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Toward (car)borane-based molecular magnets

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Abstract In a previous work, we reported the electronic structure of dimer diradicals composed of two $S = ½$ *closo*-carborane $CB_{11}H_{12}^{\cdot}$ structural units (Theor. Chem. Acc. (2013) 132: 1329). That work has been extended here in order to describe a linear dimer, a linear and a cyclical trimer, and a tetrahedral structure of these units connected by means of a $–CH_2–$ bridge. A mapping of the resulting spin states onto a Heisenberg spin Hamiltonian is proposed for these new chains providing the evaluation of spin-exchange coupling constants.

Keywords Carboranes · Spin population · Heisenberg spin Hamiltonian · Heisenberg coupling constants

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1 Introduction

The magnetic properties in individual molecules, connected to the total spin S of the system, can be manifested macroscopically with properties such as ferromagnetism, antiferromagnetism, and ferrimagnetism [1]. Molecular magnets encompass active fields of research within current and future fundamental and applied sciences [2], such as spintronics, quantum computing, information storage, and nanomedicine [3–5].

As regards to polyhedral heteroborane clusters and particularly the very stable icosahedral carboranes [6], little is known about their magnetic properties. In 1996, Michl et al. [7] obtained the crystal structure of a carborane-based stable free radical: dodecamethylcarba-*closo*-dodecaboranyl $(CB_{11}Me_{12})^{\cdot}$. According to their measurements using electron-spin resonance (ESR) spectroscopy, one can flip

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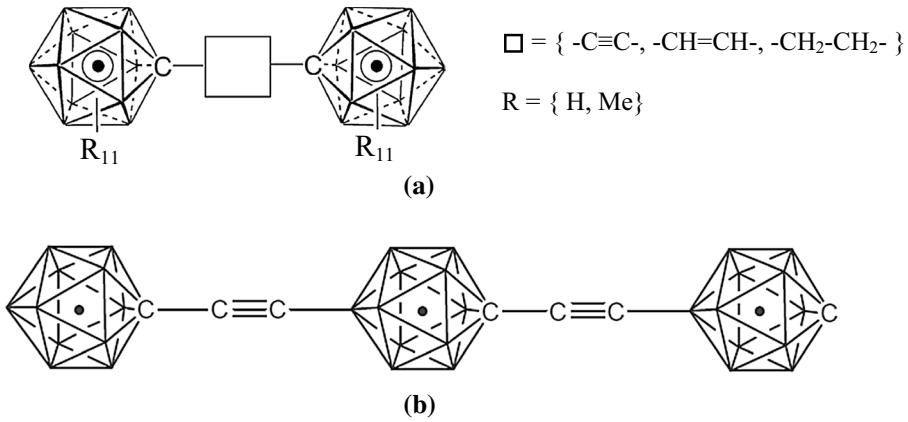

Fig. 1 **a** Two icosahedral $(CB_{11}R_{12})^{\cdot}$ radicals connected through the carbon atom from the icosahedral cage with different bridge units □ = {–C≡C–, –CH=CH–, $–CH_2–CH_2–$} and substituents *R* on each non-connected vertex of the cage, with *R* = {H, Me}. **b** Three carborane radical units $CB_{11}H_{12}^{\cdot}$ connected through the carbon cage atom with acetylene bridge units, with the same cage orientation. In all cases, the *dot* represents an unpaired electron

the spin of the unpaired electron of this radical using a magnetic field of 37 Gauss, which corresponds to a radiofrequency of 104 MHz. Later on, in 2007, these radical units were experimentally connected by means of acetylene and ethylene bridges [8], through the carbon atom of each carborane cage, as displayed in Fig. 1a, with bridge units {–C≡C–} and {–CH=CH–}. In this work [8], they did not report on ESR measurements for the diradicals. The electronic structure of singlet ($S = 0$) and triplet ($S = 1$) electronic states derived from the simplified systems of Fig. 1a was then analyzed, where each methyl group was simplified with a hydrogen atom, with acetylene [9], ethylene, and ethane [10] bridge units (Fig. 1a, with □ = {–C≡C–, –CH=CH–, $–CH_2–CH_2–$} and R = H). The quantum chemical computations showed that the ground state of the diradicals, independently from the bridge unit, is of singlet nature with a very close—almost degenerate—triplet state, {0.004, 0.080, 0.0005 eV} above in energy for the bridge units □ = {–C≡C–, –CH=CH–, $–CH_2–CH_2–$}, respectively.

