

Multiconfigurational character of the ground states of polycyclic aromatic hydrocarbons. A systematic study

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Abstract A systematic study of the electronic structure of polycyclic hydrocarbons from naphthalene to a system containing 80 fused benzene has been carried out. Geometries were optimized for closed shell singlet, open shell singlet, triplet and multiplet states at B3LYP/cc-pVDZ level of theory, D1 (second order Møller–Plesset) and D1 (second-order approximate coupled-cluster) diagnostics have been calculated for studied molecules. Complete active space self-consistent field (10,10)/6-31G(d) single point energy calculations have been carried out for all optimized structures. Multireference character of the ground state becomes important when the number of atoms in the polycyclic hydrocarbon exceeds 40–50. At this point, D1 diagnostics reaches 0.04–0.05 and the squared configuration interaction expansion coefficient for dominant configuration drops to about 0.6. However, only for the three largest systems predominantly polyradicalic ground states have been detected. All other polycyclic hydrocarbons showing significant multiconfigurational character of singlet ground state have only two dominant configurations which are closed shell singlet and doubly excited singlet, respectively. Thus, small polycyclic hydrocarbons have mostly single reference singlet ground state, the medium size systems have notably multireference ground state (singlet or triplet) with only moderate polyradicalic character. The ground state of largest systems is singlet polyradical.

Keywords DFT · Complete active space · Multiconfigurational ground state · Graphene

Introduction

Graphene nanoribbons are segments of graphene that can be considered as unrolled single-walled carbon nanotubes. According to a number of experimental and theoretical research works, these materials are shown to be promising for applications in nanoelectronics [1–10]. The electronic structures of graphene ribbons and closely related linear acenes have recently been a subject of intense theoretical studies. In 2004, Bendikov et al. [11] reported that the oligoacenes larger than hexacene showed triplet instability of the closed shell singlet ground state at hybrid density functional theory (DFT) B3LYP/6-31G(d) level. The lowest energy state for highest oligoacenes has been interpreted as diradical with antiferromagnetic (AFM) spin ordering. In more sophisticated investigation of linear acenes reported by Hachmann et al. [12] oligoacenes up to dodecacene have been studied using complete active space self-consistent field (CASSCF) calculations in the framework of the density matrix renormalization group (DMRG) algorithm [12] with unrestricted B3LYP/6-31G(d) optimized geometries used by Bendikov [11]. In agreement with this study, singlet ground state has been identified for all larger acenes. The larger acenes were found to be polyradicalic species having one unpaired electron every five to six rings. The analysis of Hachmann [12] found further support in recent works of Jiang and Dai [13] where oligoacenes up to 40 repeat units have been studied using spin polarized DFT, and Qu et al. [14] where DMRG method has been applied. Finally, dos Santos used periodic boundary conditions for AFM states and the results were in line with the findings of Bendikov [11] and Jian and Dai [13]. On the other hand, Deleuze et al. [15] arrived at the conclusion that polyacenes have closed shell singlet ground state at least up to heptacene and very small S0-T1 adiabatic excitation energies in the limit of indefinitely large polyacene. According to Deleuze et al. giant symmetry breaking effects in unrestricted

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single-reference treatments of polyacenes are unphysical and high level treatment of electronic correlations are necessary for its compensation. Deleuze et al. also studied graphene nanoribbons using the formalism of crystalline orbitals [16]. They found that for singlet states, symmetry-breakings in spin-densities are necessarily the outcome of a too approximate treatment of static and dynamic electron correlation in single-determinant approaches, and is thus nothing other than a methodological artefact. However, it has been shown that this problem can be at least partially solved using “spin decontamination” technique [17]. Rayne and Forest [18, 19] studied polyacenes and rectangular graphene nanoribbons assuming closed shell singlet ground state. They concluded that graphene [m \times n] nanoribbons have closed shell ground state with vanishing S₀-T₁ energy gap at polymeric limit (m \rightarrow ∞ and/or n \rightarrow ∞). In a very recent paper Lichka et al. [20] reached a conclusion that graphene nanoribbons present strong multiradical character and D2 [21] diagnostic confirms multiconfigurational character of the ground state. Rivero et al. [22] predicted polyradical character of polycyclic aromatic hydrocarbons using projected Hartree-Fock theory.

As seen the results in the literature are rather contradictory, therefore, we decided to carry out a detailed study of the ground state electronic structure of a series of fused aromatic hydrocarbons of increasing size, starting from simplest naphthalene up to largest polycyclic systems containing 80 fused benzene rings, close relatives of graphene nanoribbons.

