.9	-17.7	0.085	8	0.890	0.110	78
<b>5</b>	-5.4 <sup>26</sup>	-5.2 <sup>26</sup>	0.128	13	0.785	0.215	59
<b>6</b>	-32.6 <sup>26</sup>	-7.5 <sup>26</sup>	0.412	41	0.925	0.075	85
<b>7</b>	0.0	192.4	0.083	8	0.293	0.707	6

<sup>a</sup>Open shell singlet energy minus RB3LYP singlet energy; <sup>b</sup>triplet energy minus open shell singlet energy

The diradical character of the investigated compounds is numerically expressed by means of the  $y$ NOON and  $y$ PUHF values (Table I). It is worth pointing out that both approaches assume that the diradical index ranges from 0 % for the closed-shell state to 100 % for the pure diradical state. Taking into account that **1–6** are pure diradicals, the  $y$ NOON values are relatively low. In addition, the value for the singlet hydrocarbon **7** (8 %) is identical to that for the triplet fluoranthene **4**. On the other hand, the  $y$ PUHF value for **7** (6 %) is negligible in comparison to the significantly higher  $y$ PUHF values for triplet hydrocarbons. In addition, the orbital overlap  $T$  decreases with increasing diradical character. It turns out that, in spite of the simplicity of the scheme using the unrestricted natural orbitals (UNOs), it successfully reproduces the diradical character of the investigated molecules.

The unpaired electrons reside in the delocalized singly occupied molecular orbitals (SOMOs) of each diradical. As an illustration, the SOMO, SOMO-1, and spin density map for triplet **1** (**1T**) are presented in Fig. 2. The SOMO and SOMO-1 are almost degenerate (-0.173 and -0.182 eV). Obviously, SOMO and SOMO-1 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 the  $\alpha$  and  $\beta$  spin electrons. The frontier orbitals for the  $\alpha$  and  $\beta$  spin electrons of triplet **1** and singlet **7**, calculated using the unrestricted symmetry-broken method (**1OS** and **7OS**), are depicted in Figs. 3 and 4, respectively. A remarkable feature of Fig. 3 is that the  $\alpha$ -HOMO and  $\beta$ -LUMO of **1OS** occupy practically the same part of space, involving approximately 0.51+0.49 electrons. The same situation was found in the case of the  $\beta$ -

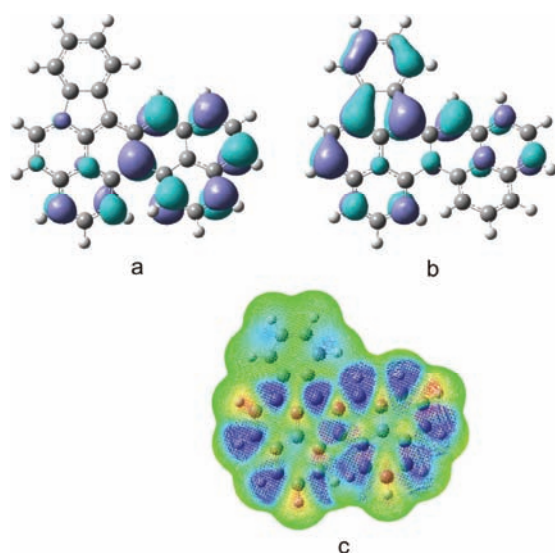


Fig. 2. SOMO (a), SOMO-1 (b), and spin density map (c) for **1T**. In the spin density map, the blue and red regions indicate the highest and lowest spin density values, respectively. In the grayscale presentation the dark regions indicate the highest spin density values.

