# Helical Folding-Induced Stabilization of Ferromagnetic Polyradicals Based on Triarylmethyl Radical Derivatives

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S *Supporting Information*

ABSTRACT: Magnetic ordering in purely organic π-conjugated materials is a challenging, rare, and desirable event. The interest lies on the unique magnetic properties derived from high-spin carbon-based polymers/macromolecules tailored through appropriate synthetic routes. Ground-breaking achievements have been reported regarding magnetic ordering in an organic polymer using spin clusters as building blocks. This strategy leads to two-dimensional extended polyradicals with a concomitant loss of appealing macroscopic properties such as expected magnetic anisotropy in elongated shaped macromolecules containing carbon-bearing radicals. Here we provide compelling evidence of a secondary structure-induced stabilization of ferromagnetic polyradicals with robust magnetic properties and strongly suggest revisiting a discarded attempt to obtain polymeric linear-like radicals. An alternative synthetic approach is also proposed, based on polyradicals obtained from discrete molecular precursors (oligomers) long enough to ensure a secondary structure, rather than from polymerization processes.
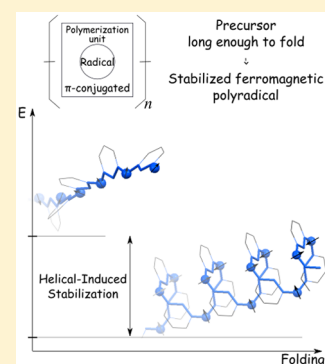
1. INTRODUCTION

Purely organic magnetic materials constitute a promising approach for the miniaturization of devices with interesting optical, electronic and magnetic properties, all using low cost chemical elements.[1−4] Despite significant advances in the field, critical issues remain when aiming at achieving a strong enough ferromagnetic ordering over a wide range of temperatures and a structural control on the final products.[5]

To date, the most successful strategies relied on synthesizing high-spin macromolecules and/or polymers with very large numbers of carbon bearing unpaired electrons interacting through bond.[5−14] Particularly, odd alternant polycyclic hydrocarbons with a 1,3-connection are widely used, as envisioned by Mataga.[15] In these systems, topological arguments ensure nondisjoint, degenerate singly occupied molecular orbitals (SOMOs)[16,17] and ground states with the highest multiplicity.[18] The π-conjugation in these systems implies that there are large parts of space shared by the SOMOs, which increases greatly the interactions dominated by the exchange integral. Note, however, that the fact of being degenerate and orthogonal ensures an almost zero orbital overlap among them, which results in the relative stabilization of the high-spin states. However, within the commonly adopted synthetic route, disruption and even suppression of magnetic interactions is commonly observed, associated with an incomplete generation of the radical centers from the precursor, or an out-of-plane torsion breaking the π-conjugation.[10,13] In fact, recent work has shown that such torsions, which in turn define the interaction among unpaired electrons through the 1-3-phenylene unit, are capable of reversing the nature of the ground state in related triradicals.[19] This is especially the case for linear, star-branched, and dendritic connectivity, as recognized a long time ago by

Rajca and co-workers.[5] Precisely to circumvent this problem, an alternative approach based on the use of organic spin clusters was proposed.[5] These building blocks constituted one of the mainstreams in the field of organic magnetism.[12] As a result, most of the subsequent related research led to two-dimensional (2D) extended polyradicals[5,14] at the expense of other architectures with lower dimensionalities, as for instance linear or rod 1D chains. Nonetheless, interesting properties associated with an elongated 1D-like polyradical are not present in 2D materials, magnetic anisotropy among them. The contribution of classical dipole—dipole interactions to magnetic anisotropy is known to be a relevant one.[11] Thus, energy barriers for coherent rotation of magnetization are expected to relate to the molecular shape of the polyradicals as well as to its spin density; the latter being especially large in elongated shapes.

In the present work, we investigate the structural and magnetic properties of two 1D-like polyradicals based on odd alternant hydrocarbons. Relying on consistent arguments in favor of the structural and chemical stability we provide compelling evidence of helical-induced stabilization of ferromagnetic polyradicals with robust magnetic properties. Interestingly, one of the systems under study was already synthesized by Rajca and co-workers,[8] although its use as a magnetic building block was, at that time, discarded because of the uncontrollable impact of chemical defects on the magnetic properties. Considering the novel and interesting predicted properties of these 1D-like elongated magnetic organic systems, further research seems mandatory. To this end, a plausible

scheme, based on Rajca and co-workers results,[7] is proposed for an effective synthetic strategy to reach medium-size oligomers.