Computational details

All geometry optimizations have been carried out using D3 dispersion corrected [23] B3LYP functional as implemented in Turbomole 6.5 [24]. Dunning’s correlated consistent cc-pVDZ basis set [25] was applied for all except for CASSCF calculations where 6-31G(d) set has been used [26]. All CASSCF calculations were performed with Gaussian 09 rev. D.01 [27]. Geometries of all structures have been optimized for closed shell singlets using a restricted method (RB3LYP), while open shell singlets, triplets, and multiplets were minimized with an unrestricted method (UB3LYP). All closed shell singlet solutions were tested for triplet instabilities. The geometry optimizations were run using Fermi thermal smearing, starting from triplet state in order to find the lowest energy multiplet solutions. To estimate the multireference character of the ground states, D1 diagnostics [28] were calculated at second-order approximate coupled-cluster (CC2) and second order Møller–Plesset (MP2) levels for closed shell singlet states, for large systems only D1(MP2) diagnostics have been estimated. Single point CASSCF calculations have been carried out for all optimized geometries using active space with ten electrons and ten orbitals. This is

the largest active space we could afford. According to [12] taking into account the dynamic correlation almost does not change triplet-singlet gap for the acenes suggesting that CASSCF wavefunction describes reasonably well the electronic structure of polyacenes. Moreover, given the size of the system under the study taking into account the dynamic correlation is not currently possible. Structures of studied hydrocarbons are shown in Fig. 1. For the parallelogramic structures all possible combinations of **n** and **m** have been studied in the ranges **m**=1–4 and **n**=2–10 where **m** and **n** are the number of fused benzene rings in columns and rows, respectively. Moreover, a large structure with **m**=8 and **n**=10 has been calculated. These hydrocarbons are denoted as **P_{m,n}**, where **1,n** are acenes. Another group of polycyclic hydrocarbons (rectangular) is geometrical isomers of the first group are denoted as **R_{m,n}**.

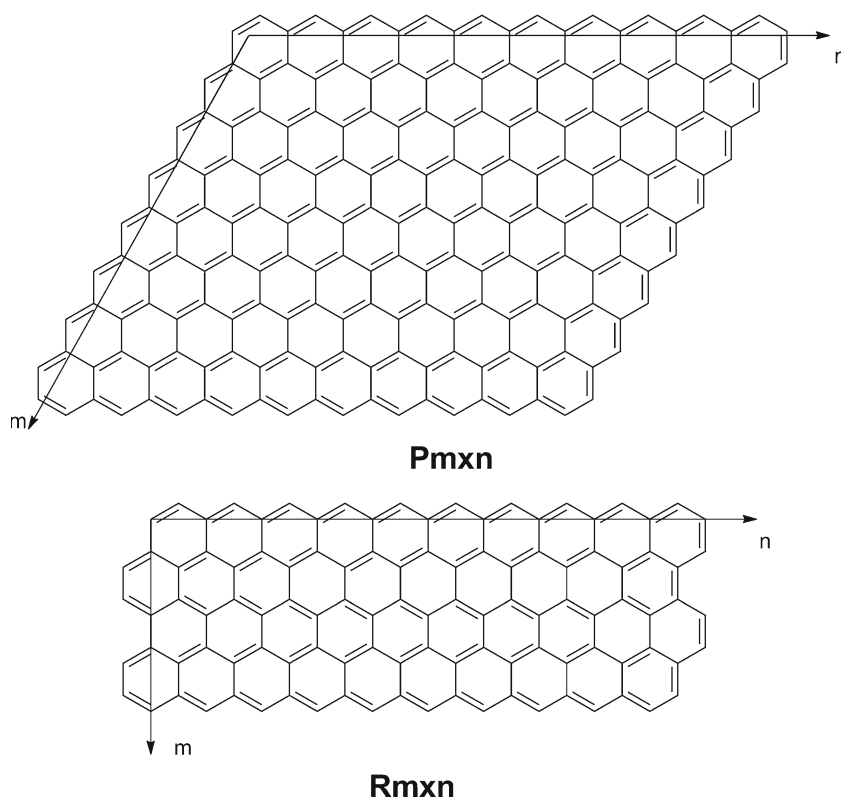
Results and discussion

B3LYP/cc-pVDZ level of theory and D1 diagnostic

First, all structures have been optimized at RB3LYP/cc-pVDZ level and restricted solutions were tested for triplet instability. For **1,n** systems (acenes) the triplet instability is detected for **1,6** (hexacene) in agreement with Bendikov et al.’s work [11]. The complete set of data is shown in Fig. 2. The area below black marks corresponds to the hydrocarbons of rectangular series stable at RB3LYP/cc-pVDZ level of theory. Red marks correspond to the first polycyclic hydrocarbons of parallelogramic series showing triplet instability. All systems above imaginary lines connecting black marks (rectangular) and red marks (parallelogramic) show triplet instability at RB3LYP/cc-pVDZ level.

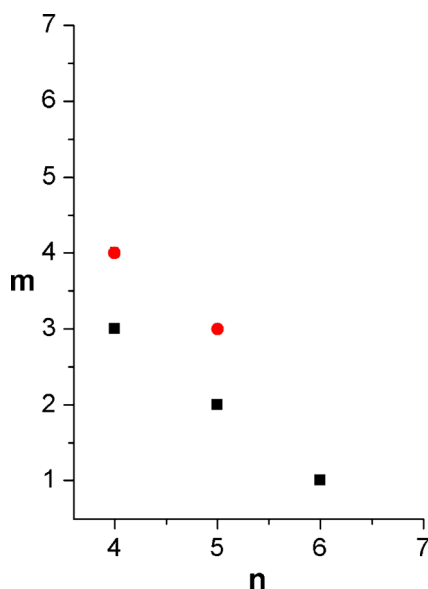
Triplet instability is often considered as an indication for multiconfigurational character of the ground state, however, the size of the system first presenting triplet instability depends on the Hartree–Fock (HF) exchange fraction and the basis set and, therefore, cannot be taken as the final proof of multiconfigurational character of the ground state.

