Quantitative prediction and interpretation of spin energy gaps in polyradicals: the virtual magnetic balance

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Abstract

Open-shell organic molecules possessing more than two unpaired electrons and sufficient stability even at room temperature are very unusual, but are being recently synthesized and promise a number of fascinating applications. Unfortunately, reliable structural information is not available and only lower bounds can be estimated for the energy splittings between the different spin states. On these grounds we introduce, in this paper, an effective 'virtual magnetic balance', purposely tailored for polyradicals and devised to parallel experimental works with a robust and user-friendly tool. The main target of this tool is to provide reliable structures and quantitative splittings of spin states of large, complex molecules with reasonable computation times and in a theoretical framework allowing the disentanglement of the different stereo-electronic effects contributing to the overall experimental result. A recently synthesized tetraradical with remarkable chemical stability has been used as a case study.

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Introduction

The interest for organic molecules coupling high-spin electronic ground states with significant chemical stability is strongly increasing in recent years, both from fundamental and applicative points of view.[1-6] As a matter of fact, this situation contradicts the very general tendency toward spin pairing, which leads, of course, to conventional chemical bonding. At the same time, most representatives of this class exhibit poor stability, which limits their use as building blocks for magnetic materials and in the development of spintronics. The situation is even worse when going from diradicals (two unpaired electrons) to higher polyradicals (four unpaired electrons in the case considered in the present study), which can be even more interesting for several applications, eventually including quantum computing. A promising synthetic route toward stable organic polyradicals would be to protect the magnetic centers with cumbersome and inert chemical groups, but this proposal faces against a number of experimental and theoretical difficulties. From the experimental point of view, the group of Rajca has recently succeeded in synthetizing several organic polyradicals[4, 7, 8] and, in particular, a very promising tetraradical molecule based on aminyl groups, which is the object of the present investigation.[9] Full experimental characterization of such species is, however, not yet fully feasible, and, in particular, several difficulties are encountered in the experimental estimate of the energy gap among the different spin states. Indeed the latter quantity is usually derived by a best fit procedure, which is known to suffer of a significant uncertainty, and only lower bound can sometimes

be determined for magnetic splittings[2, 8, 10, 11].

From the theoretical point of view, methods rooted into the density functional theory (DFT) (and the broken-symmetry approximations pioneered by Noodleman[12, 13]), which are the battle-horse of contemporary quantum chemistry, are not sufficiently reliable for quantitative studies of polyradicals.[14, 15] Time dependent DFT (TDDFT) has been also used with success in this connection by resorting to the Spin-Flip ansatz,[16] which is able to take static correlation into account within a formally single reference approach. Still within DFT based methods, Phillips and Peralta[17] developed a complex strategy based on analytical derivatives with respect to the spin direction, to evaluate the energy gap between the lowest triplet and singlet states. Of course, the most sophisticate multi-reference wave function approaches can provide reliable energy splittings.[18-27] However, at least in their conventional implementations, such approaches have prohibitive computation times for the large systems of interest in the present context. One promising route is offered by the recent development of the multi-configuration pair-density functional theory, which requires, however, further testing and validation.[28, 29] Another promising route is based on the Spin-Flip restricted active space configuration interaction (RAS-CI) method developed in the Head-Gordon group's [30-33] following an original suggestion put forward by Krylov.[34, 35] Spin-Flip RAS[36] shares the same configurational space of the so called difference dedicated configuration interaction (DDCI) approach, originally proposed by Miralles et al.,[37] in its simplest implementation (DDCI1) (see Supporting Information). It has, however, been shown that the DDCI1 model is not sufficient for obtaining quantitative splittings between quasi degenerate spin states, and that the complete DDCI scheme must be applied to obtain robust results.