One can proceed further from Fig. 1a and connect the simplified carborane cage $CB_{11}H_{12}^{\cdot}$ in 1D, 2D, and 3D [11]. From a theoretical point of view, elongation of the 1D chain was carried out by connecting three carborane units with acetylene bridge units, as shown in Fig. 1b, thus having three unpaired electrons, one on each cage [11]. The electronic structure computations showed that for the linear triradical, the ground state is of high-spin nature ($S = 3/2$), with a doublet state ($S = 1/2$) lying 0.013 eV above in energy.

As we shall explain below (vide infra Results ad Discussion), one can further consider the possibility of connecting the radical carborane cages (as magnetic units with $S = 1/2$) with methylene as a bridge unit, into different architectural constructs in 1D, 2D, and 3D. In this work, we will consider a "linear" dimer, a "linear" and "cyclic" three-unit structure, and a "tetrahedral" (four-unit) structure. The reason for generating such structures stems from the possibility of determining the electronic structure for the low-lying spin states of the system. Hence, one could then map these results onto a Heisenberg spin Hamiltonian, thus allowing the connection between experimental and theoretical studies of these polyradical networks [12, 13]. This approach has been applied even to large systems [14] requiring the determination of the corresponding coupling constants.

The organization of this article is as follows. Section 2 summarizes the theoretical concepts and the notation used in this work. In Sect. 3, we report the computational details and the results found in four carborane compounds with different geometrical arrangements as well as the corresponding discussion. Finally, in the last section, we point out the concluding remarks of this work.

1.1 The theoretical models

The phenomenological Heisenberg spin Hamiltonian in Eq. 1 predicts the energy of the different spin states of a many-electron system, provided the spin and electron (orbital) degrees of freedom are independent from each other,

$$\hat{H} = E_0 - 2\sum_{A<B} J_{AB}\hat{S}_A\hat{S}_B \tag{1}$$

where E_0 is a constant meaning the origin of the energy scale chosen for that model; *A* and *B* are the magnetic sites within the system, J_{AB} is the coupling constant between them, and $\hat{S}_A$ and $\hat{S}_B$ are the spin operators assigned to those centers.

In Noodleman's treatment [15, 16], the expectation values of the Hamiltonian $\hat{H}$ in Eq. 1 are calculated through Slater determinants. One of these determinants is the highest pure spin multiplet (*HS*) in which all its orbitals are singly occupied with spin up (a ferromagnetic disposal). The other determinants are mixed spin symmetry and lowered spin symmetry; they are denominated broken-symmetry (*BS*) states possessing singly occupied orbitals with spin down (an antiferromagnetic disposal). Consequently, the differences in the energies corresponding to the determinants are

$$E_{HS} - E_{BS} = -2 \sum_{A<B} J_{AB} \left[\left\langle \hat{S}_A \hat{S}_B \right\rangle^{HS} - \left\langle \hat{S}_A \hat{S}_B \right\rangle^{BS} \right] \quad (2)$$

There are different possibilities to formulate the *BS* determinants so that Eq. 2 constitutes a system of linear equations in the variables J_{AB} provided that the two-center expectation values $\langle \hat{S}_A \hat{S}_B \rangle^{HS}$ and $\langle \hat{S}_A \hat{S}_B \rangle^{BS}$ individually, or their differences $(\langle \hat{S}_A \hat{S}_B \rangle^{HS} - \langle \hat{S}_A \hat{S}_B \rangle^{BS})$, have previously been evaluated. The information on the spin attributed to the fragments *A* and *B* may be obtained from the partitioning of the expectation values of the spin operator

$$\left\langle \hat{S}^2 \right\rangle = \sum_A \sum_B \left\langle \hat{S}_A \hat{S}_B \right\rangle \quad (3)$$

The one-center local spin (*LS*) quantity $\langle \hat{S}_A^2 \rangle$ allows one to determine the spin state of an atom or group of atoms in a molecule or cluster, while the spin correlation between fragments *A* and *B* is described by the expectation value $\langle \hat{S}_A \hat{S}_B \rangle$. This value provides an important tool for linking experimental results interpreted in terms of the Heisenberg spin Hamiltonian to quantum chemical calculations. We will consider the general algebraic expression for $\langle \hat{S}_A \hat{S}_B \rangle$ reported in Refs. [17–21]. The terms $\langle \hat{S}_A^2 \rangle$ and $\langle \hat{S}_A \hat{S}_B \rangle$ (arising from the spin atomic operator formulation) will be identified, respectively, with $\langle \hat{S}^2 \rangle_A$ and $\langle \hat{S}^2 \rangle_{AB}$ in those references.