Thus, in the extreme case of RHF/STO-3G model, even benzene, the molecule with definitely closed shell ground state, shows triplet instability. The stable ground state, however, is a clear indication of the closed shell singlet ground state. As can be seen from Fig. 2 the stability of closed shell ground state depends on three factors, the number of benzene rings, the geometry of edges and the molecular shape. Thus, the largest polycyclic hydrocarbons with stable closed shell singlet ground state are **P_{3,3}** and **R_{4,3}** while the largest stable acene is pentacene. The higher the **n/m** ratio of polycyclic hydrocarbon the smaller the system presenting instability of the closed shell singlet ground state. Rectangular structures

Fig. 1 Studied polycyclic hydrocarbons

maintain closed shell structure of the ground states for larger systems than parallelogramic ones.

For the systems presenting instability of the closed shell ground state, the geometries were reoptimized to the lowest energy state (open shell singlet) using broken symmetry unrestricted method. Table 1 shows the relative energies of triplet (T) and open shell singlet states (OSS) taking as reference

**Fig. 2** Limits of closed shell singlet ground state stability at B3LYP/cc-pVDZ level for m,n rectangular (black square) and parallelogramic (black circle) polycyclic hydrocarbons

closed shell singlet states. As seen, for most of the systems singlet or OSS state is the lowest energy state. The exceptions are **P3,10**, **P8,10**, **R3,10**, **R4,9**, and **R4,10**. While **P3,10**, **R3,10**, **R4,9**, and **R4,10** show triplet ground states, the ground state of the largest **P8,10** system is a multiplet with six unpaired electrons at B3LYP/cc-pVDZ level. The properties of the broken symmetry solutions for oligoacenes and graphene nanoribbons has been discussed in the literature [15, 16] where authors arrived at a conclusion that the low energy broken symmetry solution is an artefact. Indeed, strong spin contamination is observed for large systems (Table 1). Thus, for **P8,10** OSS state the expectation value for $\langle S^2 \rangle$ is 4.12, notably higher than the theoretical value of 0, characteristic for singlets. The same is true for triplets. For systems **P3,8**, **P4,8**, **P4,9**, **P4,10**, **P8,10**, **R3,10**, and **R4,10** the expectation values of $\langle S^2 \rangle$ notably exceed the theoretical value of 2.0 and, therefore, their energies cannot be trusted. For some of the large systems (**P4,8**, **P4,9**, **P4,10**, **P8,10**) higher multiplicity states more stable than triplet have been located using Fermi annealing technique (Table 1). These states have four unpaired electrons for **P4,8**, **P4,9**, **P4,10** (multiplicity=5) and six unpaired electrons for largest studied system **P8,10** (multiplicity=7). Another interesting point is that spin contamination of the high spin state is very low, the theoretical values of $\langle S^2 \rangle$ are 6 for the multiplicity 5 and 12 for the multiplicity 7 are an indication of single reference character of these states. Therefore, their energies can be trusted. Unfortunately, the direct comparison of high spin states energies with those of

Table 1 The relative energies of triplet (**T**), multiplet (**M**), and open shell singlet (**OSS**) states with respect to the closed shell singlet (kcal mol⁻¹) and the corresponding $\langle S^2 \rangle$ expectation values obtained at B3LYP/cc-pVDZ levels

