# Characterization and Quantification of Polyradical Character

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S *Supporting Information*

ABSTRACT: The decomposition of $\langle \hat{S}^2 \rangle$ into atomic and diatomic contributions (local spin analysis) is used to detect and quantify the polyradical character of molecular systems. A model triradical system is studied in detail, and the local spin analysis is used to distinguish several patterns of local spin distributions and spin–spin interactions that can be found for different electronic states. How close a real molecular system is to an ideal system of k perfectly localized spin centers is utilized to define a measure of its k-radical character. The spin properties and triradical character of the lowest-lying electronic states of a number of all σ, all π, and σ–π organic triradicals are discussed in detail. The local spin contributions exhibit good correlation with experimental triradical stabilization energies.

Spin Distribution in Triradicals
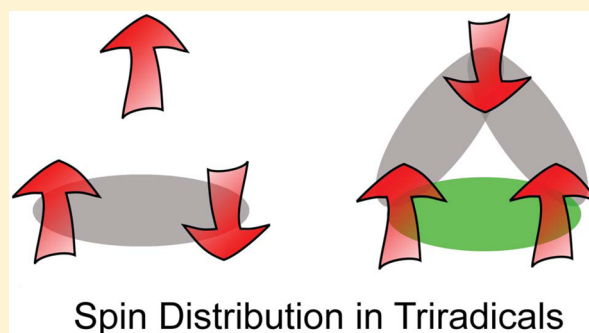
INTRODUCTION

A polyradical can be considered as a molecule with N electrons occupying N near degenerate orbitals. The design of organic high-spin polyradicals is of major relevance for the development of new organic and organometallic magnetic materials.[1] As opposed to the simplest case of diradicals,[2] the more general case of organic polyradicals adds extra complexity to the puzzle of radical character quantification, as most of the indices and quantities that have been proposed in the literature to detect and quantify the diradical character of molecular systems[3−11] cannot be trivially generalized beyond diradicals.

Probably, the most significant feature of a polyradical system is the presence of some local spin. The spin density is typically used to characterize the spin properties of molecular systems, but when the overall system is a singlet there is no spin density. Yet, in some cases (e.g. singlet diradicals) the existence of some local spin is still assumed. In the last years there has been a growing interest in recovering local spins from the analysis of ab initio wave functions.[12−18] Mayer showed[14] that the most appropriate approach to the problem starts from the decomposition of the expectation value of the spin-squared operator into a sum of atomic and diatomic contributions as

$$\langle \hat{S}^2 \rangle = \sum_A \langle \hat{S}^2 \rangle_A + \sum_{A, B \neq A} \langle \hat{S}^2 \rangle_{AB} \tag{1}$$

A proper formulation of eq 1 can provide nonzero one- and two-center terms for pure singlets, thus overcoming the limitation of the spin density (see below).

In this work we make use of the local spin analysis to tackle the characterization and quantification of the polyradical character, with particular emphasis on triradicals. The manuscript is organized as follows. First we overview the essentials of the method. Next, a model triradical system is introduced and discussed in light of the local spin analysis. This provides us

with reference values for the atomic and diatomic contributions of $\langle \hat{S}^2 \rangle$ in the ideal case of three perfectly localized spins for different electronic states. Finally, the spin properties of a number of all σ, all π, and σ–π triradicals such as trimethylenebenzene (TMB),[19−24] tridehydrobenzene isomers (TDB),[24−27] and dehydro-m-xylylene (DMX),[24,28,29] are characterized in detail in their lowest-lying doublet and quartet electronic states. Direct comparison with the appropriate reference values obtained for the model system permit to actually quantify the triradical character of these species.

LOCAL SPIN ANALYSIS

In general, any decomposition of physical quantities into atomic (and diatomic) contributions relies on the identification of the atom within the molecule. This can be achieved by subdividing the physical space into atomic regions or domains. The one- and two-electron integrals restricted over these atomic domains lead to atomic and diatomic quantities, respectively. Recently,[18] we have introduced a general formulation for the decomposition of the expectation value of $\langle \hat{S}^2 \rangle$ in the most general framework of three-dimensional space analysis. The corresponding atomic and diatomic contributions of eq 1 can be formally expressed as

$$\langle \hat{S}^2 \rangle_A = \frac{3}{4} \int_{\Omega_A} u(\vec{r}_1) d\vec{r}_1 + \frac{1}{2} \int_{\Omega_A} \int_{\Omega_A} \Lambda(\vec{r}_1, \vec{r}_2; \vec{r}_1, \vec{r}_2) d\vec{r}_1 d\vec{r}_2$$
$$- \frac{1}{2} \int_{\Omega_A} \int_{\Omega_A} \Lambda(\vec{r}_1, \vec{r}_2; \vec{r}_2, \vec{r}_1) d\vec{r}_1 d\vec{r}_2 \tag{2}$$

and

$$\langle \hat{S}^2 \rangle_{AB} = \frac{1}{2} \int_{\Omega_A} \int_{\Omega_B} \Lambda(\vec{r}_1, \vec{r}_2; \vec{r}_1, \vec{r}_2) d\vec{r}_1 d\vec{r}_2$$

$$- \frac{1}{2} \int_{\Omega_A} \int_{\Omega_B} \Lambda(\vec{r}_1, \vec{r}_2; \vec{r}_2, \vec{r}_1) d\vec{r}_1 d\vec{r}_2 \qquad (3)$$

where we have used the density of effectively unpaired electrons first defined by Takatsuka[30] and utilized by several authors[31−34] as

$$u(\vec{r}) = 2\rho(\vec{r}) - \int \rho(\vec{r}; \vec{r}') \rho(\vec{r}'; \vec{r}) d\vec{r}' \qquad (4)$$

and the so-called spin-free cumulant[35,36]

$$\Lambda(\vec{r}_1, \vec{r}_2; \vec{r}_1', \vec{r}_2') = \Gamma(\vec{r}_1, \vec{r}_2; \vec{r}_1', \vec{r}_2') - \frac{1}{2} \rho^s(\vec{r}_1; \vec{r}_2') \rho^s(\vec{r}_2; \vec{r}_1') \qquad (5)$$

expressed through the first-order spin-density matrix

$$\rho^s(\vec{r}; \vec{r}') = \rho^\alpha(\vec{r}; \vec{r}') - \rho^\beta(\vec{r}; \vec{r}') \qquad (6)$$

and the spinless cumulant (sum of the four respective spin-dependent cumulant contributions)

$$\Gamma(\vec{r}_1, \vec{r}_2; \vec{r}_1', \vec{r}_2') = \sum_{\sigma,\sigma'}^{\alpha,\beta} \Gamma^{\sigma,\sigma'}(\vec{r}_1, \vec{r}_2; \vec{r}_1', \vec{r}_2') \qquad (7)$$