We have constructed these systems of equations with each of the determinants of type *BS,* which represent all possible spin orientations of the individual centers plus the determinant that describes the *HS* state. In our scheme, each cage of the $CB_{11}H_{12}^{\cdot}$ radical, which possesses an unpaired electron, has been regarded as a magnetic site while the contribution of the bridges $–CH_2–$ has been neglected. We have evaluated the different coupling constants J_{AB} (as well as the E_0 quantity) in systems of two, three, and four magnetic sites that have been summarized in the following subsections. Likewise, we have followed the working hypothesis considering the magnetic sites as equivalent (whenever possible), and consequently, only a few different coupling constants must be evaluated. The spin symmetry of the multiplet states has been identified with the S_z quantum number of the *HS* and *BS* Slater determinants. In order to describe the four polyradicals mentioned in the Introduction, we have considered the cases described below.

1.1.1 Two magnetic sites system

The general solution of the Hamiltonian consists of one single *J* for two singlet (*S*) and triplet (*T*) states

$$E_T = E_0 + J_{12} \left\langle \hat{S}^2 \right\rangle_{12}^{T}$$

$$E_s = E_0 + J_{12} \left\langle \hat{S}^2 \right\rangle_{12}^{S}$$

1.1.2 Three magnetic sites systems

In this case, the general solution of the Hamiltonian yields two doublet (D_1 and D_2) and one quartet states (*Q*).

One single *J*:

$$E_Q = E_0 + J_{12} \left\langle \hat{S}^2 \right\rangle_{12}^{Q} + J_{13} \left\langle \hat{S}^2 \right\rangle_{13}^{Q} + J_{23} \left\langle \hat{S}^2 \right\rangle_{23}^{Q}$$

$$E_D = E_0 + J_{12} \left\langle \hat{S}^2 \right\rangle_{12}^{D} + J_{13} \left\langle \hat{S}^2 \right\rangle_{13}^{D} + J_{23} \left\langle \hat{S}^2 \right\rangle_{23}^{D}$$

$$J_{12} = J_{23}; J_{12} = J_{13}$$

Two different *Js*:

$$E_Q = E_0 + J_{12} \left\langle \hat{S}^2 \right\rangle_{12}^{Q} + J_{13} \left\langle \hat{S}^2 \right\rangle_{13}^{Q} + J_{23} \left\langle \hat{S}^2 \right\rangle_{23}^{Q}$$

$$E_{D_1} = E_0 + J_{12} \left\langle \hat{S}^2 \right\rangle_{12}^{D_1} + J_{13} \left\langle \hat{S}^2 \right\rangle_{13}^{D_1} + J_{23} \left\langle \hat{S}^2 \right\rangle_{23}^{D_1}$$

$$E_{D_2} = E_0 + J_{12} \left\langle \hat{S}^2 \right\rangle_{12}^{D_2} + J_{13} \left\langle \hat{S}^2 \right\rangle_{13}^{D_2} + J_{23} \left\langle \hat{S}^2 \right\rangle_{23}^{D_2}$$

$$J_{12} = J_{23}$$

1.1.3 Four magnetic sites system

One single *J*:

In the four magnetic site system case, a singular value decomposition may also be used to solve the resulting overdetermined system of linear equations [22], which arises from considering the different spin configurations (*Q* now means quintuplet)

$$E_Q = E_0 + J_{12} \left\langle \hat{S}^2 \right\rangle_{12}^{Q} + J_{13} \left\langle \hat{S}^2 \right\rangle_{13}^{Q} + J_{14} \left\langle \hat{S}^2 \right\rangle_{14}^{Q} + J_{23} \left\langle \hat{S}^2 \right\rangle_{23}^{Q} + J_{24} \left\langle \hat{S}^2 \right\rangle_{24}^{Q} + J_{34} \left\langle \hat{S}^2 \right\rangle_{34}^{Q}$$

$$E_T = E_0 + J_{12} \left\langle \hat{S}^2 \right\rangle_{12}^{T} + J_{13} \left\langle \hat{S}^2 \right\rangle_{13}^{T} + J_{14} \left\langle \hat{S}^2 \right\rangle_{14}^{T} + J_{23} \left\langle \hat{S}^2 \right\rangle_{23}^{T} + J_{24} \left\langle \hat{S}^2 \right\rangle_{24}^{T} + J_{34} \left\langle \hat{S}^2 \right\rangle_{34}^{T}$$

