Monatsh Chem (2011) 142:1013–1019
DOI 10.1007/s00706-011-0557-8

ORIGINAL PAPER

The diradical character of polyacenequinododimethides

**Slavko Radenković · Svetlana Marković ·
Ratko Kuč · Nevena Stanković**

Received: 18 May 2011 / Accepted: 13 June 2011 / Published online: 19 July 2011

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

---

S. Radenković (✉) · S. Marković · R. Kuč · N. Stanković
Faculty of Science, University of Kragujevac,
P.O. Box 60, 34000 Kragujevac, Serbia
e-mail: slavkoradenkovic@kg.ac.rs

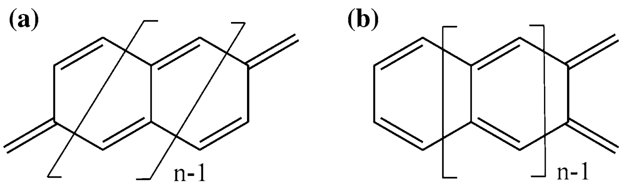

Fig. 1 Structures of **a** polyacene-2,x-quinododimethides (2,x-dimethylene-2,x-dihydropolyacenes) and **b** polyacene-2,3-quinododimethides (2,3-dimethylene-2,3-dihydropolyacenes). The number of hexagons is indicated by n, whereas x denotes the position of the second methylene group in polyacene-2,x-quinododimethides

symmetry-broken method, which allows 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 occupies 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.

The electronic structure of singlet diradicals with Kekulé structures has attracted much attention [15–27]. Experimental and theoretical methods have been used to investigate the diradical character of Chichibabin's hydrocarbon [15], substituted fluoranthenes [17], linear polyacenes [18, 21, 23, 27], phenalenyl-based hydrocarbons [19, 20, 22, 24–27], and zethrenes [25]. On the other hand, the question of whether a Kekuléan system can exist in a triplet ground state has been less thoroughly examined. An assumption that a sufficiently small highest occupied molecular orbital (HOMO)–lowest unoccupied molecular orbital (LUMO) gap should allow the promotion of an electron to produce a diradical resulted in the proposal of cyclohepta[*def*]fluorene [28], nonacene, and higher linear polyacenes [29–31] as possible representatives of triplet Kekuléan hydrocarbons. However, cyclohepta[*def*]fluorene has never been synthesized. In addition, Bendikov et al. [18] showed that the RB3LYP wavefunction becomes unstable for polyacenes as small as hexacene, and all higher polyacenes, implying that the energies calculated 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 [23].

The only Kekuléan hydrocarbon whose triplet state has been confirmed experimentally is 2,2-dimethyl-2*H*-dibenzo[*cd*,*k*]fluoranthene [17, 32]. In a series of recent papers [33–35] we presented density functional theory (DFT) calculations on fluoranthenes. Our investigations showed that some fluoranthenes are diradicals, implying that their triplet ground state is energetically more favorable in comparison with 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 π-electrons. This leads to aromatic stabilization which is stronger than the destabilization caused by the unpaired electrons.

The assumption that some polyacenequinododimethides [14] are triplet Kekuléan hydrocarbons has never been confirmed. In this paper we present a detailed study of the electronic structure of polyacenequinododimethides in their singlet and triplet states. Our ultimate goal is to determine whether some polyacenequinododimethides are triplet Kekuléan hydrocarbons.

Results and discussion

The results of our investigation using the 6-311G(d,p) basis set for a series of polyacene-2,x-quinododimethides (Fig. 1a) and polyacene-2,3-quinododimethides (Fig. 1b) are summarized in Tables 1 and 2. To examine the effect of diffuse functions, the 6-311+G(d,p) basis set was employed for **5a** (Table 1) and **5b** (Table 2). It was revealed that the addition of diffuse functions invokes only negligible changes in geometry and energy. For this reason all further discussion is based on results obtained at the B3LYP/6-311G(d,p) level of theory.