Note that the spin free cumulant $\Lambda(\vec{r}_1, \vec{r}_2; \vec{r}_1' \vec{r}_2')$ does not vanish for open-shell single determinant wave functions, due to the contributions from the spin density. The Ω_A and Ω_B in eqs 2 and 3 denote integration over the atomic domains of atoms A and B, respectively. In this work we have used those provided by the recently introduced topological fuzzy Voronoi cells (TFVC) scheme.[37] They can be regarded as a computationally more efficient (but somewhat less theoretically sound) alternative to Bader's QTAIM domains. Yet, the behavior of both methods is strikingly similar.[37]

The interpretation of the $\langle \hat{S}^2 \rangle_A$ and $\langle \hat{S}^2 \rangle_{AB}$ values, henceforth local spin analysis, has been recently discussed in detail in the context of a chemical bonding analysis of main-group diatomics.[38] We will give here a brief review of its features. The most relevant is that, contrary to the simplest population analysis of the spin density, the local spin analysis can yield nonzero atomic and diatomic contributions for pure singlet states. The atomic $\langle \hat{S}^2 \rangle_A$ value denotes and quantifies the existence of some local atomic spin *within* the molecule, whereas the magnitude and sign of the diatomic contributions inform about the nature of the couplings between these local spins.[12,39,40]

In the simplest case of two perfectly localized parallel spins on centers A and B, $\langle \hat{S}^2 \rangle_A = 3/4$ and $\langle \hat{S}^2 \rangle_{AB} = 1/4$, for an overall value of $\langle \hat{S}^2 \rangle = 2$. The $\langle \hat{S}^2 \rangle_A$ value is consistent with the corresponding $\langle \hat{S}^2 \rangle$ value for a one-electron system, and the positive sign of $\langle \hat{S}^2 \rangle_{AB}$ indicates that the two local spins are parallel. If the two spins are not perfectly localized, the value of $\langle \hat{S}^2 \rangle_A$ increases and $\langle \hat{S}^2 \rangle_{AB}$ decreases, indicating a partial triplet character on the given center and a concomitant decrease of the diatomic contribution.

When two perfectly localized spins are coupled as a singlet, a proper multireference wave function is needed to account for the spin properties of the system. In that case, the local spin analysis yields $\langle \hat{S}^2 \rangle_A = 3/4$ and $\langle \hat{S}^2 \rangle_{AB} = -3/4$. The former is again consistent with a one-electron system, and the negative sign of the diatomic term now indicates that the local spins are entangled (coupled as a singlet), for an overall value of $\langle \hat{S}^2 \rangle = 0$.

If the two spins are not perfectly localized, both the values of $\langle \hat{S}^2 \rangle_A$ and $\langle \hat{S}^2 \rangle_{AB}$ tend to decrease. In the limiting case of a closed-shell single-determinant description, the local spin contributions exactly vanish.

Thus, the $\langle \hat{S}^2 \rangle_A$ and $\langle \hat{S}^2 \rangle_{AB}$ values can be used to quantify the presence of local spin, by comparison with the ideal values expected for perfectly localized electrons. For instance, in the case of benzene, a local spin value on the C atoms of ca. 0.12 was obtained,[18] induced by the fluctuation of the π electrons. Both CASSCF and UHF wave functions similarly account for this effect. This value is far from the 3/4 expected for a perfectly localized electron, so the hexaradical character of benzene is non-negligible but certainly minimal. Also, in the series of singlet ortho-, meta-, and para-benzyne, local spins of 0.32, 0.54, and 0.96, respectively, were obtained on the pairs of formal carbon radical centers, reflecting the increasing radical character, particularly from ortho to meta. The value for para-benzyne exceeded the ideal value of a singly localized electron (3/4), suggesting the additivity of the spins of the σ and π electrons on the radical center. Such σ and π decomposition (more precisely, $\sigma-\sigma$, $\pi-\pi$, and $\sigma-\pi$, due to the two-electron nature of the spin-squared operator) is very useful whenever it is possible to apply and was recently used to unravel the complex electronic structure of C_2, best described as a diradicaloid.[38]

COMPUTATIONAL DETAILS

All wave functions for the molecular systems studied have been obtained at the CASSCF level with the cc-pVTZ basis set. For the simple triradical model systems the STO-3G basis set in combination with CASSCF or UHF levels of theory has been used instead. The first- and second-order density matrices have been obtained using a modified version of Gaussian03[41] and an auxiliary program[42] that reads and processes the CASSCF outputs. All local spin components are given in atomic units. All calculations have been carried out at the geometrical structure of the molecules optimized at the current level of theory, unless otherwise indicated. The local spin analysis has been performed with the program APOST-3D[43] using the TFVC atomic definition.[37,44]

RESULTS AND DISCUSSION

In the past we have made use of simple model systems to derive the limiting values of $\langle \hat{S}^2 \rangle_A$ and particularly $\langle \hat{S}^2 \rangle_{AB}$ in the case of perfectly localized spins.[38] This permits establishing to which extent the local spin components obtained for a real system match those of the perfectly localized one. From now on we will focus on triradicals. The simplest model of a triradical is made up of three H atoms described with minimal basis, placed at the vertices of a triangle. For such a system one can have a quartet state ($S = 3/2$) or two doublet states ($S = 1/2$). Since the local spin analysis is independent of the particular S_z projection for nonsinglet states,[16] in the case of the quartet we can consider the $M_S = 3/2$ state, which is readily described with a ROHF wave function. The perfectly localized spins situation is achieved for large H−H distances. A pictorial representation of the results of the local spin analysis obtained at the dissociation limit for the quartet state is given in Figure 1.