Molecule	T	$\langle S^2 \rangle$	OSS	$\langle S^2 \rangle$	M^a	$\langle S^2 \rangle$	D1 MP2	D1 CC2
1,2(Naphthalene)	62.19	2.02	–	–	–	–	0.026	0.032
1,3(Anthracene)	41.48	2.02	–	–	–	–	0.028	0.036
1,4(Tetracene)	27.45	2.02	–	–	–	–	0.030	0.043
1,5(Pentacene)	17.64	2.03	–	–	–	–	0.032	0.048
1,6(Hexacene)	10.57	2.03	–0.08	0.35	–	–	0.033	0.053
1,7(Heptacene)	5.36	2.03	–1.67	0.84	–	–	0.035	0.056
1,8(Octacene)	1.44	2.04	–4.05	1.08	–	–	0.036	0.059
1,9(Nanocene)	–1.53	2.04	–6.62	1.25	–	–	0.037	0.062
1,10(Decacene)	–12.88	2.04	–18.2	1.41	–	–	0.055	0.122
P2,2 (pyrene)	48.29	2.04	–	–	–	–	0.029	0.038
P2,3	32.06	2.04	–	–	–	–	0.032	0.049
P2,4	19.41	2.04	–	–	–	–	0.037	0.064
P2,5	10.15	2.05	–0.12	0.27	–	–	0.041	0.079
P2,6	3.49	2.05	–2.31	0.87	–	–	0.046	0.096
P2,7	–1.25	2.06	–5.42	1.11	–	–	0.051	0.113
P2,8	–4.60	2.07	–8.51	1.30	–	–	0.055	0.129
P2,9	–6.96	2.09	–6.96	2.08	–	–	0.060	0.143
P2,10	–8.68	2.14	–14.4	1.83	–	–	0.064	0.157
P3,3	20.79	2.07	–	–	–	–	0.038	0.068
P3,4	10.99	2.08	–0.01	0.24	–	–	0.045	0.087
P3,5	3.34	2.09	–2.26	0.86	–	–	0.053	0.109
P3,6	–2.35	2.12	–5.96	1.13	–	–	0.061	0.136
P3,7	–6.44	2.24	–9.77	1.37	–	–	0.070	0.168
P3,8	–9.33	2.87	–13.5	1.69	–	–	0.083	0.204
P3,9	–11.50	3.48	–17.3	2.00	–	–	0.102	–
P3,10	–13.65	2.56	–11.6	1.86	–	–	0.138	–
P4,4	3.63	2.07	–2.14	0.80	–	–	0.053	–
P4,5	–2.29	2.08	–6.02	1.17	–	–	0.062	–
P4,6	–6.76	2.09	–10.4	1.48	–	–	0.074	–
P4,7	–10.00	2.11	–14.9	1.83	–	–	0.106	–
P4,8	–12.47	2.24	–19.4	2.18	–13.0	6.20	0.198	–
P4,9	–15.35	2.87	–23.9	2.48	–18.3	6.22	0.239	–
P4,10	–19.37	3.48	–28.3	2.81	–22.4	6.27	0.222	–
P8,10	–48.06	5.29	–40.5	4.12	–48.4	12.4	0.198	–
R3,1 (Phenanthrene)	63.44	2.04	–	–	–	–	0.026	0.034
R3,2	46.69	2.03	–	–	–	–	0.028	0.037
R3,3	25.74	2.04	–	–	–	–	0.033	0.050
R3,4	10.93	2.04	–	–	–	–	0.038	0.072
R3,5	0.89	2.05	–3.06	0.90	–	–	0.047	0.104
R3,6	–5.52	2.06	–7.90	1.14	–	–	0.057	0.139
R3,7	–9.33	2.07	–11.85	1.30	–	–	0.067	0.166
R3,8	–11.41	2.07	–15.12	1.55	–	–	0.076	0.173
R3,9	–12.44	2.08	–18.40	1.90	–	–	0.081	0.178
R3,10	–15.46	3.13	–12.14	2.01	–	–	0.160	0.177
R4,1 (Chrysene)	58.40	2.02	–	–	–	–	0.027	0.035
R4,2	43.98	2.03	–	–	–	–	0.030	–
R4,3	22.10	2.04	–	–	–	–	0.034	–
R4,4	6.23	2.05	–0.35	0.58	–	–	0.043	–

Table 1 (continued)

Molecule	T	$\langle S^2 \rangle$	OSS	$\langle S^2 \rangle$	M ^a	$\langle S^2 \rangle$	D1 MP2	D1 CC2
R4,5	-4.20	2.06	-6.22	1.07	–	–	0.056	–
R4,6	-10.23	2.08	-11.7	1.20	–	–	0.073	–
R4,7	-13.26	2.09	-15.5	1.39	–	–	0.091	–
R4,8	-14.61	2.10	-19.0	1.79	–	–	0.124	–
R4,9	-15.31	2.20	-14.8	2.07	–	–	0.195	–
R4,10	-16.92	2.78	-3.62	2.17	–	–	0.135	–

D1 diagnostics at MP2 and CC2 levels. Calculated at MP2/cc-pVDZ//B3LYP/cc-pVDZ and CC2/cc-pVDZ//B3LYP/cc-pVDZ levels, respectively

^a For **P4,8**, **R4,9**, and **P4,10** multiplicity is 5, for **P8,10** multiplicity is 7

triplet and especially open singlet states is not possible due to their unreliable energies. For triplet state of **P4,8** where spin contamination is still relatively small ($\langle S^2 \rangle = 2.24$) the triplet and high spin state are practically degenerated, the high spin state is only 0.5 kcal mol⁻¹ more stable than triplet.

B3LYP/cc-pVDZ model reproduces well experimental singlet-triplet gap for naphthalene, anthracene, tetracene, pentacene, and hexacene (61.0, 43.1, 29.5, 19.8 and 12.4 kcal mol⁻¹, respectively, [29–34]) where the single reference solution is still a good approximation. For large systems where closed shell singlet solution becomes unstable, OSS state with AFM spin ordering is the ground state. However, strong spin contamination, a reflection of multiconfigurational nature of the ground state, makes DFT or any other single reference method unreliable to treat large polycyclic hydrocarbons. We estimated D1 diagnostics at CC2 and MP2 levels for studied systems to visualize the range of the applicability of the single reference methods to polycyclic hydrocarbons (Table 1). Authors [15] calculated T1 diagnostics for acenes up to heptacene and arrived at the conclusion that these molecules do not show any significant multireference character. In difference to T1 diagnostic, D1 diagnostic is strictly size intensive and can, thus also be used for large systems and to compare results for molecules of different size. Values of D1(MP2) > 0.04 and D1(CC2) > 0.05 indicate that the system cannot be properly described using the corresponding single reference methods [28]. As seen from Table 1, in the case of acenes D1(CC2) diagnostics exceeds 0.05 for hexacene, precisely where B3LYP/cc-pVDZ model shows triplet instability, and the appearance of the triplet instability is generally a good indication where D1 diagnostics exceed critical value. For large systems D1(MP2) correlates better with triplet instability than D1(CC2), which show values slightly larger than 0.05 even for the systems having stable singlet closed shell solution.