$$E_S = E_0 + J_{12} \left\langle \hat{S}^2 \right\rangle_{12}^{S} + J_{13} \left\langle \hat{S}^2 \right\rangle_{13}^{S} + J_{14} \left\langle \hat{S}^2 \right\rangle_{14}^{S} + J_{23} \left\langle \hat{S}^2 \right\rangle_{23}^{S} + J_{24} \left\langle \hat{S}^2 \right\rangle_{24}^{S} + J_{34} \left\langle \hat{S}^2 \right\rangle_{34}^{S}$$

$$J_{12} = J_{13}; J_{12} = J_{14}; J_{12} = J_{23}; J_{12} = J_{24}; J_{12} = J_{34}; J_{23} = J_{24}; J_{23} = J_{34}; J_{24} = J_{34}$$

The determination of coupling constants solving these linear equation systems is based on the previous evaluation

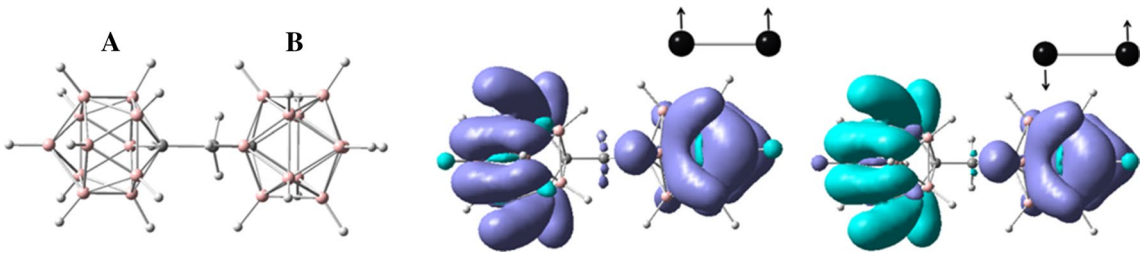

Fig. 2 Geometrical arrangement and calculated spin densities of the linear dimer constituted by two carborane radical units $CB_{11}H_{12}^{\cdot}$ connected through the carbon cage atoms with an methylene bridge unit

Table 1 Local spin populations, energies (au), $\langle \hat{S}^2 \rangle$ expectation values, and coupling constants (in cm^{-1}) for the linear dimer studied in this work in the *HS* and *BS* states

Local spins					
HS state			*BS* state		
	A	B		A	B
A	0.746	0.248	A	0.745	−0.244
B	0.248	0.753	B	−0.244	0.746
	Energy		$\langle \hat{S}^2 \rangle$	$J_{AB}(YA)$	$J_{AB}(LS)$
HS state	−675.703373		2.0076	6.004	6.101
BS state	−675.703345		1.0073		