The $\langle \hat{S}^2 \rangle_A$ and $\langle \hat{S}^2 \rangle_{AB}$ values and the atomic $\langle \hat{S} \rangle_z$ values (half of the atom-condensed spin-density) are also shown. The local spin, $\langle \hat{S}^2 \rangle_A$, on each hydrogen atom is 3/4, consistent with that of a single electron. The diatomic spin contributions $\langle \hat{S}^2 \rangle_{AB}$ are
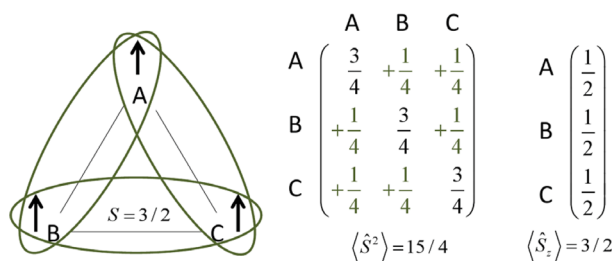
Figure 1. Pictorial representation of the local spin analysis for perfectly localized spins in quartet state.

equal to $+1/4$ for any $A \neq B$, indicating the parallel arrangement of the local spins. The spin density on each H atom equals to 1, and so is the number of effectively unpaired electrons. When the spins are not perfectly localized, the values of $\langle \hat{S}^2 \rangle_A$ increase, indicating partial high-spin contributions on the centers (triplet and quartet, in this case). Consequently, the $\langle \hat{S}^2 \rangle_{AB}$ terms decrease. For instance, a ROHF/STO-3G wave function with an H−H distance of 1 Å yields $\langle \hat{S}^2 \rangle_A = 0.80$ and $\langle \hat{S}^2 \rangle_{AB} = 0.23$ using the TFVC scheme.[37] As there is only one atomic orbital per atom, a Mulliken-type approach would yield the $\langle \hat{S}^2 \rangle_A$ and $\langle \hat{S}^2 \rangle_{AB}$ values of 1 independently of the interatomic distance. As discussed in ref 38, the previous result is only possible using topological atomic definitions.

In the case of the doublet states one can encounter two limiting situations for perfectly localized spins, represented in Figure 2. The upper panel describes a situation in which two of
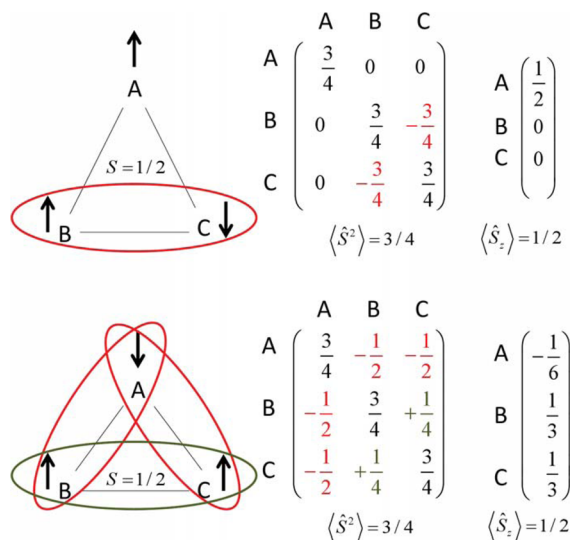

Figure 2. Pictorial representation of the local spin analysis for perfectly localized spins in doublet states.

the perfectly localized spins are coupled as a singlet (centers B and C), whereas the third spin does not show any coupling with them, i.e., $\langle \hat{S}^2 \rangle_{AB} = \langle \hat{S}^2 \rangle_{AC} = 0$. The spin density is zero for the centers B and C and 1 for the center A. This represents a case in which the triradical is best pictured as a diradical + a radical center.

Another situation is depicted in the lower panel of 2. In this case, the three perfectly localized spins interact with each other. The spins on centers B and C exhibit parallel arrangement, as indicated by the $\langle \hat{S}^2 \rangle_{BC} = +1/4$ value, and are antiparallel with the local spin on center A. The diatomic spin contributions $\langle \hat{S}^2 \rangle_{AB} = \langle \hat{S}^2 \rangle_{AC}$ are equal to $-1/2$. The negative sign is an

indication that the spins on the centers are antiparallel, but the actual value differs from the $-3/4$ that one obtains for a pair of isolated spins coupled as a singlet. The atomic spin densities are nonzero but cannot be trivially associated with three perfectly localized spins: the spin density on center A amounts to $-1/3$, whereas that of centers B and C is $2/3$, for an overall value of 1. This illustrates once again the limitation of use of the spin density for the description of local spins. The simple pictorial representation of 2 can only be derived from the local spin analysis.

Of course, multireference wave functions are necessary to properly describe the doublet states. For this model system the exact wave function is achieved at the CASSCF(3,3) level of theory. The limiting situations depicted in the upper and lower panels of Figure 2 can be put into correspondence with the spin-adapted configurations of Figures 3c and 3d of ref 24, respectively.

At the dissociation limit (i.e., for large H−H distances), the two doublet states become degenerate. With our model system we have observed that when the B−C distance is shorter than the A−B or A−C ones, the picture of the upper panel of Figure 2 is lower in energy. On the contrary, as the B−C distance stretches with respect to the other two, the lower panel picture prevails. For instance, when the A−B and A−C distances are 1 Å but the B−C distance is shortened to 0.9 Å, the local spin analysis of the ground-state CASSCF/STO-3G wave function yields $\langle \hat{S}^2 \rangle_B = \langle \hat{S}^2 \rangle_C = 0.15$ and $\langle \hat{S}^2 \rangle_A = 0.57$. The diatomic spin components are $\langle \hat{S}^2 \rangle_{AB} = \langle \hat{S}^2 \rangle_{AC} = -0.00(4)$ and $\langle \hat{S}^2 \rangle_{BC} = -0.05$. Contrary to the quartet state, at such short distances the H atoms exhibit some covalent bonding that results in a significant reduction of the local spins.[38] Nevertheless, the atomic and diatomic spin contributions reflect a diradical + radical picture (the diradical in this case being rather unsubstantial). If the B−C distance is stretched to 1.1 Å the atomic and diatomic spin components are $\langle \hat{S}^2 \rangle_B = \langle \hat{S}^2 \rangle_C = 0.41$ and $\langle \hat{S}^2 \rangle_A = 0.11$ and $\langle \hat{S}^2 \rangle_{AB} = \langle \hat{S}^2 \rangle_{AC} = -0.08$ and $\langle \hat{S}^2 \rangle_{BC} = 0.08$. Again, these values are far from those of the perfectly localized spins ideal case. Yet, the local spin analysis does indicate that the system is better described by the picture of the lower panel of Figure 2, the centers B and C exhibiting a more significant radical character than center A.

Thus, the magnitude and sign of the diatomic spin terms differentiate between doublet and quartet states. Moreover, they also reveal that two patterns of spins distribution may occur in the lowest spin state. One type is best characterized as a system in which one can distinguish a singlet diradical and an additional isolated radical center. In the other one the three spin centers exhibit interactions with each other.