In the past years, an extension of the original DDCI approach[37, 38] has been proposed by our group to efficiently tackle diradical systems, and validated for several compounds[20, 23, 39, 40], displayed in Figure 1. These benchmarks included diradical differing in the atoms bearing the magnetic sites (either C, N, NO or Cu) and spanned molecules of increasing dimensions, from the relatively small benzyne series (**1**-**3**) to the larger amynil diradical (**9**) and Copper based dication (**11**). As reported in Table 1, the agreement achieved for all these compounds with the available experimental estimates is remarkable, and the DDCI based approach succeeds in differentiating even similar compounds (e.g. **4** and **5**).
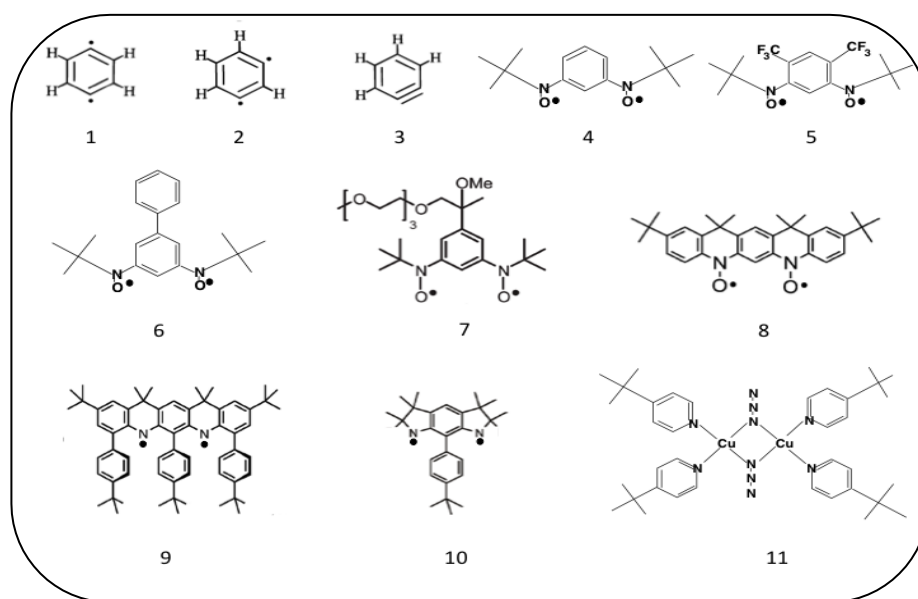
Figure 1 – Previously investigated diradicals by means of DDCI based approaches: **1** *p*-benzyne ; **2** *m*-benzyne ; **3** *o*-benzyne ; **4** *m*-phenylene bis(tert-butyl nitroxide) diradical1[9] ; **5** *4,6-bis*(trifluoromethyl)- N,NA-di-tert-butyl-*1,3*-phenylene *bis*(aminoxyl) diradical[10] ; **6** biphenyl-3,5-diyl bis(tert-butyl nitroxide) diradical[11] ; **7** *bis*(aminoxyl) diradical[12] ; **8** diaryl nitroxide diradical[4] ; **9** amynil diradical[13] ; **10** aza-m-xylylene diradical[14] ; **11** *bis*(μ-azido)*tetrakis*(4-*tert*-butylpyridine) dicopper(II) dication diradical.[15]

Diradical	Type	ΔE_{ST}	
		Exp	**Calc.**
1		3.8^{16}-5.5^{17}	5.3 ([8]
2	C•	21.0^{16}	19.7^{8}
3		37.5^{16}	36.9^{8}
4		1.0^{9}	0.8^{6}
5		0.2^{10}	0.1^{6}
6	NO•	$>0.7^{11}$	0.9^{6}
7		1.3^{12}	0.9^{6}
8		0.6^{4}	0.6^{7}
9	N•	$>2.0^{13}$	5.4^{5}
10		10.0^{14}	10.0^{5}
11	(N-Cu)•	0.3^{15}	0.4^{8}

Table 1 – Comparison between the computed values of single-triplet energy gap (ΔE_{ST}) and the available experimental estimates. The ">" symbol indicated that only experimental lower bounds could be determined. All energy gaps are reported in kcal/mol.