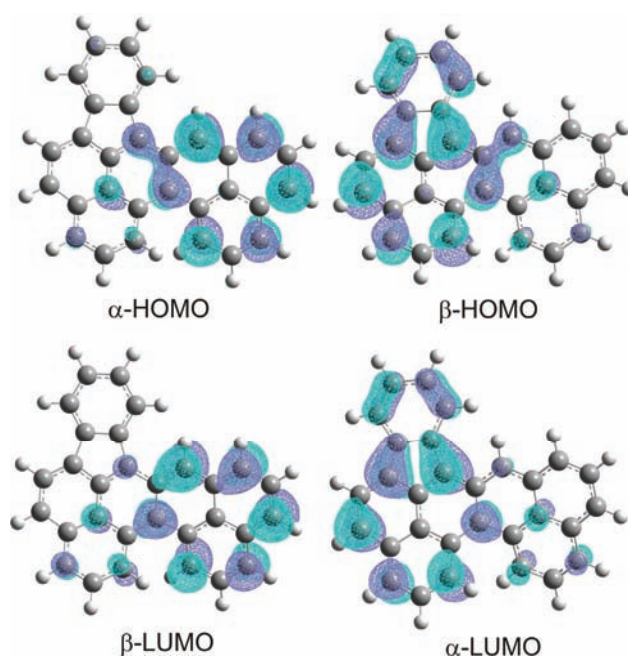


Fig. 3. Frontier orbitals for **10S**.

-HOMO and  $\alpha$ -LUMO. In this way, there are no unpaired electrons in **10S**, yet two of them occupy different parts of space, thus allowing the  $\pi$ -electrons to delocalize. The situation is quite different in **70S** (Fig. 4). Here, the  $\alpha$ -HOMO and



$\beta$ -HOMO, as well as the  $\alpha$ -LUMO and  $\beta$ -LUMO, are of almost identical shapes. Thus, the HOMO and LUMO are occupied with 1.71 and 0.29 electrons, respectively. In addition, there is a noticeable shared region between the HOMO and LUMO, which is in agreement with the high  $T$  value for **7** (Table I). The frontier orbitals for the  $\alpha$  and  $\beta$  spin electrons clearly reflect the triplet and singlet nature of the compounds **1** and **7**.

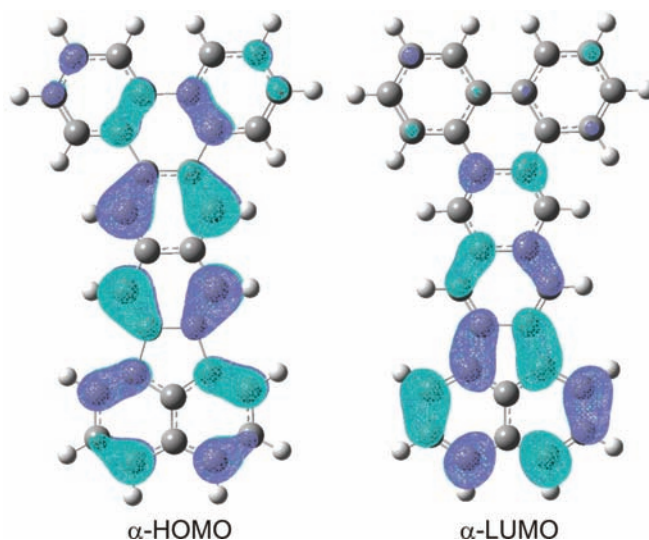


Fig. 4. Frontier orbitals for **7OS**. The shapes of the  $\beta$ -HOMO and  $\beta$ -LUMO are almost identical to those of the  $\alpha$ -HOMO and  $\alpha$ -LUMO.

#### CONCLUSIONS

The unrestricted symmetry-broken method was applied to the triplet 2,2-dimethyl-2*H*-dibenzo[*cd,k*]fluoranthene (**6**) and the singlet fluorantheno[8,9-*b*]triphenylene (**7**). The excellent agreement with the experimental results confirms the applicability of the symmetry-broken method to the Kekuléan fluoranthenes **1–5**. The triplet ground state of **1–6** was confirmed by the negative singlet–triplet gap values. These compounds tend to delocalize their  $\pi$ -electrons and thus they take up diradical structures. Even in the singlet state, these Kekuléan hydrocarbons show a pronounced diradical character, and their structures are best presented with those of singlet diradicals. Such structures provide a possibility for an electron pair to occupy different parts of space and allows for the achievement of aromatic stabilization. The diradical index  $\gamma_{\text{NOON}}$  is not in good agreement with the diradical character of the investigated molecules. On the other hand,  $\gamma_{\text{PUHF}}$  successfully reproduces the diradical character of the investigated molecules.