The $\langle \hat{S}^2 \rangle_A$ and $\langle \hat{S}^2 \rangle_{AB}$ values obtained for an actual molecular system can be used to quantify its polyradical character, by comparing them with the corresponding reference values expected for perfectly localized spins. In the case of the $\langle \hat{S}^2 \rangle_{AB}$ terms, however, different values should be taken as reference depending on the state and nature of the spin distribution of the system, which would add unnecessary complications. Thus, one can simply focus on the values of the atomic spin contributions and define a RMSD measure of k-radical character as

$$\Delta^{(k)} = \sqrt{\frac{\sum_A (\langle \hat{S}^2 \rangle_A - \langle \hat{S}^2 \rangle_A^{id})^2}{n}} \tag{8}$$

where the $\langle \hat{S}^2 \rangle_A^{id}$ represent the atomic ideal values, and n is the total number of atoms/fragments considered in the local spin analysis (the hydrogen atoms can often be safely ignored). The smaller the $\Delta^{(k)}$ value the closer the system is to a reference picture of k perfectly localized spin centers. This indicator can be computed for any system in any state, and its value depends upon the particular choice of the $\langle \hat{S}^2 \rangle_A^{id}$ terms.

Table 1. k-Radical Character Index for $k = 3$, $\Delta^{(3)}$, for a Set of Molecules[a]

molecule	$\Delta^{(3)}$	
	doublet	quartet
TMB	0.232 (0.231)	0.248
2-DMX	0.227	0.287
5-DMX	0.263	0.253
1,2,3-TDB	0.207	0.181
1,2,4-TDB	0.279	0.165
1,3,5-TDB	0.200	0.168

[a]The value in paretheses for TMB corresponds to the lowest-lying $^2B_1$ state.

We are now in a position to tackle actual triradical systems. Local spin analysis will be undertaken in order to shed light into their electronic distribution. In particular, for the doublet states the analysis will be used to distinguish which of the two pictures better correspond to the actual spin distribution. The triradical character will be quantified by the corresponding $\Delta^{(3)}$ values. Figure 3 collects the structures and numbering schemes of the set of triradicals that are considered in this work.
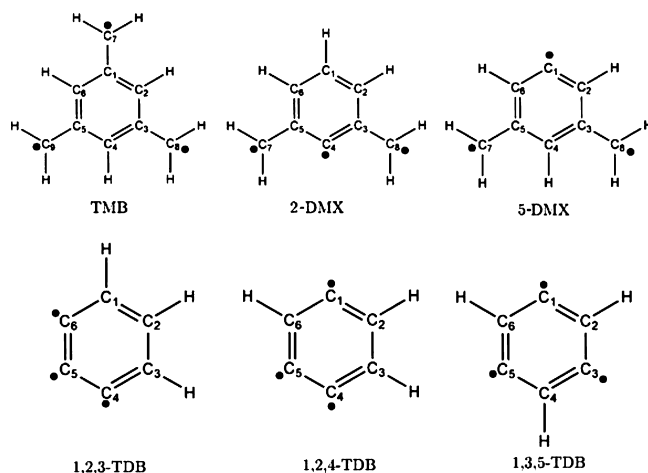

Figure 3. Numbering scheme of trimethylenebenzene (TMB), dehydro-m-xylylene isomers (2-DMX and 5-DMX), and tridehydrobenzene isomers (1,2,3-TDB, 1,2,4-TDB, and 1,3,5-TDB).

Let us discuss first in detail the σ,σ,σ-triradical trimetylene-benzene (TMB). The results of the local spin analysis are gathered in Table 2. We have analyzed the ground $^4A'$ state, with D_{3h} symmetry, and the Jahn–Teller distorted $^2A_2$ and $^2B_1$ doublets, of C_{2v} symmetry with proper CASSCF wave functions. The active space included 9 electrons and 9 orbitals, 6 π orbitals of the ring, and the 3 orbitals associated with the unpaired electrons. The $^2A_2$ and $^2B_1$ states are 15.55 and 15.74 kcal/mol higher in energy, respectively, with respect to the ground $^4A'$ state. These energies are in good agreement with previous theoretical predictions.[19–22,24]

The main local spins centers of TMB in the quartet state are the external carbon atoms labeled C_7, C_8, and C_9, which formally bear the unpaired electrons. The local spin value is 0.41. The centers 2, 4, and 6 also present a substantial value of $\langle \hat{S}^2 \rangle_C = 0.32$. This result can be explained by the resonance structures of the molecule; in most of them the unpaired electron is formally located on these centers.[22] The local spin value on carbons 1, 3, and 5 (0.14) is similar to that obtained for the carbon atoms of benzene[17] or the central carbon atom of the allyl radical. In fact, the TMB molecule can also be considered as formed from three pseudoallyl radicals, as shown in Figure 4. The local spin on each symmetrically equivalent pseudoallyl moiety is 0.82, and the diatomic spin terms between them are 0.22. Thus, the overall picture of the molecule would be similar to the ideal case of 1, with a small deviation from the perfectly localized spins situation induced by electron delocalization among the pseudoallyl moieties.

Turning back to the atomic and diatomic contributions, the latter are very small in absolute value (less than 0.1 in all cases). This is because the spin is partially localized over several centers which exhibit many similar (and small) interactions. Nevertheless, the sign of these terms provides valuable information about the alignment of the partial local spins: the positive sign of $\langle \hat{S}^2 \rangle_{C_7C_8}$ and the equivalent $\langle \hat{S}^2 \rangle_{C_7C_9}$ and $\langle \hat{S}^2 \rangle_{C_8C_9}$ indicate that the local spins on these centers are parallel and so on. The overall local spin distribution derived from the analysis of the quartet state is also depicted on 4.

The case of the excited doublet states is somewhat more complex. The system undergoes a Jahn–Teller distortion[20] that lowers the symmetry of the molecule to C_{2v}. Two, almost degenerate, double states, $^2A_2$ and $^2B_1$, result from the elongation and shortening of the C_1–C_7 distance, respectively. The molecule can not be conceived as three pseudoallyl moieties anymore (at least not in a unique manner), and the local spin contributions on the symmetry-equivalent carbon atoms of the quartet state are now different. In the $^2A_2$ state, the local spin on the external C atoms increases with respect to that of the quartet state. Also, the carbon atoms of the benzene ring exhibit smaller local spin values and more similar among them. This indicates that the spin is more efficiently localized on atoms 7–9, and the remaining centers play a minor role. The $\langle \hat{S}^2 \rangle_{C_8C_9}$ diatomic contribution is positive and similar to the value of the quartet state, indicating parallel arrangement of the local spins on C_8 and C_9. Instead, the $\langle \hat{S}^2 \rangle_{C_7C_8} = \langle \hat{S}^2 \rangle_{C_7C_9} = -0.24$ value clearly indicates that the spin on center C_7 is flipped with respect to that of the quartet state. In the $^2B_1$ state, the local spins on the carbon atoms of the benzene ring, C_2, C_4, and C_6, are smaller than for the quartet state. As in the $^2A_2$ state, this indicates that the spins are more localized on centers 7–9. The large and negative $\langle \hat{S}^2 \rangle_{C_8C_9} = -0.37$ value indicates a relatively strong antiferromagnetic interaction between centers 8 and 9. Interestingly, the very small $\langle \hat{S}^2 \rangle_{C_7C_8}$ and $\langle \hat{S}^2 \rangle_{C_7C_8}$ diatomic terms suggest that the spin on atom 7 is not coupled to atoms 8 and 9. The local spin analysis on the $^2B_1$ state thus indicates that it is best described as an isolated radical center (atom 7) plus a diradical (atoms 8 and 9).