The approach is now extended to polyradicals with more than two unpaired electrons exploiting the implementation of a number of computational breakthroughs in our BALOO[40] code which allows for the computation of accurate splittings for large open-shell systems at a reasonable (albeit not negligible) cost. Triradicals, which have been recently reviewed by Winkler and Sanders[41], are currently under investigation and will be the subject of a forthcoming paper. Herein we will consider the tetraradical displayed in Figure 1, which, according to a recent experimental investigation, is rather stable even at room temperature and has a quintet (high-spin) ground state.[4, 9] The aim of our study is two-fold. On the one hand we provide a reliable estimation and an interpretation of the energy splittings among the several spin states of this very interesting molecule. On the other hand, we show that experimental studies of polyradicals can be systematically paralleled by reliable quantum mechanical investigations thanks to the general availability of a powerful, open-source, and user-friendly 'virtual magnetic balance'.
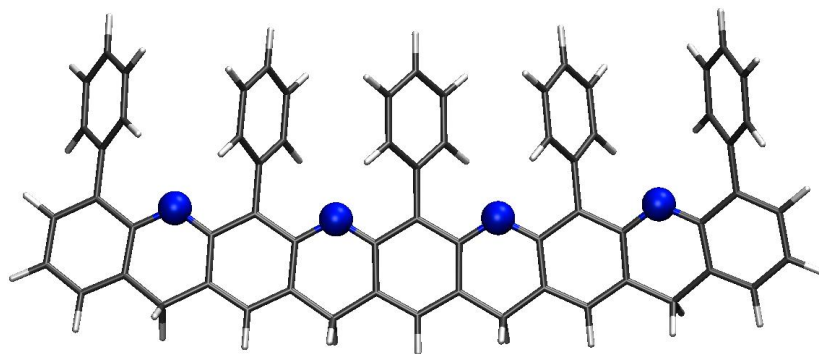

Figure 1 – The aminyl tetraradical studied in the present paper. The radical centers are the nitrogen atoms (blue) whose p orbitals perpendicular to the molecular plane are the magnetic orbitals.

Computational Route to Magnetic Splittings

The system under study, displayed in Figure 1, was obtained from the aminyl tetraradical reported by Rajca *et al.* [9] after removal of all the aliphatic chains and saturation with hydrogen atoms. This substitution is expected to have a negligible effect on the global geometric and electronic structure of the aminyl molecule in the backbone region, involved in the magnetic properties. The four pendant phenyl groups (see Figure 1) were instead included in the model molecule, as they were already found to have small although not negligible effects on the shape of the magnetic orbitals, at least for the corresponding diradical aminyl molecule.[20] The resulting tetraradical contains four spin centers localized on the four nitrogen atoms connected by aromatic rings. The magnetic half-occupied orbitals are essentially based on the atomic p orbitals of the nitrogen atoms perpendicular to the nearly planar polycyclic scaffold and have π symmetry.

The first step of our computational strategy is a DFT geometry optimization of the molecule in the high-spin quintet state at the B3LYP/cc-pVDZ level of theory, using the unrestricted Kohn-Sham approach. This

calculation was performed with the Gaussian09 package.[42] A nearly planar structure was obtained for the polycyclic backbone, with the side phenyl rings slightly bent (10°-12°) with respect to the common plane of the three central phenyl rings. Conversely, the pendant phenyls are not coplanar with the backbone, but rotated by 45° to 55°, indicating that no appreciable conjugation should be expected between them or with the polycyclic scaffold. Thereafter, a restricted Open-shell Hartree-Fock-SCF (ROHF-SCF) calculation was carried out using the Gamess program,[43] on the same spin state and geometry and with the same basis set of the previous DFT calculation. The resulting 1162 canonical molecular orbitals (MOs) were then modified using the QUIOLA program, [40] with the aim of enforcing fragment localization and concentrating the charge of the lowest virtual MOs near the spin centers[44, 45] (see also Supporting Information). As mentioned above, the magnetic orbitals have negligible contributions from the pendant phenyls, so that the MOs localized on these moieties (for a total of 574 MOs) are expected to play a negligible role in tuning the energy splittings. As a consequence, the orbitals localized on the pendant phenyls, which were included in the HF calculation, are neglected in the subsequent DDCI step. Excitations from the 1s orbitals of the heavy atoms are also discarded, whereas correlation is taken into full account for the remaining 588 MOs localized on the backbone.