Careful inspection of the data in Table 1 reveals that only in the cases of **1a** and **2a** do the results for the RB3LYP singlet and UB3LYP symmetry-broken singlet coincide. For $n > 2$, the energy difference between open-shell singlet and closed-shell singlet ($\Delta G_{\mathrm{OS-CS}}$) of polyacene-2,$x$-quinododimethides is negative, and decreases with increasing size of the molecules considered (Fig. 2). Similarly, $\Delta G_{\mathrm{OS-CS}}$ is negative for all molecules from the series of polyacene-2,3-quinododimethides (Table 2). On the other hand, $\Delta G_{\mathrm{OS-CS}}$ for this series first decreases, achieves its minimal value for the molecule **5b**, and then slowly increases (Fig. 2). It is reasonable to assume on the basis of the behavior of $\Delta G_{\mathrm{OS-CS}}$ for polyacene-2,3-quinododimethides that $\Delta G_{\mathrm{OS-CS}}$ will remain negative for even larger molecules ($n > 8$). These results clearly indicate that singlet states of polyacene-2,x-quinododimethides and polyacene-2,3-quinododimethides are best described using the unrestricted symmetry-broken method.

Table 1 Difference in free energy/kJ mol^{-1} between open-shell symmetry-broken singlet and closed-shell RB3LYP solution ($\Delta G_{\mathrm{OS-CS}}$), singlet–triplet gap ($\Delta G_{\mathrm{T-OS}}$), spin contamination for the open-shell singlet ($\langle S^2 \rangle$), and diradical index y_{PUHF}/%

Compound	$\Delta G_{\mathrm{OS-CS}}$	$\Delta G_{\mathrm{T-OS}}$	$\langle S^2 \rangle$	y_{PUHF}
Benzene-2,4-quinododimethide (**1a**; $x = 4$)	0.00	119.85	0.00	14.43
Naphthalene-2,6-quinododimethide (**2a**; $x = 6$)	0.00	63.80	0.00	30.85
Anthracene-2,6-quinododimethide (**3a**; $x = 6$)	−6.56	37.41	0.45	49.33
Naphthacene-2,8-quinododimethide (**4a**; $x = 8$)	−15.08	25.10	0.80	62.82
Pentacene-2,9-quinododimethide (**5a**; $x = 9$)	−23.33 (−22.53)[a]	19.48 (19.46)[a]	1.00	70.99
Hexacene-2,10-quinododimethide (**6a**; $x = 10$)	−30.25	17.29	1.17	76.33
Heptacene-2,11-quinododimethide (**7a**; $x = 11$)	−38.25	17.13	1.35	80.04
Octacene-2,12-quinododimethide (**8a**; $x = 12$)	−45.53	17.88	1.56	82.68

[a] Results in parenthesis obtained using the 6-311+G(d,p) basis set

Table 2 Difference in free energy/kJ mol^{-1} between open-shell symmetry-broken singlet and closed-shell RB3LYP solution ($\Delta G_{\mathrm{OS-CS}}$), singlet–triplet gap ($\Delta G_{\mathrm{T-OS}}$), spin contamination for the open-shell singlet ($\langle S^2 \rangle$), and diradical indices y_{PUHF}/% and y_{NOON}/%

Compound	$\Delta G_{\mathrm{OS-CS}}$	$\Delta G_{\mathrm{T-OS}}$	$\langle S^2 \rangle$	y_{PUHF}	y_{NOON}
Benzene-2,3-quinododimethide (**1b**)	−1.69	83.93	0.00	18.16	8.1
Naphthalene-2,3-quinododimethide (**2b**)	−10.38	29.71	0.62	53.55	10.2
Anthracene-2,3-quinododimethide (**3b**)	−31.22	14.93	1.06	79.89	15.7
Naphthacene-2,3-quinododimethide (**4b**)	−53.22	12.54	1.17	92.31	21.4
Pentacene-2,3-quinododimethide (**5b**)	−67.74 (−68.73)[a]	14.22 (13.89)[a]	1.24	99.10	96.9
Hexacene-2,3-quinododimethide (**6b**)	−65.34	17.50	1.33	96.71	86.8
Heptacene-2,3-quinododimethide (**7b**)	−62.42	19.08	1.47	93.96	77.9
Octacene-2,3-quinododimethide (**8b**)	−63.01	24.92	1.66	90.42	75.7