Rm,n show lower values of D1(CC2) and D1(MP2) diagnostics compared to **Pm,n** polycyclic hydrocarbons, correlating also with triplet instability of the ground state at B3LYP/cc-pVDZ level. Moreover, no high spin states more stable than triplets have been detected for hydrocarbons of **Rm,n** series.

Therefore, the combination of D1 diagnostics and triplet instability data is an indication of the applicability limits for single determinant treatment for polycyclic hydrocarbons. As seen from Table 1, in the case of acenes a significant multireference character of the ground state could be expected for hydrocarbons larger than octacene. In the case of **Pm,n** series notable multireference character could be expected already for **P2,7**, **P3,5**, and **P4,4**, while for **Rm,n** series the hydrocarbons starting from **R3,6** and **R4,5** should have appreciable multireference character.

CASSCF(10,10)/6-31G(d) level of theory

The results of CASSCF(10,10)/6-31G(d) calculations are listed in Table 2. The CASSCF(10,10) single point calculations have been carried out for all available geometries; singlets, OSS, triplets, and multiplets. At first glance, the most striking difference between DFT and CASSCF results is that multiplet states found for **P4,8**, **R4,9**, **P4,10**, and **P8,10** are by far the less stable states compared to singlets and triplets. This is a consequence of the shortcomings of the single reference DFT approach. Multiplet states have only one dominant configuration, the squared CI coefficient of this configuration is of 0.90 for **P4,8**, **R4,9**, and **P4,10**, while for **P8,10** the same coefficient is of 0.98 (Table 3). Therefore, multiplet states are described well by DFT. On the other hand, triplet and especially singlet states of these hydrocarbons are notably multiconfigurational, the dominant configuration contributes to singlet states only 40, 32, 23, and 4 %, for **P4,8**, **R4,9**, and **P4,10**, respectively (Table 3). The contributions from dominant configuration to triplets are of 55, 65, 28, and 4 %, correspondingly.

In the case of the largest studied system **P8,10**, the dominant configurations for both singlet and triplet states are not even singlet and triplet (Table 3). In fact, **P8,10** in both singlet and triplet states has contributions from at least 15 different configurations with almost equal participation which are multiradicalic. The most stable is the singlet state by only 1.5 kcal mol⁻¹. Since CASSCF method lacks dynamical correlation and the dynamical correlation is generally more

Table 2 CASSCF(10,10)/6-31G(d) single point relative energies estimated for triplet (T), multiplet (M), and open singlet shell (OSS) geometries at B3LYP/cc-pVDZ level with respect to closed shell singlet (kcal mol⁻¹)

Molecule	OSS	T	M ^a	N
1,2(Naphthalene)	–	65.3	–	0.31
1,3(Anthracene)	–	48.2	–	0.38
1,4(Tetracene)	–	32.8	–	0.43
1,5(Pentacene)	–	15.3	–	0.46
1,6(Hexacene)	5.17	18.6	–	0.45
1,7(Heptacene)	8.63	18.0	–	0.51
1,8(Octacene)	4.39	3.36	–	0.62
1,9(Nanocene)	4.32	14.11	–	0.59
1,10(Decacene)	9.53	6.98	–	1.08
P2,2 (pyrene)	–	48.17	–	0.36
P2,3	–	44.05	–	0.36
P2,4	–	30.47	–	0.38
P2,5	8.44	12.19	–	0.42
P2,6	0.56	6.46	–	0.47
P2,7	–7.78	–0.94	–	0.80
P2,8	–8.73	–7.28	–	1.07
P2,9	–6.14	–2.21	–	0.97
P2,10	3.53	–8.93	–	1.12
P3,3	–	26.57	–	0.35
P3,4	12.2	21.16	–	0.35
P3,5	13.50	10.24	–	0.44
P3,6	13.83	0.44	–	0.95
P3,7	8.94	–3.22	–	1.14
P3,8	3.78	4.61	–	1.21
P3,9	–4.56	–7.56	–	1.27
P3,10	1.48	–3.42	–	1.32
P4,4	0.24	0.32	–	0.49
P4,5	–1.25	5.61	–	0.61
P4,6	0.26	9.53	–	1.06
P4,7	3.57	4.35	–	1.12
P4,8	2.60	4.95	15.3	1.38
P4,9	3.06	1.21	13.1	1.56
P4,10	7.42	12.4	19.5	1.94
P8,10	–2.84	–1.34	21.2	3.49
R3,1(Phenanthrene)	–	68.26	–	0.36
R3,2	–	56.74	–	0.34
R3,3	–	41.68	–	0.32
R3,4	–	18.97	–	0.36
R3,5	0.49	–0.51	–	0.59
R3,6	–4.66	–4.79	–	0.92
R3,7	–2.40	–1.23	–	1.17
R3,8	–11.74	–15.00	–	1.27
R3,9	–15.91	–19.19	–	1.27
R3,10	–3.11	–8.95	–	1.52
R4,1(Chrysene)	–	67.11	–	0.33
R4,2	–	69.51	–	0.35