The canonical and localized magnetic orbitals are displayed in Figure 2. In the bottom panel, the four MOs localized on the nitrogen atoms show very similar features, which emphasize a significant spread (40% of the total charge) over the neighboring carbon atoms. This limited localization on the spin centers was already found for the parent aminyl diradical[20] and seems to be a general feature of the aminyl systems coupled with aromatic bridges.
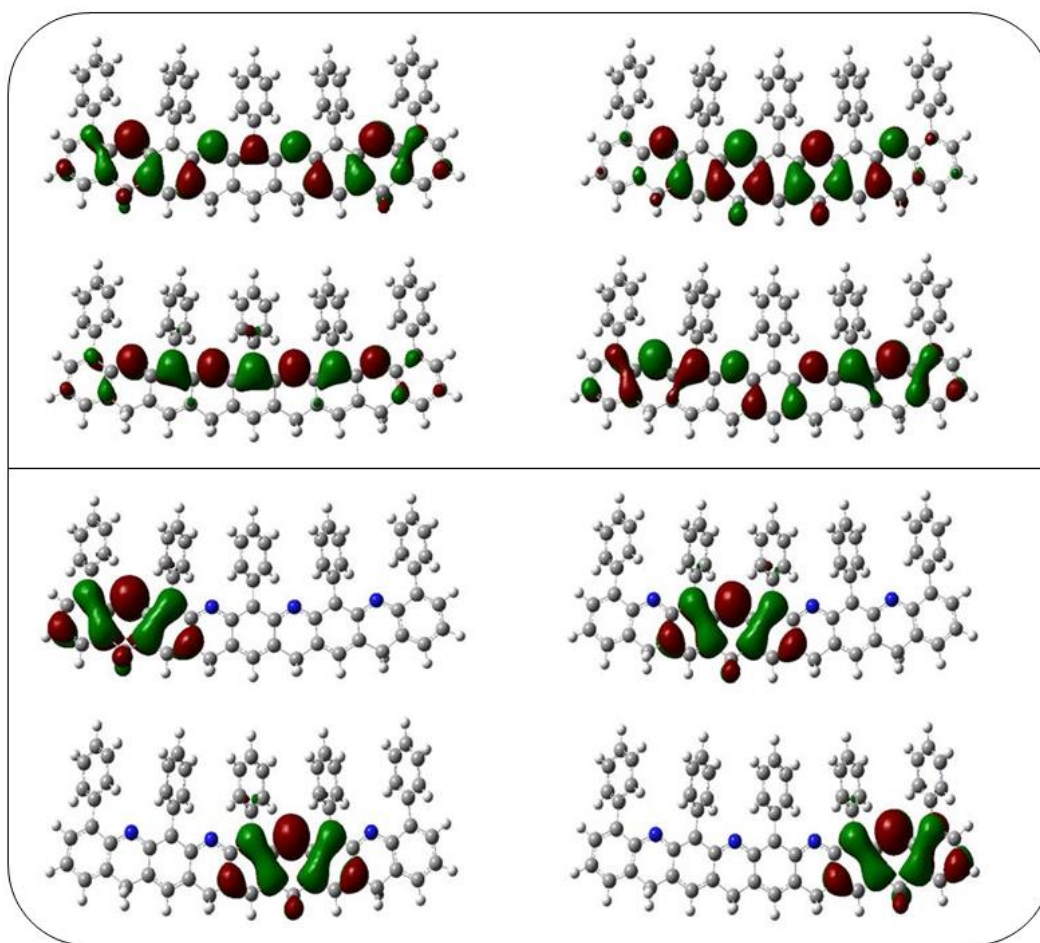
Figure 2 – The four canonical (top panel) and localized (bottom panel) magnetic molecular orbitals as obtained by restricted Hartree-Fock calculation carried out for the high spin quintet state.

As mentioned before, all post-HF calculations were performed with the BALOO package[40] coded in our group and previously employed for magnetic energy splitting calculations on medium-to-large sized molecules. [21, 23, 39, 44] Although the code can employ Configuration State Functions (CSF) (which are generally more effective in terms of computational resources) in this work we have preferred to use Slater Determinants (SD), as this choice has the advantage of collecting states with different spin in a single calculation.

A preliminary study of static correlation effects was made for the CAS(4,4) configurational space, which includes the so-called exchange and kinetic exchange effects, but lacks spin polarization and correlation contributions. The CAS(4,4) with null spin component along z, includes 36 SDs distributed in the following way: 6 SDs of single occupation (one electron for each magnetic site), 24 SDs with 2 electrons on one site and the remaining electrons one for site (charge transfer (CT) configurations), 6 SDs with two electron pairs on two sites (double charge transfer configurations).

The CAS energy differences are reported in the first line of Table 1 for the three lowest states. The most stable state is the quintet, the first and second excited states are a triplet and a singlet, at 592 and 1275 cm^{-1}, respectively. Inspection of the CI coefficients shows that the most important configurations needed to simultaneously describe the lowest quintet, triplet and singlet states are the six SDs of single occupation,

whose contribution exceeds 99.9% for all states. Therefore SDs of CT nature have very small effects on the lowest states, at least at this level of calculation. From the data reported in Table 1 it is also apparent that the CAS-CI calculation provides a physically meaningful picture of the spin states, all the transition energies being close to those obtained by more sophisticated calculations. A deeper analysis of the CAS(4,4) states is therefore significant for elucidating the physically relevant effects and it is reported in some detail in the Supplementary Material.