[a] Results in parenthesis obtained using the 6-311+G(d,p) basis set

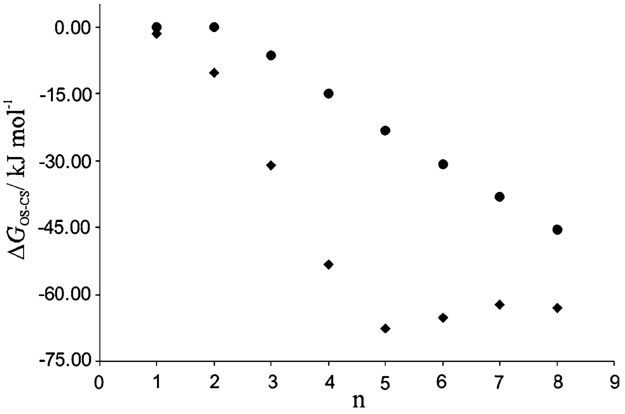

Fig. 2 Dependence of the difference in free energy/kJ mol^{-1} between open-shell symmetry-broken singlet and closed-shell RB3LYP singlet ($\Delta G_{\mathrm{OS-CS}}$) on the number n of hexagons of polyacene-2,x-quinododimethides (*circles*) and polyacene-2,3-quinododimethides (*diamonds*)

The negative values of $\Delta G_{\mathrm{OS-CS}}$ for all examined polyacenequinododimethides indicate a diradical character of these molecules. The diradical character of the molecules under investigation is assessed by means of the diradical index y_{PUHF}, obtained using the unrestricted symmetry-broken method. In the case of polyacene-2,x-quinododimethides, the values of y_{PUHF} increase with increasing molecular size (Table 1; Fig. 3a). It is noticeable that all molecules in the series beyond **4a** have more than 50% diradical character. Analogous results for polyacene-2,3-quinododimethides show that y_{PUHF} is not a monotonic function of the number of hexagons in these molecules (Table 2; Fig. 3a). With $y_{\mathrm{PUHF}} = 99.10\%$ **5b** has the maximal diradical character in the given series, whereas larger molecules have somewhat lower y_{PUHF} values, although still higher than 90%. By comparing the values of y_{PUHF} for the same-size molecules of the polyacene-2,x-quinododimethides and polyacene-2,3-quinododimethides series it is evident that polyacene-2,3-quinododimethides have significantly more pronounced diradical character. The same conclusion can be obtained by comparing the values of $\Delta G_{\mathrm{OS-CS}}$ from Tables 1 and 2. The growth of the diradical character along the series of polyacene-2,x-quinododimethides is expected, and can be explained with the fact that wider molecule area provides higher possibility for achieving aromatic stabilization. A peculiar change of the diradical index along the series of polyacene-2,3-quinododimethides was the reason to evaluate their diradical character using the CAS(8,8)/6-