Table 2 (continued)

Molecule	OSS	T	M ^a	N
R4,3	–	31.19	–	0.25
R4,4	–3.00	8.78	–	0.33
R4,5	–8.43	–4.91	–	0.84
R4,6	–3.96	–3.90	–	1.19
R4,7	–4.39	–8.74	–	1.21
R4,8	–10.3	–10.3	–	1.32
R4,9	2.95	–1.42	–	1.50
R4,10	12.4	2.88	–	2.00

The number of electrons outside closed shell (N)

important for the singlet states than for triplet ones, the ground state of **P8,10** is likely to be a singlet polyradical. All dominant configurations in **P8,10** are polyradicalic by nature ranging from bi- to hexaradical. Therefore, the ground state of **P8,10** can be defined as polyradicalic singlet state in agreement with the finding of [20] for graphene nanoribbons. For smaller polycyclic hydrocarbons the situation is different. As can be seen from Table 3 in the vast majority of cases there is only one or two dominant configurations that accounts for more than 50 % of the contribution. Thus, in the case of polyacenes even for decacene, the contribution from the dominant configuration is still 50 % in singlet and 79 % in triplet. The second most important configuration for decacene contributing with 24 % is doubly excited singlet state (Table 3). The next five configurations are polyradicalic (di- and tetradicalic) contributing 80 % in total. Therefore, the oligoacenes up to at least decacene can still be described reasonably well as closed shell singlets with only moderate polyradicalic character.

Polycyclic hydrocarbons of **P2,n** series have one dominant configuration contributing more than 50 % up to **P2,8** for singlets and in the case of triplets even **P2,10** still has 79 % from single triplet configuration. Two dominant configurations contributing to the singlet state of **P2,10** the largest member of this series, are closed shell singlet (47 %) and double excited singlet configurations (34 %) (Table 3). The next six configurations are tetradicalic summing 90 % in total. For triplet states the contribution of the dominant triplet configuration is higher than 75 % in all cases (Table 3). Our calculations predict that polyradicalic character of polyacenes becomes important only for decacene and larger acenes, although multiconfigurational character of the ground state is detected for smaller systems starting from hexacene, unlike [12] where hexacene is already considered as biradical.

As systems become larger, the contributions of polyradicalic configurations increase. For singlet states of **P3,n** and **P4,n** series the dominant closed shell configuration accounts for more than 50 % of contribution up to **P3,6** and **P4,5**, respectively. The second most important configuration

Table 3 Squared CI expansion coefficients for dominant configurations in studied molecules at CASSCF(10,10)/6-31G(d) level of theory for singlet state using RHF geometry (S), triplet (T) and multiplet (M) states using UHF geometry

Molecule	S 2222200000	S 2222020000	T 2222uu000	M
1,2(Naphthalene)	0.84	–	0.77	–
1,3(Anthracene)	0.81	0.02	0.79	–
1,4(Tetracene)	0.79	0.03	0.77	–
1,5(Pentacene)	0.77	0.04	0.75	–
1,6(Hexacene)	0.77	0.04	0.79	–
1,7(Heptacene)	0.75	0.04	0.82	–
1,8(Octacene)	0.70	0.07	0.77	–
1,9(Nanocene)	0.67	0.04	0.81	–
1,10(Decacene)	0.50	0.23	0.79	–
P2,2 (pyrene)	0.82	0.02	0.75	–
P2,3	0.82	0.02	0.81	–
P2,4	0.81	0.03	0.82	–
P2,5	0.79	0.03	0.79	–
P2,6	0.77	0.05	0.81	–
P2,7	0.62	0.22	0.82	–
P2,8	0.50	0.31	0.79	–
P2,9	0.54	0.28	0.81	–
P2,10	0.47	0.34	0.79	–
P3,3	0.82	0.01	0.81	–
P3,4	0.82	0.01	0.82	–
P3,5	0.79	0.04	0.84	–
P3,6	0.54	0.27	0.82	–
P3,7	0.47	0.33	0.81	–
P3,8	0.44	0.37	0.82	–
P3,9	0.43	0.30	0.82	–
P3,10	0.39	0.36	0.72	–
P4,4	0.75	0.07	0.82	–
P4,5	0.70	0.12	0.84	–
P4,6	0.50	0.31	0.86	–
P4,7	0.50	0.33	0.84	–
P4,8	0.39	0.30	0.54	0.90 ^a
P4,9	0.32	0.30	0.65	0.90 ^a
P4,10	0.22	0.20	0.28	0.90 ^a
P8,10	0.04 ^b	–	0.04 ^c	0.98 ^d
R3,1(Phenanthrene)	0.82	0.01	0.75	–
R3,2	0.82	0.01	0.77	–
R3,3	0.84	0.01	0.82	–
R3,4	0.82	0.01	0.84	–
R3,5	0.72	0.11	0.81	–
R3,6	0.57	0.26	0.79	–
R3,7	0.44	0.33	0.81	–
R3,8	0.44	0.34	0.79	–
R3,9	0.43	0.30	0.81	–
R3,10	0.33	0.27	0.42	–
R4,1(Chrysene)	0.84	0.01	0.81	–