2. COMPUTATIONAL DETAILS

Calculations for the polymer and oligomer compounds have been carried out using the B3LYP[20] hybrid density functional theory (DFT)-based method including dispersion corrections as proposed by Grimme;[21] the resulting method being referred to hereafter as B3LYP-D. For the polymers, periodic calculations have been carried out using Crystal09 code,[22,23] with the standard 6-21G* basis set for all atoms (H, C), whereas for the decaradical, the Gaussian 09 suite of programs[24] was used employing a 6-31G* basis set.[25,26] ITOL values have been fixed to 7,7,7,7,14 to force stringent numerical convergence of energy and gradients and 3 k-points in the 1D irreducible Brillouin zone. Denser k-point meshes do not significantly affect the energy differences defining structure stability or values of magnetic coupling constants.

The description of the magnetic properties is based on Heisenberg−Dirac−Van Vleck (HDVV) model Hamiltonian:

$$\hat{H}^{HDVV} = -\sum_{\langle i,j \rangle} J_{ij} \hat{S}_i \cdot \hat{S}_j \tag{1}$$

where J_{ij} is the exchange coupling constant between the $\hat{S}_i$ and $\hat{S}_j$ localized spin moments and the $\langle i,j \rangle$ symbol indicates that the sum refers to nearest-neighbor interactions only. According to eq 1, a positive value of the exchange coupling constant J_{ij} corresponds to ferromagnetic (FM) interactions, while negative values describe an antiferromagnetic (AFM) interaction (parallel and antiparallel spins, respectively).

The number, sign, and magnitude of the most relevant J_{ij} determine the low-energy spectrum of the problem and consequently the magnetic ordering of the system. The extraction of the different J_{ij} is based on the mapping approach described in previous work.[27,28] In short, the procedure maps the diagonal elements of the HDVV Hamiltonian to the energy expectation value of different broken symmetry (BS) solutions. This is equivalent to map eigenvalues of the Ising model Hamiltonian, as in eq 2, to expectation energy values of the different BS solutions.

$$\hat{H}^{Ising} = -\sum_{\langle i,j \rangle} J_{ij} \hat{S}_i^z \hat{S}_j^z \tag{2}$$

where $\hat{S}_i^z$ and $\hat{S}_j^z$ are the z-component of the $\hat{S}_i$ and $\hat{S}_j$ localized spin operators in the HDVV Hamiltonian. A more detailed description concerning the different magnetic solutions relevant to the present work and their algebraic expressions is presented in the Supporting Information. Nevertheless, it is worth mentioning that, based on spin-flip TD-DFT,[29] a general and elegant formalism for the extraction of magnetic coupling constants in systems with an arbitrary (finite) number of interacting spins has been presented that does not require employing BS solutions.[30] Nevertheless, in the case of dinuclear complexes, BS-DFT and spin-flip TD-DFT lead to similar results provided in the former spin projection is properly taken into account.[31] Note, in addition, that BS-DFT is equally applicable to finite and periodic systems and is chosen here to provide an appropriate comparison.

3. STRUCTURAL FEATURES, CHEMICAL STABILITY, AND MAGNETIC PROPERTIES

The structures investigated in the present work can be regarded as derivatives of m-xylylene diradical extended in 1D (referring to the σ skeleton), with an increasing steric protection of the radical centers, as indicated in Figure 1.

Polymer **1** is a good model to investigate magnetic interactions and the different adopted conformations. Polymer **2** is a Gomberg-based[32] polyradical. To the best of our knowledge, polyradical **1** has never been synthesized. On the
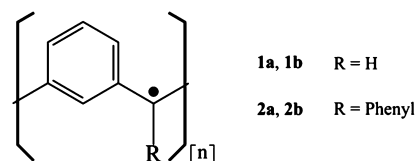

Figure 1. Schematic representation of investigated polymers. The different notation for each polymer indicates the conformation adopted (a stands for linear and b for helical).

contrary, polyradical **2** was synthesized by Rajca and co-workers,[8] following the carbopolyanion method. The obtained precursor polymer was reported to have an average number of 30 potential radical sites. However, the material that was obtained when attempting to synthesize polyradical **2** presented a saturation of the magnetization curve fitting with an average spin value of $S = 2$ only. The failure of spreading the magnetic interaction along all potential radical sites was assigned to chemical defects, such as incomplete oxidation of the carbopolyanion precursor. However, no further experimental attempts aiming at improving the generation of radical centers in these linear polyradicals have been pursued. This was largely motivated by the success of spin clusters as building blocks for synthesizing 2D extended polyradicals, as proposed by Rajca and co-workers.