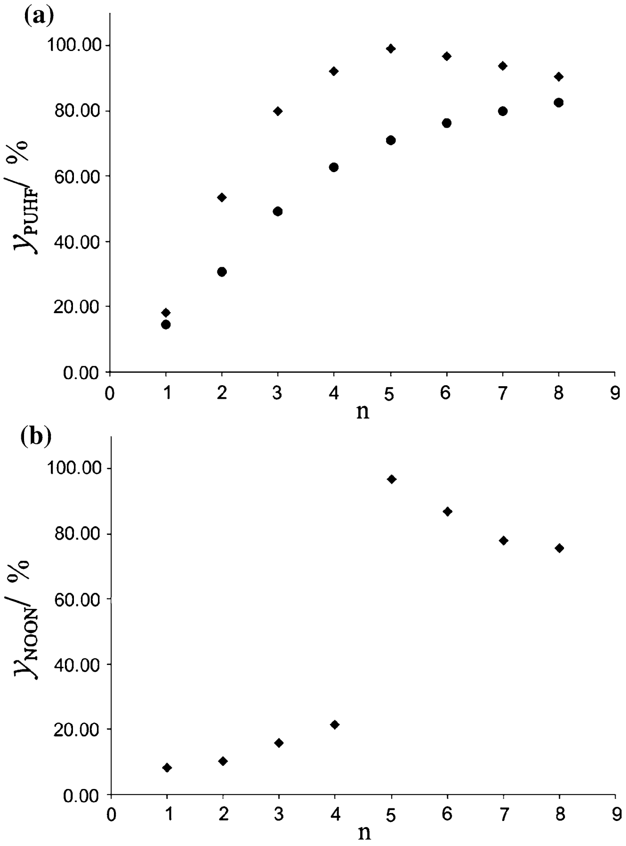

Fig. 3 **a** Dependence of the diradical index y_{PUHF}/% on the number n of hexagons of polyacene-2,x-quinododimethides (*circles*) and polyacene-2,3-quinododimethides (*diamonds*). **b** Dependence of the diradical index y_{NOON}/% on the number n of hexagons of polyacene-2,3-quinododimethides

311G(d,p) method. Table 2 presents the diradical index y_{NOON} determined according to natural orbital occupation number (NOON) analysis, i.e., on the basis of the occupation number of the LUMO, resulting from the CAS calculation. The values of y_{NOON} for the first four members of the series of polyacene-2,3-quinododimethides are significantly lower than the values of y_{PUHF}. On the other hand, both methods agree about the very high diradical character for larger molecules, and maximal diradical character of **5b** (Fig. 3b).

The diradical character of molecules under study can be analyzed by examining the spatial distribution of the HOMO and LUMO electrons in the singlet diradical structures. As an example, Fig. 4 shows frontier orbitals obtained using the unrestricted symmetry-broken method for **7a**. Analogous results are obtained for **7b** (Fig. 5). Two characteristic features of Figs. 4 and 5 are immediately recognized. First, it is obvious that α-HOMO and β-HOMO of **7a** and **7b** are delocalized over the entire molecules, but have very small sharing regions. The same observation holds for α-LUMO and β-LUMO. Second, α-HOMO and β-LUMO, as well as β-HOMO and α-LUMO, occupy practically the same part of space. In this way there are no unpaired electrons in any singlet diradical, yet two of them occupy different parts of space, thus allowing the π-electrons to delocalize.

The main goal of the present work is to elucidate whether triplet state is the ground state for some polyacenequinododimethides. The values of the singlet–triplet gaps (ΔG_{T-OS}) for these two classes of molecules are given in Tables 1 and 2. Positive values of ΔG_{T-OS} reveal that all examined molecules exist in the singlet ground state. Another conclusion arising from analyzing the dependence of ΔG_{T-OS} on the number of hexagons is that ΔG_{T-OS} remains positive even for higher members of the given series ($n > 8$), indicating that their ground state would be a singlet (Fig. 6).

Taking into account the relatively low singlet–triplet gaps for higher members of the polyacenequinododimethides series, it is reasonable to expect that promotion of an electron from the HOMO to the LUMO can be easily achieved. Such electron promotion would lead to a triplet diradical structure. As an illustration of the spin density distribution, spin density maps for triplet **4a** and **4b** are presented in Fig. 7. It is obvious that the strongest spin density is located on the carbon atoms of methylene groups in **4a** and **4b**. The repulsion between two unpaired electrons causes the spin density to be practically equal to zero

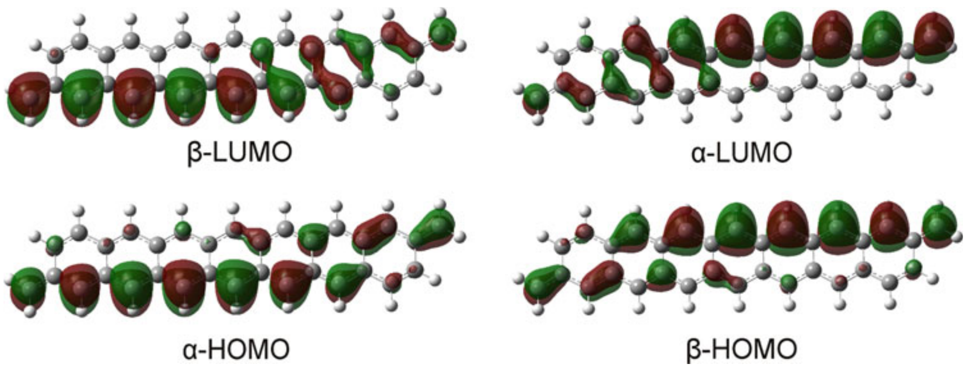

Fig. 4 Frontier orbitals for heptacene-2,11-quinododimethide (**7a**) calculated using the unrestricted symmetry-broken method