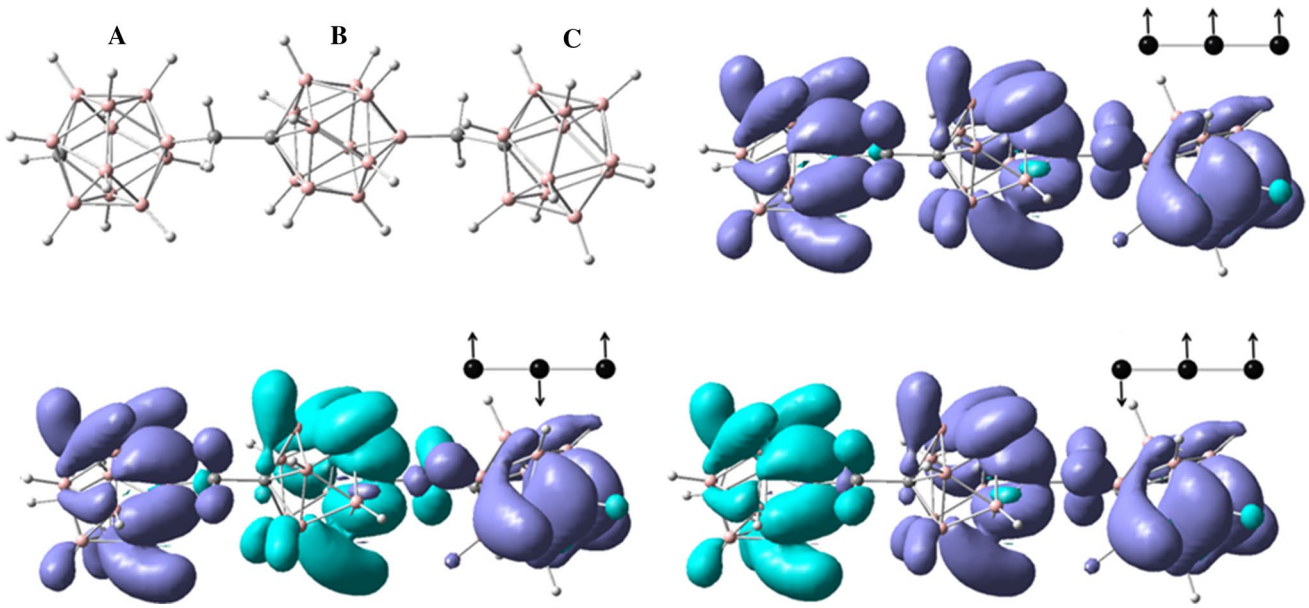

Fig. 3 Geometrical arrangement and calculated spin densities of the linear trimer constituted by three carborane radical units $CB_{11}H_{12}^{\cdot}$ connected through the carbon cage atoms with an methylene bridge unit

of the local spin (*LS*) quantities $\langle \hat{S}_A \hat{S}_B \rangle$ according to the algorithms reported in Refs. [17–21]. Alternatively, in the case of a unique *J* constant, these quantities can also be calculated using the Yamaguchi (*YA*) procedure [23–25] in which the coupling constants are evaluated in terms of energies and spin-squared expectation values

$$J_{AB}(YA) = \frac{E_{HS} - E_{BS}}{\left\langle \hat{S}^2 \right\rangle^{HS} - \left\langle \hat{S}^2 \right\rangle^{BS}} \tag{4}$$

In the next section, we report values for the constants *Js* arising from both approaches.

Table 2 Local spin populations, energies (au), $\langle \hat{S}^2 \rangle$ expectation values, and coupling constants (in cm^{-1}) for the linear trimer ($D_{\infty h}$-like) studied in this work in the *HS* and two *BS* states

Local spins							
HS state				*BS*1 state			
	A	B	C		A	B	C
A	0.713	0.232	0.241	A	0.701	−0.223	0.235
B	0.232	0.708	0.240	B	−0.223	0.688	−0.229
C	0.241	0.240	0.753	C	0.235	−0.229	0.745
*BS*2 state							
		A			B		C
A		0.702			−0.227		−0.239
B		−0.227			0.694		0.236
C		−0.239			0.236		0.752
		Energy		$\langle \hat{S}^2 \rangle$		$J_{AB}(LS)$	$J_{AC}(LS)$
HS state		−1032.644247		3.7600		−65.279	21.875
*BS*1 state		−1,032.644799		1.7449			
*BS*2 state		−1,032.644619		1.7450			

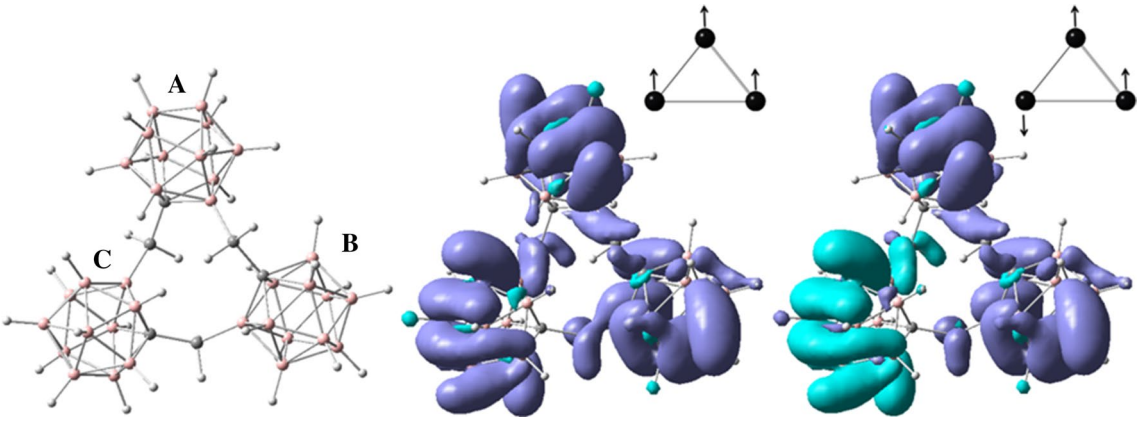

Fig. 4 Geometrical arrangement and calculated spin densities of the cyclical trimer constituted by three carborane radical units $CB_{11}H_{12}$ connected through the carbon cage atoms with methylene bridge units