The rationale of the energy splitting comes from the high delocalization of the magnetic orbitals on the neighboring parts of the skeleton (no more than 60% on nitrogen) that causes a relevant overlap among them. Consequently, the exchange integral between contiguous magnetic orbitals is rather high (~ 1000 cm^{-1}) leading to a strong stabilization of the high spin state, according to the Hund rule. Differently from the situation observed for diradicals, where the singlet state is destabilized by the direct exchange, in the present case also the lowest triplet and singlet states are stabilized by the strong value of this term (see Supporting Information). It is noteworthy that the high value of the exchange seems to be a peculiarity of aminyl based systems, whereas similar nitrosyl systems are characterized by much lower exchange values (about 70 cm^{-1}) with magnetic orbitals strongly localized (more than 95%) on the NO groups.

Next, extensive variational CI calculations were carried out, in most cases complemented with a perturbative treatment in the Møller-Plesset partition. The configurational space was selected automatically according to the so-called Difference Dedicated Configuration Interaction (DDCI) protocol[38, 46, 47] which couples a balanced description of the states with different spin eigenvalue, with configurational spaces of reasonable dimensions. This protocol is aimed to provide reliable energy differences, rather than accurate individual total energies of each state, and avoids the huge number of double excitations from doubly occupied MOs to empty MOs. The DDCI protocol can be implemented at different levels of accuracy and computational effort, leading to the so called DDCI1, DDCI2 and DDCI3 models (see Ref.s [46, 48, 49] and Supporting Information). The different DDCI spaces of increasing dimension were obtained extending the recipe devised for diradicals[46] to the more demanding case of tetraradicals by means of a number of well-defined excitations outside the CAS(4,4) reference space.

Due to the huge number of MOs required in the present case, the dimension of the different DDCI spaces becomes rapidly too demanding from a computational point of view, so that a mixed variational/perturbative approach has been used. The Complementary Space Perturbative Approach (CSPA) included in the BALOO suite of programs was devised to perform variational CI calculations followed by second-order perturbative estimate of both energies and wave functions.[50] In particular, the MO space is divided into active and inactive subspaces and only configurations within the active space are considered for variational CI calculation, whereas those involving inactive MOs are used for perturbative corrections. The use of purposely-tailored MOs (see above) permits to obtain energy differences of high accuracy with a reasonable computational effort. The results of the several DDCI calculations, sometimes involving huge variational spaces (last column), are reported in Table 1. The different DDCI classes[46, 49] were ordered in terms of increasing complexity with the purpose of analyzing their specific effects on the energy shifts.

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Table 1 – Energy splittings for the aminyl tetraradical displayed in Figure 1, as obtained by CAS-CI and DDCI calculations. E_Q, E_T and E_S are the energy of the lowest quintet, triplet and singlet states, respectively. Energy differences are reported in cm^{-1}. For DDCI calculations the two numbers in parentheses in the first column indicate the percentage of occupied and empty MOs in the active space, respectively, whereas the remaining space is treated at CSPA level. The DDCI3(π/π) label means that all π MOs are included in the active space, whereas the σ MOs are treated at CSPA level. The +P symbol indicates a standard perturbative correction. The last column reports the dimension of the CI space in million units of Slater determinants.

Level of theory	E_T-E_Q	E_S-E_Q	CI dim
CAS-CI	592	1275	36
CAS-CI + P	475	1008	
DDCI1 (100/33)	822	1782	1.4
DDCI2 (100/33)	752	1626	2.2
DDCI3 (20/12)	600	1301	5.3
DDCI3 (25/16)	597	1294	11.8
DDCI3 (30/20)	593	1285	23.3
DDCI3 (40/20)	591	1280	33.8
DDCI3 (50/25)	587	1272	67.4
DDCI3(π/π)	594	1289	41.1
Experimental[9]	>100		