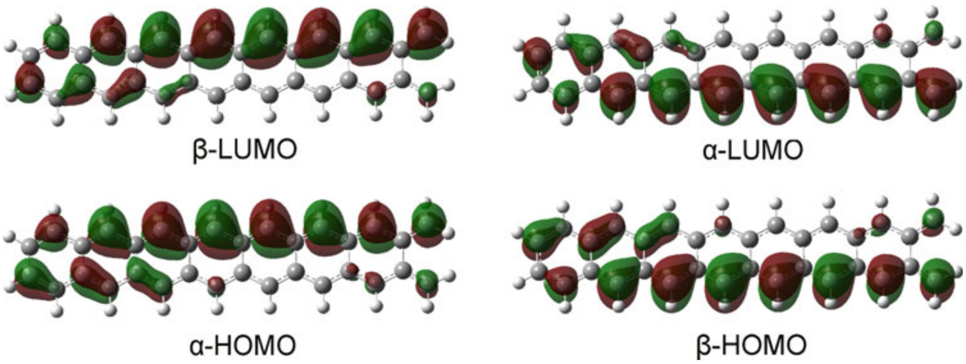

Fig. 5 Frontier orbitals for heptacene-2,3-quinododimethide (**7b**) calculated using the unrestricted symmetry-broken method

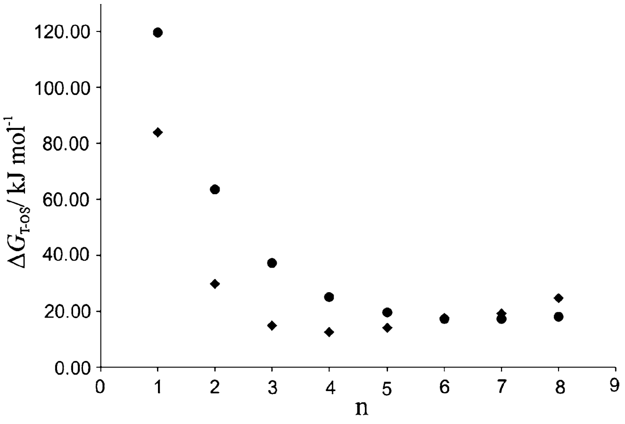

Fig. 6 Dependence of the singlet–triplet gap $\Delta G_{\mathrm{T-OS}}$/kJ mol^{-1} on n for polyacene-2,*x*-quinododimethides (*circles*) and polyacene-2,3-quinododimethides (*diamonds*)

in the middle of molecule **4a**. On the other hand, the spatial arrangement of the two methylene carbon atoms in **4b** limits delocalization of spin density to only one part of the given molecule.

The optimized geometries of **5a** and **5b** are presented in Fig. 8. These geometries were obtained at the UB3LYP/6-311G(d,p) and UB3LYP/6-311+G(d,p) levels using the symmetry-broken method, which gives the best description of the ground state of these molecules as discussed above. It is obvious that the addition of diffuse functions does not cause any significant changes in geometry. It is worth mentioning that the unrestricted symmetry-broken method produces planar structures for all molecules, except for **1b**. All structures for triplet states are also planar. On the other hand, RB3LYP singlet structures are nonplanar in the case of the first five members of the polyacene-2,3-quinododimethides series (**1b**, **2b**, **3b**, **4b**, and **5b**), whereas higher members of this series ($n > 5$) and all polyacene-2,*x*-quinododimethides are planar. Figure 8 shows that C–C bonds which are double according to the Kekulé structures have lengths in the range 135.2–139.2 pm, whereas the lengths of single bonds range from 141.1 to 145.7 pm. These intervals are typical for the C–C bond length in aromatic hydrocarbons. This fact reveals that the structure of a