Figure 5 provides a simpler representation of the local spin analysis of the two doublet states of TMB. Direct comparison with Figure 2 indicates that the diatomic contributions are still less than half the value expected for perfectly localized electrons. The $\Delta^{(3)}$ values (i.e., with respect to an ideal

Table 2. Local Spin Values and Atom-Condensed Spin Densities for TMB in Different Electronic States (Relative Energies in kcal/mol in Parentheses)

state	$\langle \hat{S}^2 \rangle_{CC}$	C_1	C_2	C_3	C_4	C_5	C_6	C_7	C_8	C_9	$\langle S_z \rangle_C$
$^4A_2$ (0.00)	C_1	0.14									−0.10
	C_2	−0.06	0.32								0.44
	C_3	0.01	−0.06	0.14							−0.10
	C_4	−0.02	0.06	−0.06	0.32						0.44
	C_5	0.01	−0.02	0.01	−0.06	0.14					−0.10
	C_6	−0.06	0.06	−0.02	0.06	−0.06	0.32				0.44
	C_7	−0.08	0.07	−0.02	0.07	−0.02	0.07	0.41			0.55
	C_8	−0.02	0.07	−0.08	0.07	−0.02	0.07	0.08	0.41		0.55
	C_9	−0.02	0.07	−0.02	0.07	−0.08	0.07	0.08	0.08	0.41	0.55
$^2A_2$ (15.55)	C_1	0.14									−0.05
	C_2	−0.07	0.26								0.24
	C_3	0.01	−0.05	0.14							−0.06
	C_4	−0.02	0.02	−0.06	0.25						0.14
	C_5	0.01	−0.02	0.01	−0.06	0.14					−0.06
	C_6	−0.07	0.05	−0.02	0.02	−0.05	0.26				0.24
	C_7	−0.02	−0.04	0.03	−0.15	0.03	−0.04	0.58			−0.22
	C_8	−0.01	0.02	−0.08	0.05	−0.02	0.02	−0.24	0.43		0.33
	C_9	−0.01	0.02	−0.02	0.05	−0.08	0.02	−0.24	0.08	0.43	0.33
$^2B_1$ (15.74)	C_1	0.14									−0.07
	C_2	−0.05	0.24								0.17
	C_3	0.01	−0.06	0.14							−0.05
	C_4	−0.03	0.04	−0.06	0.28						0.29
	C_5	0.01	−0.02	0.01	−0.06	0.14					−0.05
	C_6	−0.05	0.01	−0.02	0.04	−0.06	0.24				0.17
	C_7	−0.08	0.03	−0.02	0.05	−0.02	0.03	0.38			0.46
	C_8	0.00	0.02	−0.05	−0.03	0.02	−0.08	−0.01	0.54		−0.01
	C_9	0.00	−0.08	0.02	−0.03	−0.05	0.02	−0.02	−0.37	0.54	−0.02
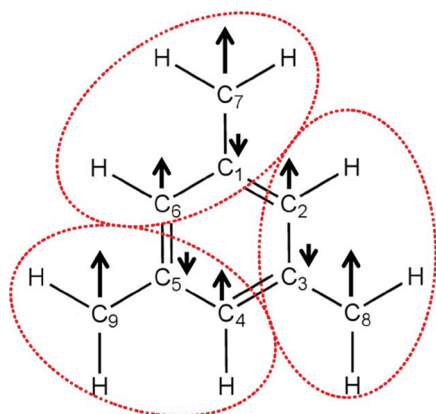
Figure 4. Numbering scheme of TMB and local spin distribution of the quartet state. Three pseudoallyl moieties are encircled in red.
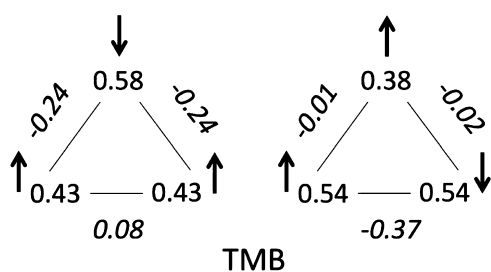
Figure 5. Pictorial local spin representation of the lowest-lying $^2A_2$ (left) and $^2B_1$ (right) doublet states of the TMB π,π,π-triradical.

triradical) are very similar for the two doublet states (0.232 and 0.231 for the $^2A_2$ and $^2B_1$ states, respectively) and somewhat larger than the value for the quartet state (0.248). Thus, the $^2B_1$ state exhibits the larger triradical character among the three considered electronic states.

For the remaining triradicals we restrict ourselves to analyze the pictorial representations given in Figures 6 and 7, and the respective $\Delta^{(3)}$ values. The full results of the local spin analysis
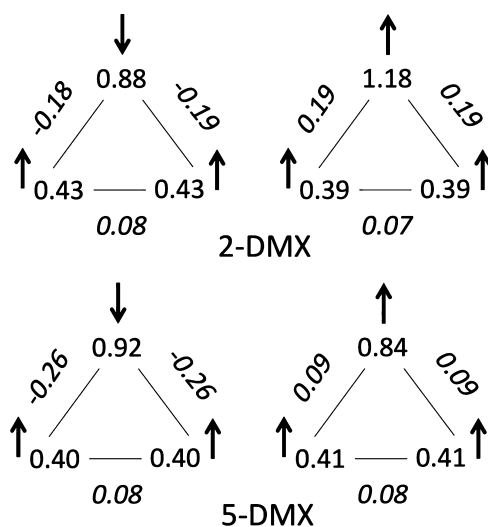
Figure 6. Pictorial representation of the local spin distribution of the 2-DMX and 5-DMX σ,π,π-triradicals in their lowest lying doublet ($^2B_2$, left) and quartet ($^4B_2$, right) states.
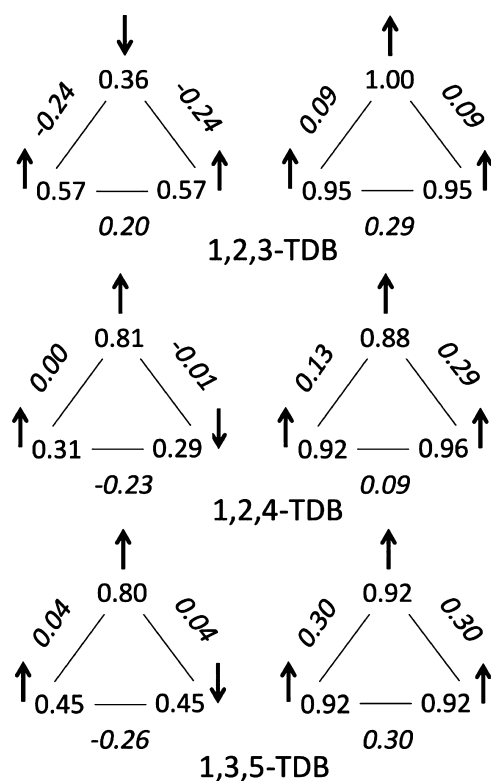
Figure 7. Pictorial representation of the local spin distribution of the 1,2,3-TDB, 1,2,4-TDB, and 1,3,5-TDB σ,σ,σ-triradicals in their lowest lying doublet (left) and quartet (right) states.