Table 3 (continued)

Molecule	S 2222200000	S 2222020000	T 2222uu000	M
R4,2	0.82	0.01	0.81	–
R4,3	0.86	0.01	0.84	–
R4,4	0.82	0.01	0.82	–
R4,5	0.59	0.23	0.82	–
R4,6	0.44	0.36	0.81	–
R4,7	0.43	0.38	0.81	–
R4,8	0.39	0.34	0.81	–
R4,9	0.33	0.33	0.80	–
R4,10	0.20	0.23	0.32	–

^a Multiplicity=5^b Dominant configuration 2222u0d00^c Dominant configuration 2duu2000u2^d Multiplicity=7

is the double excited singlet state. For the largest molecule of **P3,n** series: **P3,10** a sum of the two first configurations accounts for 75 % of contributions, while the rest of the configurations are polyradicalic by nature. The triplet states of **P3,n** hydrocarbons have only one dominant triplet configuration that accounts for more than 70 % of the total.

For singlet states of polycyclic hydrocarbons of **P4,n** series, two singlet configurations; (2222200000) and (2222020000) dominate up to **P4,9**, where the sum of squared CI expansion coefficients is still 0.62, the rest of the configurations are polyradicalic by nature. There are only two examples of hydrocarbons of parallelogramic series where polyradicalic contributions dominate in the singlet states: **P4,10** and **P8,10**, which are the largest ones. In all other cases two singlet configurations predominate with only moderate contributions from the polyradicalic states. In the case of triplet states of **P4,n** series, the triplet configuration dominates up to **P4,9** (Table 3), decreasing rapidly to 0.28 for **P4,10**, and disappearing completely for **P8,10** where the most important configuration is tetradicalic (2duu2000u2) representing only 4 % of the total contribution.

As seen from Table 2, CASSCF reproduces reasonably well the experimental singlet triplet gap for naphthalene, anthracene, tetracene pentacene, and hexacene (61.0, 43.1, 29.5, 19.8 and 12.4 kcal mol⁻¹), respectively [29–34], which also are in line with the results obtained by Hachmann using density matrix renormalization group method [12]. As has been shown, the lack of dynamic correlation does not affect significantly singlet triplet gap of polyacenes [12] lowering it by only 1–2 kcal mol⁻¹, and CASSCF calculations allow to estimate this value at least semiquantitatively. Two different types of geometries were used for CASSCF singlet state calculations, RB3LYP and broken symmetry UB3LYP optimized. For acenes RB3LYP geometries result in lower CASS