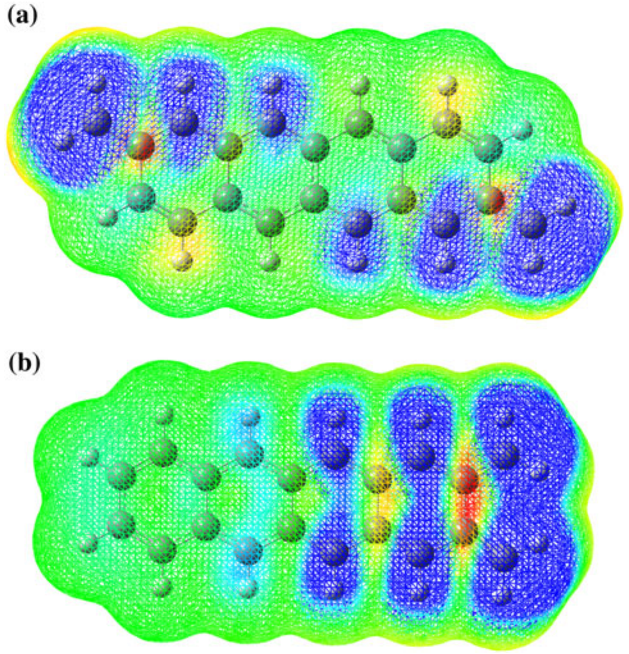

Fig. 7 Spin density maps for triplet **4a** (**a**) and **4b** (**b**). *Blue* and *red* regions indicate the highest and lowest spin density values. In the *grayscale* presentation, *dark regions* indicate the highest spin density values (color figure online)

polyacenequinododimethide cannot be properly described with a single Kekulé structure. These findings are in perfect agreement with Aihara's results [13], showing that these hydrocarbons are aromatic, and that the conjugated circuit model is not applicable to them.

Methods

All calculations were performed with the Gaussian 09 program package, revision A.02 [36], at the B3LYP/6-311G(d,p) level of theory [37, 38]. The effect of diffuse functions was examined by applying the B3LYP/6-311G+(d,p) method on **5a** and **5b**. The computed Hessian matrices showed the optimized structures to correspond to minima on the potential energy surface. The molecules