Discussion

In general terms, it is quite surprising that the energy splittings obtained by CAS and CAS+P calculations are close to those obtained by the more sophisticated and demanding calculations at the DDCI3 level. This finding is due to a comparable contribution of dynamic correlation for the three involved states, which can be traced back, once again, to the overwhelming effect of direct exchange. As matter of fact, the CT configurations included in the CAS give a very small contribution to the low-spin wave functions, actually less than 0.04% and 0.07% for the triplet and singlet states, respectively. Since the CT configurations have one additional doubly occupied MO with respect to those with four unpaired electrons, they show a different sensitivity to the inclusion of correlation,[18, 20] that could enhance their contribution to the low-spin states. In fact, these weights remain very low even at DDCI3 level (<0.1% and <0.2% for the lowest singlet and triplet states, respectively), and give rise to just a modest decrease of the energy splitting, as can be appreciated on going from DDCI2 to DDCI3. Spin polarization effects, which are included already at DDCI1 level, seem to favor the quintet state, but this split appears to be dampened by the inclusion of correlation effects at DDCI2 and, even more, at DDCI3 level. As a consequence the DDCI1 recipe (which is equivalent to the spin-flip model[36]) is not able to provide quantitative results in the present situation.

Owing to the very large spaces arising from the DDCI3 recipe, only a limited fraction of the MOs can be included in the active variational space, and the DDCI calculations have to be complemented with a CSPA correction. For this reason several DDCI3 calculations were performed in order to ascertain the convergence of the energy differences *vs*. the dimension of the active CI space. The data reported in Table 1 suggest that no other significant change may be expected by further enlarging the variational active space. Therefore the energy splittings obtained by the largest DDCI3 calculation are expected to be very close to those arising from a full variational treatment of the DDCI3 space, and the values of 580 and 1270 cm^{-1} may be

confidently considered robust estimate of the triplet–quintet and singlet-quintet energy gap, respectively. It is noteworthy that already the smallest DDCI3 computation, which can be routinely performed in an essentially black-box way, leads to remarkable estimates (600 and 1301 cm^{-1}) of energy splittings. A further proof of the stability of the results is offered by the DDCI3(π/π) calculation in which all the π MOs are included in the active space, whereas the remaining σ MOs are in the inactive space.

The only available experimental estimate is a lower bound of 0.3 kcal/mol (about 100 cm^{-1}) for the triplet-quintet splitting.[9] Our estimate of 600 cm^{-1} appears thus fully reasonable and more reliable than the value of about 1700 cm^{-1} issuing from broken-symmetry DFT computations.[9] Furthermore we can provide also a sound estimate (1300 cm^{-1}) for the singlet-quintet splitting and a disentanglement of the different contributions leading to the overall experimental result by means of a theoretically sound, but feasible and essentially black-box computational procedure.

Conclusions

We have reported on a theoretically sound yet effective calculation on the spin states of a large tetraradical, which was recently synthetized and reported to be stable at ambient temperature. The protocol discussed herein is a further step toward the accurate calculation of magnetic gaps in large organic polyradicals, thus extending the range of applicability of the approach, previously validated on several diradicals, to systems with four unpaired electrons. The theoretical results confirm the experimental data in predicting a stable quintet state with a quite large energy gap (about 580 cm^{-1} according to our best computations) from the lowest triplet state. This very demanding calculation was made possible by recent developments included in the BALOO code (our 'virtual magnetic balance'), concerning both more efficient algorithms and high parallelization. Furthermore, the whole DDCI model at the heart of the computational model, could be integrated into a user-friendly nearly black-box tool, whose efficiency is further enhanced by effective partitioning between variational and second-order perturbative steps.

The data collected by our calculations provide a deep insight on the microscopic origin of the magnetic behavior, allowing for a sound rationalization of the computed energy gaps. As far as the polyradical here investigated is concerned, the calculations revealed that the energy splittings between the lowest quintet, triplet and singlet states are mainly determined by the structure of the bridges and by the peculiarity of the aminyl radicals, whose magnetic orbitals are strongly delocalized on the π cloud of the carbon skeleton. This feature has the main effect of stabilizing the high spin states, as can be inferred even by the lowest level of theory properly including static correlation, namely CAS-CI(4,4).

Together with the intrinsic relevance of the studied system, in our opinion the main interest of the present paper is the presentation of a robust and user-friendly 'virtual magnetic balance', which permits also to non-specialists to complement their experimental studies with quantitative estimates of energy splittings among the spin states for large polyradicals of current fundamental and technological interest. Finally, the strong difficulties often encountered in the accurate experimental determination of magnetic splittings in organic polyradicals suggest that our magnetic balance could play a remarkable role in the rational design of novel

organic magnets.

Acknowledgements

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