can be found in the Supporting Information. In the case of the two dehydro-m-xylylene (DMX) isomers, namely 2-DMX and 5-DMX, we have used a CASSCF wave function with an active space conformed by 9 electrons and 9 orbitals.

2-DMX is a σ,π,π-triradical. The ground state is a $^{2}B_{2}$ doublet, with a predicted doublet-quartet gap of 11.70 kcal/mol. Let us focus first on its lowest-lying $^{4}B_{2}$ quartet state. The largest local spin center is located on the C_{4} atom, which formally bears the σ unpaired electron. Its value ($\langle \hat{S}^{2}\rangle_{C_{4}} = 1.18$) exceeds the ideal one for a singly localized spin and it can be rationalized by decomposing the local spin into its $\sigma-\sigma$ (0.63), $\pi-\pi$ (0.34), and $\sigma-\pi$ (0.21) contributions, as described in ref 38. The $\sigma-\sigma$ contribution is the largest, close to the 3/4 expected for a perfectly localized spin. The $\pi-\pi$ contribution is almost identical to that on the same atom in the TMB molecule and originates from the resonant structures.

The other main local spin centers are C_{7} and C_{8}, with a value of 0.39. The $\langle \hat{S}^{2}\rangle_{C_{4}C_{7}} = \langle \hat{S}^{2}\rangle_{C_{4}C_{8}} = 0.19$ value manifests a parallel arrangement of the local spins, whereas its magnitude is more than half the value expect for the ideal triradical (1/4).

The picture of the ground $^{2}B_{2}$ state that emerges from the local spin analysis is quite similar to the one obtained for $^{4}B_{2}$ state, but with the local spin of the σ unpaired electron located on center C_{4} flipped. In the doublet state $\langle \hat{S}^{2}\rangle_{C_{4}} = 0.88$, coming from $\sigma-\sigma$ (0.63), $\pi-\pi$ (0.26), and $\sigma-\pi$ (−0.01) contributions. The local spin on centers C_{7} and C_{8} (0.43) slightly increases with respect to the quartet state, and the negative sign of the $\langle \hat{S}^{2}\rangle_{C_{4}C_{7}} = \langle \hat{S}^{2}\rangle_{C_{4}C_{8}}$ terms indicate antiparallel arrangement of these local spins. The pictorial representation of Figure 6 indicates that all partial radical centers interact with each other. The $\Delta^{(3)}$ value reported in Table 1 is again smaller for the

doublet state. The value for the quartet state is the largest among all tridicals considered.

The ground state of the 5-DMX isomer is the $^{4}B_{2}$ quartet state. The computed doublet-quartet (adiabatic) splitting in this case is just 3.61 kcal/mol. The σ unpaired electron is mainly located on center C_{1}. The local spin value (0.84) is smaller than in center C_{4} of 2-DMX, but the $\sigma-\sigma$ contribution (0.64) is very similar to that of 2-DMX. The $\pi-\pi$ (0.14) and $\sigma-\pi$ (0.07) ones are smaller than in 2-DMX, revealing a smaller contribution to the local spin of this center due to π-electron delocalization. The local spin on the other two main spin centers (0.41) is also somewhat larger than that observed for 2-DMX (0.39). Indeed, the $\Delta^{(3)}$ value for the quartet state of 5-DMX (0.253) is smaller than for 2-DMX (0.287).

The local spin analysis of the lowest lying doublet state indicates that the σ local spin on C_{1} is flipped with respect to the quartet state. Consequently, the diatomic contributions $\langle \hat{S}^{2}\rangle_{C_{1}C_{7}} = \langle \hat{S}^{2}\rangle_{C_{1}C_{8}}$ increase and have negative signs. The interaction of the local spin on C_{1} is also significant with the centers C_{2}, C_{4}, and C_{6}. This makes the $\Delta^{(3)}$ value increase to 0.263.

Finally, we have also studied three σ,σ,σ tridehydrobenzene triradicals, namely the 1,2,3-TDB, 1,2,4-TDB, and 1,3,5-TDB isomers, in both their lowest lying doublet and quartet states. For these systems we have used a CASSCF wave function with an active space conformed by 9 electrons and 9 orbitals. The three TDB isomers exhibit a doublet ground-state, and the adiabatic doublet-quartet gap are 40.30, 38.33, and 19.83 kcal/mol for the 1,2,3-TDB, 1,2,4-TDB, and 1,3,5-TDB isomers, respectively.

Briefly, the local spin analysis indicates that there are three main local spin centers on each molecule, where the formal unpaired electrons are expected. The residual local spin values on the remaining carbon atoms are similar to those found for the carbon atoms of benzene. The observed local spin values are larger in the quartet than in the doublet states. For the latter, local spin values as low as 0.29 are observed. In the quartet states the values are typically over 0.90, again exceeding the nominal 3/4 value due to the additive contributions from the σ and π electrons and from enhanced electron delocalization. The computed $\Delta^{(3)}$ values of Table 1 confirm a larger triradical character of the quartet states in all cases. Among them, the 1,2,4-TDB isomer exhibits local spin contributions closer to the ideal case of three perfectly localized parallel spins.