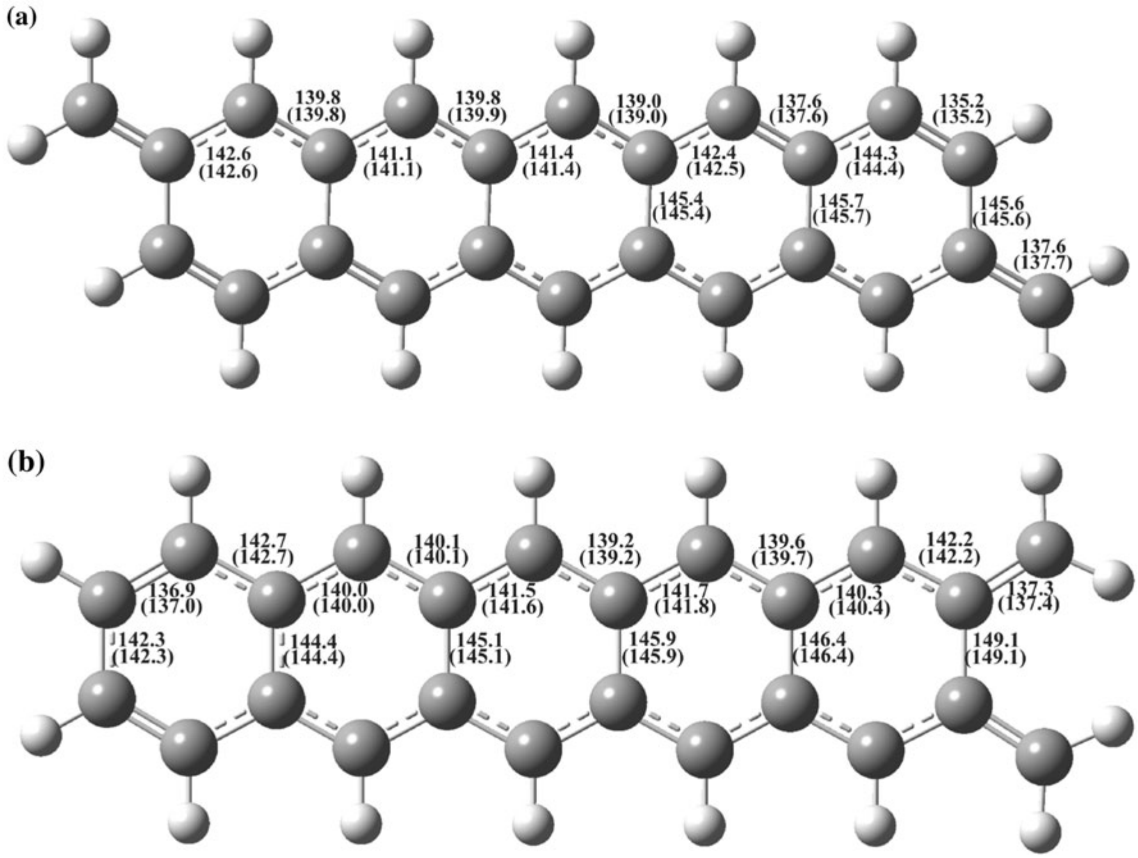

Fig. 8 Optimized geometries obtained at the B3LYP/6-311G(d,p) level using the unrestricted symmetry-broken method of **5a** (**a**) and **5b** (**b**). Results in parenthesis obtained using the 6-311+G(d,p) basis set; C–C bond lengths in pm

under investigation were calculated in their singlet and triplet states, using the restricted and unrestricted schemes for closed-shell and open-shell calculations.

The singlet diradical character of the investigated hydrocarbons was estimated using a symmetry-broken UB3LYP/6-311G(d,p) method along with geometry optimization. The diradical index y_{PUHF}, related to the HOMO and LUMO for singlet states, was defined by the weight of the doubly excited configuration in the multiconfigurational self-consistent field (MC-SCF) theory, and is formally expressed in the case of the spin-projected unrestricted Hartree–Fock (PUHF) theory [39, 40] as

$$y_{\mathrm{PUHF}} = 1 - \frac{2T}{1+T^2},$$

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

$$T = \frac{n_{\mathrm{HOMO}} - n_{\mathrm{LUMO}}}{2}.$$

For the series of polyacene-2,3-quinododimethides the singlet diradical character was also estimated using the CASSCF(8,8) method. The diradical index y_{NOON} was determined according to natural orbital occupation number (NOON) analysis [41], i.e., on the basis of the occupation number of the LUMO, resulting from the CASSCF(8,8)/6-311G(d,p) calculation. Both diradical indices range from 0% for closed-shell states to 100% for pure diradical states.

Acknowledgments This work is supported by the Ministry of Science of Serbia (grants no. 172016 and 174033).

References

1. Clar E (1964) Polycyclic hydrocarbons, vol 1. Academic, New York
2. Anthony JE (2006) Chem Rev 106:5028
3. Anthony JE (2008) Angew Chem Int Ed 47:452
4. Bendikov M, Wudl F, Perepichka DF (2004) Chem Rev 104:4891
5. Würthner F, Schmidt R (2006) Chem Phys Chem 7:793
6. Howard JB, Longwell JP, Marr JA, Pope CJ (1995) Combust Flame 101:262
7. Otero-Lobato MJ, Kaats-Richters VEM, Havenith RWA, Jenneskens LW, Seinen W (2004) Mutat Res 564:39
8. Wang J, He X, Mulder PPJ, Boere BB, Cornelisse J, Lugtenburg J, Busby WFJ (1999) Carcinogenesis 20:1137
9. Aihara J (1975) Bull Chem Soc Jpn 48:3637
10. Randić M (2003) Chem Rev 103:3449
11. Schleyer PvR, Puhlhofer F (2002) Org Lett 4:2873