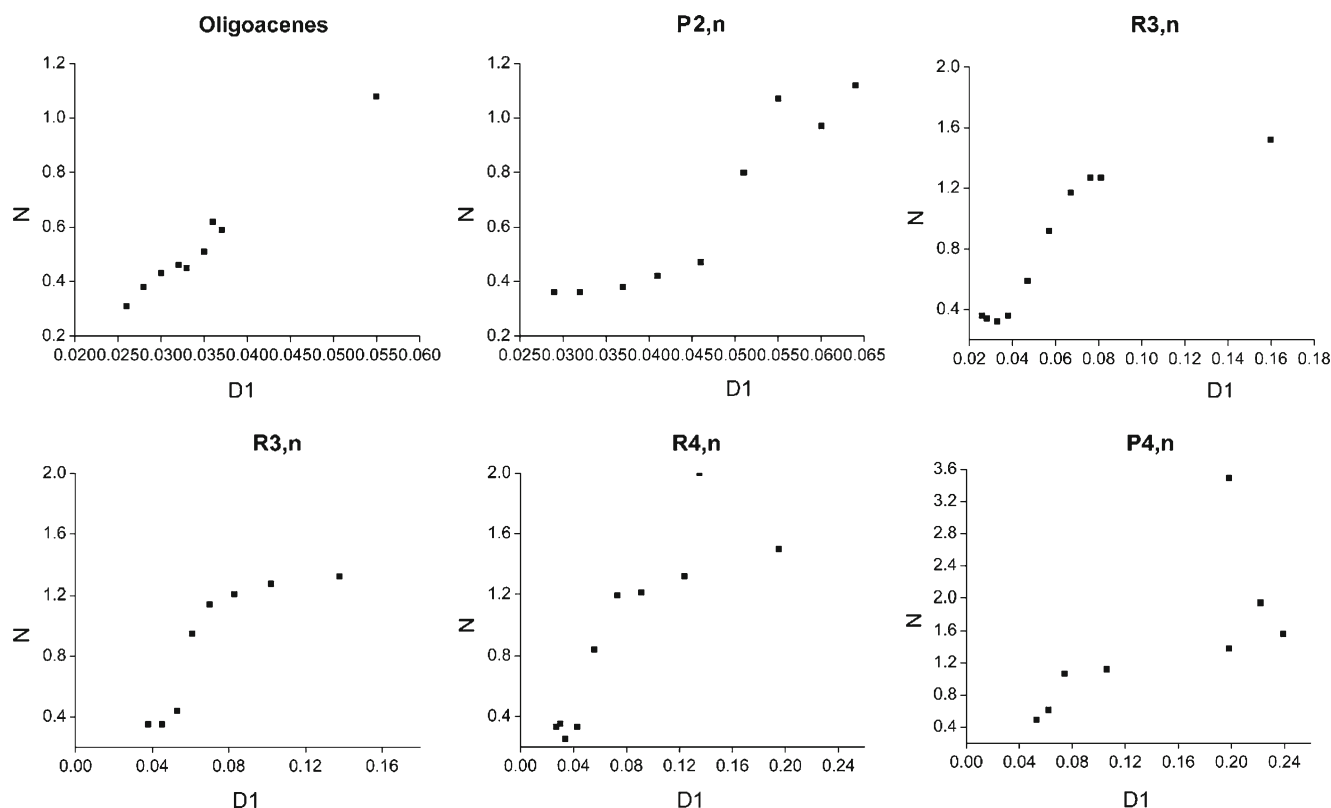


Fig. 3 D1(MP2) diagnostic against number of electrons out of closed shell (N) for studied polycyclic hydrocarbons

CF energies than these obtained by UB3LYP method (Table 2). Singlet is the ground state for acenes in agreement with the results of other authors [11–14]. For larger systems, however, the situation is different. There is no clear preference for RB3LYP or UB3LYP methods for singlet state optimizations (Table 2). Generally, for systems with significant multireference character of the ground state, the UB3LYP optimization method is preferable resulting in lower CASSCF singlet energies. As seen from Table 2 for some of the polycyclic hydrocarbons triplet states were found to be the ground state. For hydrocarbons of parallelogramic series the triplet ground state was found for **P2,10**, **P3,7**, **P3,9**, and **P3,10**. Both, B3LYP and CASSCF methods predict triplet ground state for **P3,10**. The largest energy difference was found for **P2,10** where the triplet state is almost 9 kcal mol^{-1} more stable than singlet. The majority of the systems having triplet ground state are rectangular (Table 2), the energy differences, however, are not very large, being the largest for **R3,10** ($5.84 \text{ kcal mol}^{-1}$). For the largest studied systems; **P8,10**, **P4,10**, and **R4,10** the ground state is singlet (Table 2). As can be seen from Tables 2 and 3, the electronic properties of large polycyclic hydrocarbons cannot be extrapolated from these of small ones since the properties do not change uniformly with size. This tendency can be clearly seen plotting D1 diagnostics against the number of the electrons out of closed shell obtained by CASSCF calculations. The

multireference character of the ground state that correlates with D1 diagnostic and the number of electrons out of closed shell (Fig. 3) show that for small and medium size systems these parameters increase only moderately and increase rapidly for larger systems. This sudden increase is seen for decacene, **P2,7** **P3,6** **P4,8**, and **R3,10** for oligoacenes, **P2,n**, **P3,n**, and **R3,n**, respectively.

For systems **R4,n** there is no such clear transition. This means that the extrapolation of electronic properties of small and middle sized polycyclic hydrocarbons to larger ones leads to the underestimation of their multireference character. On the other hand, for most of the studied systems except for the largest ones, the multireference character of the ground state does not necessarily mean the pure polyradicalic state.

Conclusions

Single reference methods should be used with caution for large polycyclic hydrocarbons including graphene nanoribbons due to notable multireference character of their ground state which becomes important when the number of atoms exceeds 40–50. D1(MP2) and D1(CC2) diagnostics as indicators of multireference character of the ground state correlate well with triplet instability of closed shell solutions. The use of unrestricted broken symmetry

approach can remedy to some extent the shortcomings of single reference method at the expense of spin contamination for systems with moderate multireference character of the ground state but fails for the systems with significant multireference character. CASSCF calculations demonstrate that D1(MP2) exceeds 0.04 when the squared CI expansion coefficient for the dominant configuration drop to about 0.6 which is a measure of a significant multireference character. The multireference character does not necessarily mean the polyradicalic state, however. Thus, only for the three largest studied systems, **R4,10**, **P4,10**, and **P8,10** the ground state has a definite polyradicalic character. All other polycyclic hydrocarbons showing notable multiconfigurational character of singlet ground state have only two dominant configurations; closed shell singlet and doubly excited singlet. Therefore, small polycyclic hydrocarbons have mostly single reference singlet ground state, the medium size systems have notable multireference ground state (singlet or triplet) with only moderate polyradicalic character. The ground state of the largest systems is most probably open-shell singlets with polyradical characters.

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