Table 3 Local spin populations, energies (au), $\langle \hat{S}^2 \rangle$ expectation values, and coupling constants (in cm^{-1}) for the linear trimer (D_{3h}-like) studied in this work in the *HS* and *BS* states

Local spins							
HS state				*BS* state			
	A	B	C		A	B	C
A	0.725	0.237	0.236	A	0.721	0.230	-0.229
B	0.237	0.723	0.234	B	0.230	0.715	−0.225
C	0.236	0.234	0.721	C	−0.229	−0.225	0.712
		Energy		$\langle \hat{S}^2 \rangle$		$J_{AB}(YA)$	$J_{AB}(LS)$
HS state		−1,070.728919		3.7612		−6.301	−6.779
BS state		−1,070.728977		1.7611			

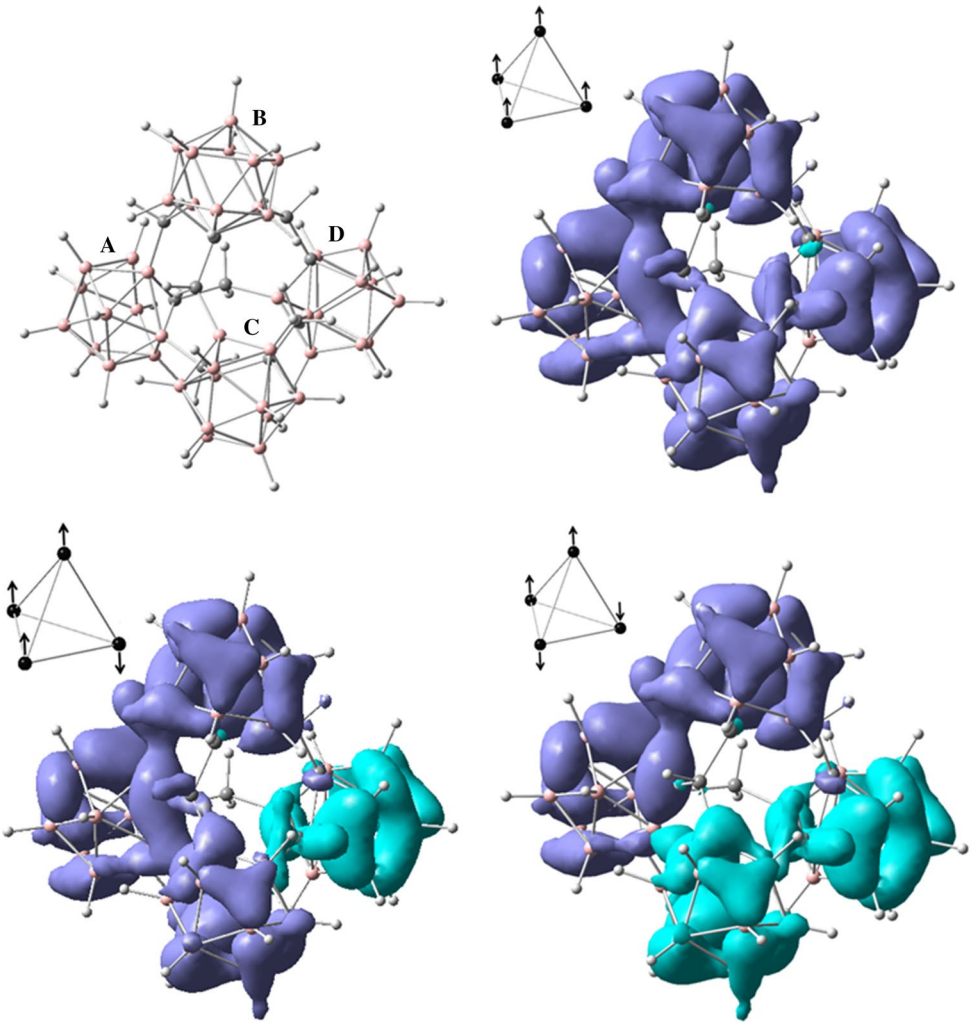

Fig. 5 Geometrical arrangement and calculated spin densities of the tetramer constituted by four carborane radical units $CB_{11}H_{12}^{\cdot}$ connected through the carbon cage atoms with an methylene bridge