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## ИЗВОД

## ДИРАДИКАЛСКИ КАРАКТЕР НЕКИХ ФЛУОРАНТЕНА

СВЕТЛАНА МАРКОВИЋ, ЈЕЛЕНА ЂУРЂЕВИЋ, СВЕТЛАНА ЈЕРЕМИЋ и ИВАН ГУТМАН

*Природно-математички факултет, Универзитет у Крагујевцу, Крагујевац*

Показано је да су неки флуорантени дирадикали, тј. да је њихово основно стање триплетно. И у енергетски неповољнијем синглетном стању ови угљоводоници показују изразит дирадикалски карактер. Дирадикалски карактер испитиваних једињења процењен је помоћу *unrestricted symmetry-broken* (URHF) и *complete active space* (CNON) метода. Нађено је да URHF вредности успешније репродукују дирадикалски карактер испитиваних угљоводоника. Показано је да SOMO и SOMO-1 орбитале за дирадикалску структуру заузимају различите делове простора са малом заједничком регијом, што резултира расподелом спинске густине преко целог молекула. Просторна дирадикалска расподела у синглетно-дирадикалским структурама је испитана на основу облика HOMO и LUMO орбитала за електроне  $\alpha$  и  $\beta$  спина. Показано је да  $\alpha$ -HOMO и  $\beta$ -LUMO (као и  $\beta$ -HOMO и  $\alpha$ -LUMO) заузимају практично исти део простора. На овај начин, у синглетном дирадикалу нема неспарених електрона, али два електрона ипак заузимају различите делове простора, што омогућава делокализацију  $\pi$ -електрона.

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## REFERENCES

1. L. K. Montgomery, J. C. Huffman, E. A. Jurczak, M. P. Grendze, *J. Am. Chem. Soc.* **108** (1986) 6004
2. K. Yamaguchi, F. Jensen, A. Dorigo, K. N. Houk, *Chem. Phys. Lett.* **149** (1988) 537
3. D. R. McMasters, J. Wirz, *J. Am. Chem. Soc.* **123** (2001) 238
4. M. Bendikov, H. M. Duong, K. Starkey, K. N. Houk, E. A. Carter, F. Wudl, *J. Am. Chem. Soc.* **126** (2004) 7416
5. T. Kubo, A. Shimizu, M. Sakamoto, M. Uruichi, K. Yakushi, M. Nakano, D. Shiomi, K. Sato, T. Takui, Y. Morita, K. Nakasuji, *Angew. Chem.* **117** (2005) 6722
6. T. Kubo, M. Sakamoto, K. Nakasuji, *Polyhedron* **24** (2005) 2522
7. J. Poater, J. M. Bofill, P. Alemany, M. Solá, *J. Phys. Chem. A* **109** (2005) 10629
8. T. Kubo, A. Shimizu, M. Uruichi, K. Yakushi, M. Nakano, D. Shiomi, K. Sato, T. Takui, Y. Morita, K. Nakasuji, *Org. Lett.* **9** (2006) 81
9. J. Hachmann, J. J. Dorando, M. Avilés, G. K. L. Chan, *J. Chem. Phys.* **127** (2007) 134309
10. M. Nakano, R. Kishi, A. Takebe, M. Nate, H. Takahashi, T. Kubo, K. Kamada, K. Ohta, B. Champagne, E. Botek, *Co. Le.* **3** (2007) 333
11. J. Huang, M. Kertesz, *J. Am. Chem. Soc.* **129** (2007) 1634
12. M. Nakano, A. Takebe, R. Kishi, H. Fukui, T. Minami, K. Kubota, H. Takahashi, T. Kubo, K. Kamada, K. Ohta, B. Champagne, E. Botek, *Chem. Phys. Lett.* **454** (2008) 97
13. K. Iketaki, K. Kanai, A. Shimizu, T. Kubo, Z. H. Wang, Y. Ouchi, Y. Morita, K. Nakasuji, K. Seki, *J. Phys. Chem. C* **113** (2009) 1515
14. T. Ishida, J. Aihara, *Phys. Chem. Chem. Phys.* **11** (2009) 7197
15. P. Baumgartner, E. Weltin, G. Wagnière, E. Heilbronner, *Helv. Chim. Acta* **48** (1965) 751
16. H. Angliker, E. Rommel, J. Wirz, *Chem. Phys. Lett.* **87**(1982) 208
17. J. Roncali, *Chem. Rev.* **97** (1997) 173
18. K. N. Houk, P. S. Lee, M. Nendel, *J. Org. Chem.* **66** (2001) 5517
19. G. J. Gleicher, D. D. Newkirk, J. C. Arnold, *J. Am. Chem. Soc.* **95** (1973) 2526