Let us focus now on the ground doublet states of the three isomers. In 1,2,3-TDB the local spin centers are the C_{4} and C_{6} atoms (0.57) and the C_{5} one (0.36). The sign of the diatomic spin contributions indicate that the local spin on C_{5} is antiparallel to that on C_{4} and C_{6}. The magnitude of the diatomic spin terms (see Figure 7, upper panel) is consistent with the picture in which all local spin centers interact with each other (see Figure 2, lower panel). On the other hand, in the 1,2,4-TDB isomer, center C_{1} exhibits a local spin close to the ideal for a fully localized spin (0.81). For the other two local spin centers the corresponding values are just 0.31 for C_{4} and 0.29 for C_{5}. The diatomic spin contributions involving C_{1} and either C_{4} or C_{5} are essentially zero, whereas we obtain $\langle \hat{S}^{2}\rangle_{C_{4}C_{5}} = -0.23$. Thus, the doublet state of 1,2,4-TDB is best described as having a radical center on C_{1} and a partial diradical on C_{4} and C_{5}. The small local spin values and diatomic spin contribution of centers C_{4} and C_{5} indicate that the two

formally unpaired σ electrons exhibit significant bonding, similarly to ortho-benzyne.[17] Note that the $\Delta^{(2)}$ value for ortho-benzyne (0.266) and the $\Delta^{(3)}$ for 1,2,4-TDB are also very similar (of course, indicating deviation from diradical and radical + diradical character, respectively).

The doublet state of 1,3,5-TDB also suffers from a Jahn–Teller distortion that breaks the D_{3h} symmetry, leading to two doublet states close in energy. The local spin analysis on the ground doublet state yields a picture similar to the 1,2,4-TDB isomer. That is, the value of the local spin on center C_5 (0.80) is significantly larger than for the other two spin centers (atoms C_1 and C_3 with local spin of 0.45). The latter exhibit a diatomic spin contribution of -0.26, pointing to the antiparallel arrangement of the local spins. The diatomic contribution involving center C_5 is very small (0.04), which essentially means that the system is better represented by the radical + diradical picture. The diradical character is more pronounced than in the 1,2,4-TDB isomer, which is reflected also in the smaller $\Delta^{(3)}$ value.

Lardin et al.[45] used isodesmic reactions in order to obtain the so-called triradical stabilization energy (TSE), namely a measure of the extent of interaction between a diradical and a radical within a triradical system. Krylov[24] obtained using experimental heats of formation a number of TSE values for the TDB isomers, using reactions in which a radical center is transferred from the triradical to a benzene molecule. The products of the isodesmic reactions are thus a phenyl radical and a benzyne diradical (ortho, meta, or para, depending on the particular reaction). The larger the value of the TSE is, the more stabilized is the triradical relative to a separated radical and diradical situation. For the 1,2,3-TDB isomer two alternative isodesmic reactions with different TSE values can be formulated, yielding as products either ortho or meta benzyne diradicals and phenyl radical. Similarly, for 1,2,4-TDB one gets three different reactions, whereas only one can be defined for 1,3,5-TDB[45] (see Figure 8 of ref 24). We have observed that the TSE values are smaller for the isomers with spin distributions consistent with a radical + diradical picture, such as 1,2,4-TDB and 1,3,5-TDB isomers (4.0 and 3.7 kcal/mol), as compared to the 1,2,3-TDB case (12.3 kcal/mol).

Moreover, for each isomer the reaction with smaller TSE value is that in which the phenyl radical is formed on the spin center of the triradical that exhibits a larger value of the local spin. For instance, in the case of 1,2,3-TDB the phenyl radical can be placed either on C_4 or on C_5 (see Figure 3). In the ground doublet state the respective local spins are 0.57 and 0.36, respectively, whereas the corresponding TSE values are 12.3 and 28.3 kcal/mol. Indeed, in Figure 8 we show that for all TDB isomers there is a good correlation between the TSE value of each reaction and the local spin value of the center where the phenyl radical is located. Note that a TSE value of zero would indicate no interaction between the radical center and the diradical. The corresponding $\langle \hat{S}^2 \rangle_A$ value for that radical center would be ca. 0.87, obtained by extrapolation of the curve of 8. This value is in good agreement with that obtained for the isolated spin center of phenyl radical (0.82, with TFVC and a CASSCF(7,7)/6-31G** wave function[17]).

CONCLUSIONS

In this work we illustrate how the local spin analysis can be used to unravel the electronic structure of triradical systems. The generalization to polyradicals is straightforward. A simple model for a triradical system is studied in the framework of
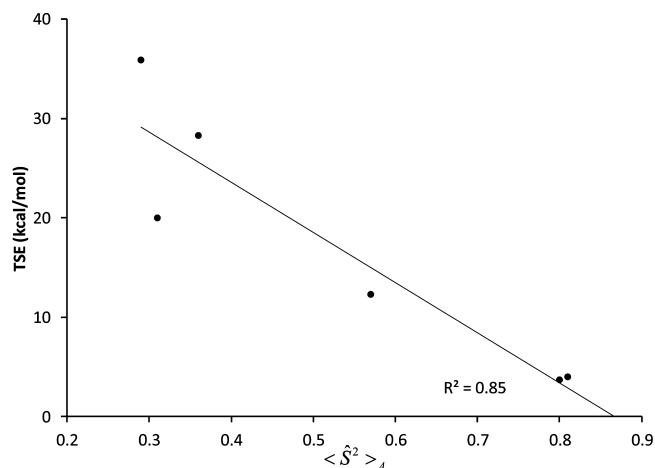

Figure 8. TSE energy vs local spin value (see text).

local spin analysis in order to obtain reference atomic and diatomic contributions to $\langle \hat{S}^2 \rangle$ for perfectly localized spins. The values of the atomic spin contributions for actual molecular systems are used to define a measure of their k-radical character, $\Delta^{(k)}$. The smaller the $\Delta^{(k)}$ the closer the system is to an ideal system of k perfectly localized spin centers. On the other hand, the magnitude and sign of the diatomic spin terms provides a picture of the entanglement between the spin carriers. In the case of triradicals we show that they can be used to distinguish not only between doublet and quartet states but also between two patterns of spins distribution that may occur in doublet states: one being characterized by a singlet diradical and an additional isolated radical center, and another one where the three spin centers exhibit interactions with each other. We have found for that for a number of all σ, all π, and $\sigma-\pi$ organic triradicals the former picture is associated with smaller triplet stabilization energies. The larger the $\langle \hat{S}^2 \rangle_A$ value of a spin center is in a triradical, the easier it is to pull apart this particular radical center from the remaining two.

ASSOCIATED CONTENT

Ⓢ Supporting Information
Complete local spin values and atom-condensed spin densities for 2-DMX, 5-DMX, 1,2,3-TDB, 1,2,4-TDB, and 1,3,5-TDB in different electronic states. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes
The authors declare no competing financial interest.