2 Results and discussion

As stated above in the Introduction, we chose the methylene bridge unit for connecting the radical carborane cages. This choice was made in order to provide separated spin densities on each magnetic unit (carborane cage) so that one can map these results onto a Heisenberg spin Hamiltonian. We successfully found solutions with a predetermined spin orientation on each cage for the dimers, using acetylene (–C≡C–) and ethylene (–CH=CH–) bridge units. However, for larger systems, such as triangular architectures, we could not find this kind of states. Notwithstanding, these solutions can be found with a methylene bridge unit. We now turn to the description of these molecular architectures.

The determination of the spin density matrices, their corresponding spin densities, and the energies E_{HS} and E_{BS} required in the *LS* and *YA* treatments has been carried out at unrestricted Becke-3-parameter-Lee–Yang–Parr functional levels (UB3LYP) using the Gaussian 09 [26] package and the atomic basis sets 6-31G(d). In all the systems, the geometries were optimized for the *HS* state at UB3LYP/6-31G(d) level. The evaluation of the one- and two-center local spins, $\langle \hat{S}_A^2 \rangle$ and $\langle \hat{S}_A \hat{S}_B \rangle$, respectively, was performed in subsequent steps using our own codes. Likewise, the solutions of the above-mentioned linear equations have been obtained from the Mathematica 9.0 [27].

The results corresponding to the linear dimer $[(CB_{11}H_{11})^{\cdot}–CH_2–(CB_{11}H_{11})^{\cdot}]$ are shown in Fig. 2 and Table 1, where *A* and *B* stand for the left and right moieties, respectively. This figure also indicates the two possible orientations of the cage spins. As can be observed, both states *HS* (triplet) and *BS* (singlet) present $\langle \hat{S}_A^2 \rangle$ quantities close to 0.75 [the canonical value is 1/2 (1 + 1/2)] meaning the two electrons are well localized in each cage. The signs of the two-center local spin components $\langle \hat{S}_A \hat{S}_B \rangle$ positive for the triplet state and negative for the singlet one confirm the predictions found in previous works [10] being their absolute values close to 0.25 (i.e., 1/2·1/2). The energies found are very similar indicating a near degenerate situation.

Table 4 Local spin populations, energies (au), $<\hat{S}^2>$ expectation values, and coupling constants (in cm^{-1}) for the tetramer studied in this work in the *HS* and two *BS* states

Local spins								
HS state					*BS*1 state			
	A	B	C	D		A	B	C	D
A	0.683	0.234	0.221	0.205	A	0.672	0.226	0.196	−0.194
B	0.234	0.735	0.235	0.218	B	0.226	0.721	0.210	−0.208
C	0.221	0.235	0.687	0.206	C	0.196	0.210	0.646	−0.180
D	0.205	0.218	0.206	0.626	D	−0.194	−0.208	−0.180	0.605
*BS*2 state								
	A		B		C		D	
A	0.593		0.189		−0.176		−0.167	
B	0.189		0.700		−0.213		−0.202	
C	−0.176		−0.213		0.637		0.188	
D	−0.167		−0.202		0.188		0.605	
	Energy		$<\hat{S}^2>$		$J_{AB}(YA)(HS/BS2)$		$J_{AB}(LS)$(overdet)	
HS state	−1,503.830274		6.0136		−132.798		−149.162	
*BS*1 state	−1,503.831593		2.9927					
*BS*2 state	−1,503.832744		1.9312					

Although in this treatment the *HS* state has been formulated by means of Slater determinants, the spin contamination is very low and the coupling constants predicted by our method are in agreement with those provided by the Yamaguchi method. We have also determined the local spins corresponding to the bridge unit considered as a whole; the values found are $\langle\hat{S}_A^2\rangle = 0.0043$ and $\langle\hat{S}_A\hat{S}_B\rangle = 0.0011$ for the *HS* state and $\langle\hat{S}_A^2\rangle = 0.0043$ $\langle\hat{S}_A\hat{S}_B\rangle = 0.0018$ for the *BS* one. These values turn out to be negligible, and consequently, the bridge units are not considered in the computations.