Theoretically, the electronic structure of polyradicals **1** and **2** has been extensively studied.[33−37] In contrast, despite early indications by Yoshizawa el al.,[37] structural effects and their impact on the $\sigma−\pi$ separation have been generally overlooked. A similar conformational preference has been recently reported by Datta et al.[38] in related calix[4]arene-based radicals. Conformational freedom in these flexible structures introduces a degree of complexity that cannot be ignored.[39] In fact, the appearance of a preferential helical conformation as a secondary structure brings interesting macroscopic properties at variance with purely linear 1D polyradicals where no ferromagnetism is expected.[40] Additionally, the secondary structure introduces an effective manner for sterically protecting the radical centers and introduces alternative interaction paths among the radical centers which compensate the rupture of the π-conjugated system as compared to the ideal planar case. These interactions spread through the π system as shown in Figure S. I. 5.

In the present work, the molecular structure of all polymers has been fully optimized for the electronic ground state (ferromagnetic solution) and for linear and helical conformations. In all cases a local minimum was located, and analysis of the corresponding structures evidence that inclusion of dispersion is crucial in defining the preference for the helical conformation. Coordinates of the primitive cells for the optimized structures including dispersion corrections are in section 1 of the Supporting Information. A preference for a helical conformation has been found for all the studied polymers, especially once dispersion terms are taken into account. The helical conformation of polymers **1** and **2** is 2.8 and 2.5 kcal/mol per magnetic center, respectively, more stable than the linear one. These values are very similar to the parallel displaced π-stacking interaction of the benzene dimer calculated by means of very accurate CCSD(T) ab initio wave function-based methods with large basis sets.[41]

Figure 2 compares the linear and helical conformation of polymers **1** and **2**. It also presents the cell parameters associated with the direction of the polymeric growth and the distances relating the carbon-bearing radicals as obtained when
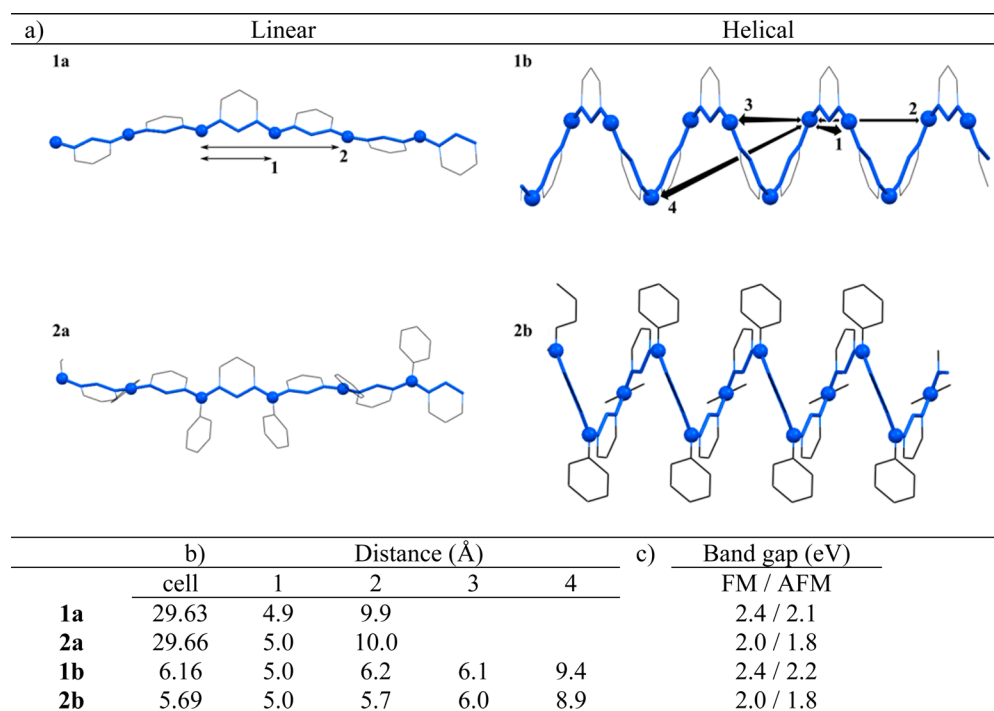
	b)	Distance (Å)				c)	Band gap (eV)
	cell	1	2	3	4		FM / AFM
1a	29.63	4.9	9.9				2.4 / 2.1
2a	29.66	5.0	10.0				2.0 / 1.8
1b	6.16	5.0	6.2	6.1	9.4		2.4 / 2.2
2b	5.69	5.0	5.7	6.0	8.9		2.0 / 1.8