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■ REFERENCES

(1) Rajca, A. *Chem. Rev.* **1994**, *94*, 871−893.

(2) Salem, L. *Angew. Chem., Int. Ed. Engl.* **1972**, *11*, 92.

(3) Noodleman, L. *J. Chem. Phys.* **1981**, *74*, 5737.

(4) Noodleman, L.; Davidson, E. R. *J. Chem. Phys.* **1986**, *109*, 131.

(5) Bachler, V.; Olbrich, G.; Neese, F.; Wieghardt, K. *Inorg. Chem.* **2002**, *41*, 4179−4193.

(6) Seierstad, M.; Kinsinger, C. R.; Cramer, C. J. *Angew. Chem., Int. Ed. Engl.* **2002**, *20*, 41.

(7) Jung, Y.; Head-Gordon, M. *Chem. Phys. Chem.* **2003**, *4*, 522−525.

(8) Herebian, D.; Wieghardt, K. E.; Neese, F. *J. Am. Chem. Soc.* **2003**, *125*, 10997−11005.

(9) Kamada, K.; Ohta, K.; Shimizu, A.; Kubo, T.; Kishi, R.; Takahashi, H.; Botek, E.; Champagne, B.; Nakano, M. *J. Phys. Chem. Lett.* **2010**, *1*, 937−940.

(10) Lopez, X.; Ruipérez, F.; Piris, M.; Matxain, J. M.; Ugalde, J. M. *Comp. Phys. Com.* **2011**, *12*, 1061−1065.

(11) Cheng, M.-J.; Hu, C.-H. *Mol. Phys.* **2003**, *101*, 1319−1323.

(12) Clark, A. E.; Davidson, E. R. *J. Chem. Phys.* **2001**, *115*, 7382−7392.

(13) Reiher, M. *Faraday Discuss.* **2006**, *135*, 97−124.

(14) Mayer, I. *Chem. Phys. Lett.* **2007**, *440*, 357−359.

(15) Mayer, I.; Matito, E. *Phys. Chem. Chem. Phys.* **2010**, *12*, 11308−11314.

(16) Alcoba, D. R.; Torre, A.; Lain, L.; Bochicchio, R. C. *J. Chem. Theory Comput.* **2011**, *7*, 3560−3566.

(17) Ramos-Cordoba, E.; Matito, E.; Salvador, P.; Mayer, I. *Phys. Chem. Chem. Phys.* **2012**, *14*, 15291−15298.

(18) Ramos-Cordoba, E.; Matito, E.; Mayer, I.; Salvador, P. *J. Chem. Theory Comput.* **2012**, *8*, 1270−1279.

(19) Yoshizawa, K.; Hatanaka, M.; Matsuzaki, Y.; Tanaka, K.; Yamabe, T. *J. Chem. Phys.* **1994**, *100*, 4453−4458.

(20) Kemnitz, C. R.; Squires, R. R.; Borden, W. T. *J. Am. Chem. Soc.* **1997**, *119*, 6564−6574.

(21) Nguyen, H. M. T.; Dutta, A.; Morokuma, K.; Nguyen, M. T. *J. Chem. Phys.* **2005**, *122*, 154308.

(22) Höltzl, T.; Veszprémi, T.; Nguyen, M. T. *Chem. Phys. Lett.* **2010**, *499*, 26−30.

(23) Neuhaus, P.; Sander, W. *Angew. Chem., Int. Ed. Engl.* **2010**, *122*, 7435−7438.

(24) Krylov, A. *J. Phys. Chem. A* **2005**, *109*, 10638−10645.

(25) Cristian, A.-M. C.; Shao, Y.; Krylov, A. I. *J. Phys. Chem. A* **2004**, *108*, 6581−6588.

(26) Nguyen, H. M. T.; Höltzl, T.; Gopakumar, G.; Veszprémi, T.; Peeters, J.; Nguyen, M. T. *Chem. Phys.* **2005**, *316*, 125−140.

(27) Slipchenko, L. V.; Krylov, A. I. *J. Chem. Phys.* **2003**, *118*, 9614−9622.

(28) Slipchenko, L. V.; Munsch, T. E.; Wenthold, P. G.; Krylov, A. I. *Angew. Chem., Int. Ed. Engl.* **2004**, *116*, 760−763.

(29) Wang, T.; Krylov, A. I. *Chem. Phys. Lett.* **2006**, *425*, 196−200.

(30) Takatsuka, K.; Fueno, T.; Yamaguchi, K. *Theor. Chim. Acta (Berlin)* **1978**, *48*, 175−183.

(31) Staroverov, V. N.; Davidson, E. R. *Chem. Phys. Lett.* **2000**, *330*, 161−168.

(32) Staroverov, V. N.; Davidson, E. R. *J. Am. Chem. Soc.* **2000**, *122*, 186−187.

(33) Staroverov, V. N.; Davidson, E. R. *J. Am. Chem. Soc.* **2000**, *122*, 7377−7385.

(34) Lain, L.; Torre, A.; Bochicchio, R. C.; Ponec, R. *Chem. Phys. Lett.* **2001**, *346*, 283−287.

(35) Kutzelnigg, W.; Mukherjee, D. *J. Chem. Phys.* **2002**, *116*, 4787−4801.

(36) Lain, L.; Torre, A.; Bochicchio, R. C. *J. Chem. Phys.* **2002**, *117*, 5497−5498.

(37) Salvador, P.; Ramos-Cordoba, E. *J. Chem. Phys.* **2013**, *139*, 071103.

(38) Ramos-Cordoba, E.; Salvador, P.; Reiher, M. *Chem.—Eur. J.* **2013**, *19*, 15267−15275.

(39) Herrmann, C.; Yu, L.; Reiher, M. *J. Comput. Chem.* **2006**, *27*, 1223−1239.

(40) Herrmann, C.; Reiher, M.; Hess, B. A. *J. Chem. Phys.* **2005**, *122*, 034102.

(41) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A., Jr.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. *Gaussian 03*, Revision C.02; Gaussian, Inc.: Pittsburgh, PA, 2003.

(42) Matito, E.; Feixas, F. *DMN program*; University of Girona (Spain) and University of Szczecin (Poland), 2009.

(43) Salvador, P.; Ramos-Cordoba, E. *APOST-3D program*; Universitat de Girona: Spain, 2012.

(44) Matito, E.; Solà, M.; Salvador, P.; Duran, M. *Faraday Discuss.* **2007**, *135*, 325−345.

(45) Lardin, H. A.; Nash, J. J.; Wenthold, P. G. *J. Am. Chem. Soc.* **2002**, *124*, 12612−12618.