In Fig. 3 and Table 2, we report the results found for the linear trimer composed of three units $CB_{11}H_{120}^{\cdot}$ bonded with two methylene groups: $[(CB_{11}H_{11})^{\cdot}–CH_2–(CB_{11}H_{10})^{\cdot}–CH_2–(CB_{11}H_{11})^{\cdot}]$. In this Table, the A, B, C moieties start from left to right as indicated in Fig. 3. The three different spin orientations of this system provide a *HS* quartet and the two different *BS* doublets. From a qualitative point of view, these results show that the electronic distribution is similar to that described in the previous system, exhibiting well-localized electrons in each cage. The energies of these states (the *HS* quartet and the two *BS* doublets) are also near degenerate, although the spin contamination is higher than in the previous compound. The negative sign of the coupling constant J_{AB} shows the ferromagnetic character of the adjacent *A* and *B* moieties while J_{AC} (positive) presents an antiferromagnetic behavior [28]. The local spins of the bridge units for this compound are also negligible and consequently have been omitted.

This triradical has also been studied with a triangular arrangement bonded with three methylene groups: $[(CB_{11}H_{10})^{\cdot}–CH_2]_3$. The results are shown in Fig. 4 and Table 3. The compound symmetry allows one to describe this aggregate by means of a *HS* state (quartet) and a *BS* one (doublet) that arise from the corresponding spin coupling. No significant differences between its *HS* and *BS* energies have been found with respect to the linear trimer, indicating the independency of each magnetic site and the small gap between the energies of those states; the spin contaminations are also similar to those found in the linear trimer. A weak ferromagnetic interaction is also observed between the adjacent moieties in agreement with the Yamaguchi treatment.

The results for the tetraradical system with a tetrahedrical arrangement, $[(CB_{11}H_9)^{\cdot}–CH_2]_4$, are shown in Fig. 5 and Table 4 in which the two *BS* states refer to the two lowest energies. This system presents one-center spin populations $\langle\hat{S}_A^2\rangle$ lower than the other elements of this series of radicals what can be interpreted as a higher interaction between the magnetic sites. Likewise, one can observe higher differences in energies between all states confirming that interpretation. The Yamaguchi coupling constant has been evaluated using the *HS* and *BS*2 states due to the last one, that is, the ground state. In this polyradical, the resulting linear equation system mentioned in Sect. 2, which allows to determine the coupling constants in the local spin approach, turns to be overdetermined, which has been indicated in Table 4. This system presents local spin values for the bridge unit (the highest ones of this series) $\langle\hat{S}_A^2\rangle = 0.0064$ and $\langle\hat{S}_A\hat{S}_B\rangle = 0.0507$ (for the *HS* state) and $\langle\hat{S}_A^2\rangle = 0.0001$ and $\langle\hat{S}_A\hat{S}_B\rangle = 0.0177$ (for the *BS* state); again, these values can be neglected as in the case of above-mentioned simplest linear dimer $(CB_{11}H_{12}^{\cdot})_2–CH_2$ compound.

We should emphasize that for all the studied systems in this work, the largest differences between two values for $\langle \hat{S}_A^2 \rangle$ corresponding to equivalent centers are within 0.109 in the *HS* state; the largest differences between $\langle \hat{S}_A \hat{S}_B \rangle$ expectation values are within 0.029; these small values confirm that the regular linear, triangular, and tetrahedral arrangements are suitable for the proposed systems.

3 Concluding remarks

In this work, we have studied a series of polyradicals derived from the connection of two, three, and four carborane radicals $CB_{11}H_{12}^{\cdot}$ bonded by methylene groups within several geometrical arrangements. This study extends and complements our previous determinations, based on local spins, on this type of radicals bonded by ethane, ethylene, and acetylene bridges. The results obtained from local spin populations and energy evaluations show a low interaction between these radicals when the bridge unit is a methylene group as well as a negligible interaction between the bridge units and the magnetic sites. The quantitative determination of coupling constants arising from our method, based on the direct partitioning of the spin-squared expectation value $\langle \hat{S}^2 \rangle$, yields values of similar magnitude to those obtained from the Yamaguchi procedure. These results confirm the ability of our local spin technique to determine electronic structures and magnetic behaviors on this type of chains within the Heisenberg Hamiltonian framework.

In future works, one could also consider spin polarization effects [29], well known from simple radicals and diradicals, in order to better understand the magnetic properties of the systems studied in this work and further polyradical molecular architectures derived from the s = 1/2 icosahedral carborane magnetic unit $(CB_{11}H_{12})^{\cdot}$. Other chemical compounds with magnetic activity are currently being studied in our laboratories.

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