12. Hajgató B, Deleuze MS, Ohno K (2006) Chem Eur J 12:5757
13. Aihara J, Makino M (2008) Chem Asian J 3:585
14. Gleicher GJ, Newkirk DD, Arnold JC (1972) J Am Chem Soc 95:2526
15. Montgomery LK, Huffman JC, Jurczak EA, Grendze MP (1986) J Am Chem Soc 108:6004
16. Yamaguchi K, Jensen F, Dorigo A, Houk KN (1988) Chem Phys Lett 149:537
17. McMasters DR, Wirz J (2001) J Am Chem Soc 123:238
18. Bendikov M, Duong HM, Starkey K, Houk KN, Carter EA, Wudl F (2004) J Am Chem Soc 126:7416
19. Kubo T, Shimizu A, Sakamoto M, Uruichi M, Yakushi K, Nakano M, Shiomi D, Sato K, Takui T, Morita Y, Nakasuji K (2005) Angew Chem 117:6722
20. Kubo T, Sakamoto M, Nakasuji K (2005) Polyhedron 24:2522
21. Poater J, Bofill JM, Alemany P, Solá M (2005) J Phys Chem A 109:10629
22. Kubo T, Shimizu A, Uruichi M, Yakushi K, Nakano M, Shiomi D, Sato K, Takui T, Morita Y, Nakasuji K (2006) Org Lett 9:81
23. Hachmann J, Dorando JJ, Avilés M, Chan GKL, J Chem Phys 127:134309/1
24. Huang J, Kertesz M (2007) J Am Chem Soc 129:1634
25. Nakano M, Takebe A, Kishi R, Fukui H, Minami T, Kubota K, Takahashi H, Kubo T, Kamada K, Ohta K, Champagne B, Botek E (2008) Chem Phys Lett 454:97
26. Iketaki K, Kanai K, Shimizu A, Kubo T, Wang ZH, Ouchi Y, Morita Y, Nakasuji K, Seki K (2009) J Phys Chem C 113:1515
27. Ishida T, Aihara J (2009) Phys Chem Chem Phys 11:7197
28. Baumgartner P, Weltin E, Wagnière G, Heilbronner E (1965) Helv Chim Acta 48:751
29. Angliker H, Rommel E, Wirz J (1982) Chem Phys Lett 87:208
30. Roncali J (1997) Chem Rev 97:173
31. Houk KN, Lee PS, Nendel M (2001) J Org Chem 66:5517
32. McMasters DR, Wirz J (1997) J Am Chem Soc 119:8568
33. Gutman I, Marković S, Jeremić S (2010) Polycyc Arom Comp 30:240
34. Marković S, Đurđević J, Jeremić S, Gutman I (2010) J Mol Mod 17:805
35. Marković S, Đurđević J, Jeremić S, Gutman I (2010) J Serb Chem Soc 75:1241
36. Frisch MJ, Trucks GW, Schlegel HB, Scuseria GE, Robb MA, Cheeseman JR, Scalmani G, Barone V, Mennucci B, Petersson GA, Nakatsuji H, Caricato M, Li X, Hratchian HP, Izmaylov AF, Bloino J, Zheng G, Sonnenberg JL, Hada M, Ehara M, Toyota K, Fukuda R, Hasegawa J, Ishida M, Nakajima T, Honda Y, Kitao O, Nakai H, Vreven T, Montgomery JA Jr, Peralta JE, Ogliaro F, Bearpark M, Heyd JJ, Brothers E, Kudin KN, Staroverov VN, Kobayashi R, Normand J, Raghavachari K, Rendell A, Burant JC, Iyengar SS, Tomasi J, Cossi M, Rega N, Millam JM, Klene M, Knox JE, Cross JB, Bakken V, Adamo C, Jaramillo J, Gomperts R, Stratmann RE, Yazyev O, Austin AJ, Cammi R, Pomelli C, Ochterski JW, Martin RL, Morokuma K, Zakrzewski VG, Voth GA, Salvador P, Dannenberg JJ, Dapprich S, Daniels AD, Farkas O, Foresman JB, Ortiz JV, Cioslowski J, Fox DJ (2009) Gaussian 09, Rev A.1. Gaussian Inc., Wallingford
37. Lee C, Yang W, Parr RG (1988) Phys Rev B 37:785
38. Becke AD (1993) J Chem Phys 98:5648
39. Yamaguchi K (1990) In: Carbo R, Klobukowski M (eds), Self-consistent field: theory and applications. Elsevier, Amsterdam, p 727
40. Yamanaka S, Okumura M, Nakano M, Yamaguchi K (1994) J Mol Struct (Theochem) 310:205
41. Dönhert D, Koutecký J (1980) J Am Chem Soc 102:1789