20. J. Aihara, *Bull. Chem. Soc. Jpn.* **48** (1975) 3637
21. J. Kolc, J. Michl, *J. Am. Chem. Soc.* **92** (1970) 4147
22. J. Michl, J. Kolc, *J. Am. Chem. Soc.* **92** (1970) 4148
23. R. P. Steiner, J. Michl, *J. Am. Chem. Soc.* **100** (1978) 6413
24. A. Castellan, J. Kolc, J. Michl, *J. Am. Chem. Soc.* **100** (1978) 6687
25. D. R. McMasters, J. Wirz, *J. Am. Chem. Soc.* **119** (1997) 8568
26. I. Gutman, J. Đurđević, *MATCH Commun. Math. Comput. Chem.* **60** (2008) 659
27. I. Gutman, J. Đurđević, A. T. Balaban, *Polycyclic Aromat. Compd.* **29** (2009) 3
28. J. Đurđević, I. Gutman, J. Terzić, A. T. Balaban, *Polycyclic Aromat. Compd.* **29** (2009) 90
29. J. Đurđević, I. Gutman, R. Ponec, *J. Serb. Chem. Soc.* **74** (2009) 549
30. I. Gutman, J. Đurđević, *J. Serb. Chem. Soc.* **74** (2009) 765
31. S. Radenković, J. Đurđević, I. Gutman, *Chem. Phys. Lett.* **475** (2009) 289
32. J. Đurđević, S. Radenković, I. Gutman, S. Marković, *Monatsh. Chem.* **140** (2009) 1305
33. I. Gutman, *Z. Naturforsch.* **65a** (2010) 473
34. D. Vukičević, J. Đurđević, I. Gutman, *J. Serb. Chem. Soc.* **75** (2010) 1093
35. S. Marković, J. Đurđević, S. Jeremić, I. Gutman, *J. Mol. Mod.*, in press
36. A. Necula, L. T. Scott, *J. Anal. Appl. Pyrolysis* **54** (2000) 65 and references therein
37. A. Necula, L. T. Scott, *Polycyclic Aromat. Compd.* **30** (2010) and references therein, in press
38. *Gaussian 03, Revision E.01-SMP*, Gaussian Inc., Pittsburgh, PA, 2003
39. C. Lee, W. Yang, R. G. Parr, *Phys. Rev. B* **37** (1988) 785
40. A. D. Becke, *J. Chem. Phys.* **98** (1993) 5648
41. D. Dönhert, J. Koutecký, *J. Am. Chem. Soc.* **102** (1980) 1789
42. K. Yamaguchi, in: *Self-Consistent Field: Theory and Applications*, R. Carbo, M. Klobukowski, Eds., Elsevier, Amsterdam, 1990, p. 727
43. S. Yamanaka, M. Okumura, M. Nakano, K. Yamaguchi, *J. Mol. Struct. (Theochem)* **310** (1994) 205.