Figure 2. (a) Schematic representation of the optimized geometries of polymers **1** and **2** adopted for a linear and helical conformation. Arrows indicate the distance between the magnetic centers, which are represented by ball atoms. (b) Lattice parameters of polymers **1** and **2** associated with the direction of the polymer growth and distances between the magnetic centers defining the different magnetic coupling constants in Table 1. (c) Calculated band gap (for the ferro and antiferro solutions, respectively) in eV of polymers **1** and **2**. All information is extracted from the optimized geometries taking into account dispersion corrections. Hydrogen atoms are not shown for clarity.

considering dispersion corrections. Note that the number of magnetic carbon atoms per cell is six in the linear conformations and three for the helical ones. The introduction of phenyl rings in polymer **2** promotes a large $\pi-\pi$ interaction along the direction of the polymer, resulting in an effective stabilization with respect to the linear conformation. Figure 2 also includes the band gap values for the different polymers in the ferro and most stable antiferromagnetic phases. For a given conformation, the almost constant band gap values around 2 eV, either for the ferro or antiferromagnetic order, indicates that the magnetic centers are stable and that magnetic properties do not alter the electronic structure of the polymer. Additionally, the similar values for the different conformations ensure a comparable behavior no matter the geometry adopted. Density of states and band diagram for ferro and antiferromagnetic solutions of polymer **2b** are presented section 3 of the Supporting Information.

Finally, concerning the discussion on structural features, it could be argued that increasing chemical stability of the radical centers might be an effective way of promoting more robust properties of the resulting 1D-like polyradical. For this purpose, steric hindrance might be considered as an approach as noted in the increase of stability when passing from the Gomberg radical[32] to the perchlorotriphenylmethyl (PTM) radical.[42] Thus, a polymer based on PTM units represents a limiting case to further verify this hypothesis, although the large steric hindrance makes it difficult to obtain stable structures, in line with the reported work on related 2D polyradical den-drimers.[9,43−45] However, currently there is a large library of available PTM-derivatives with only certain chlorine-substituted positions.[4] Such a catalogue could be used for a revisited synthesis of related polymer **2**, in order to achieve a compromise between gained stabilization of the radical centers

through steric protection and a conformational freedom to adopt a relaxed secondary structure.

In order to obtain information regarding the magnetic properties, single point calculations for different BS solutions were carried out at each of the obtained optimized geometries in the ferromagnetic ground-state solution. Table 1 summarizes the most important results found in this work. It is evidenced that for all conformations, the ferromagnetic order is the

Table 1. (a) Energetic Difference between the Ferromagnetic and the Most Stable Antiferromagnetic Phases as Predicted From the B3LYP-D Calculations, (b) Averaged Spin Density over the Radical-Bearing Carbon Atoms, and (c) Calculated Magnetic Exchange Interactions[a]

	type of structure			
polymer	linear		helix	
(a) $\Delta E_{\text{FM-AFM}}$ (cm^{-1})				
1	−1920		−2312	
2	−1134		−1447	
(b) Spin Densities				
1	0.717		0.678	
2	0.642		0.631	

	linear		helix			
polymer	J_1	J_2	J_1	J_2	J_3	J_4
(c) Magnetic Exchange Interactions (cm^{-1})						
1	328	−8	388	0.2	−10	−0.3
2	202	−6	292	0.1	−5.0	−4.0

[a]A negative energetic difference value implies a more stable ferromagnetic state. All values refer to each of the linear and helical structures, in both polymer **1** and **2**.

ground state, and the calculated value of the FM−AFM energy difference is large enough to ensure ferromagnetism even at room temperature ($J \gg kT$). This is of paramount importance when aiming at designing a material with robust magnetic properties. Additionally, Table 1 shows the averaged spin densities over the carbon atoms bearing the unpaired electrons. For a given polymer, the spin density remains almost constant no matter the conformation adopted. Comparatively, polymer **2** shows a slightly smaller spin density due to the extra phenyl ring which provides further delocalization of the unpaired electrons. Table 1 also presents the exchange interaction values for polymers **1** and **2** for the structure optimized including dispersion. Details on the definition of the magnetic cells, associated computed energies, and equations for the extraction of the magnetic coupling constants are in section 2 of the Supporting Information. It is worth noticing that a different conformation introduces changes in the magnetic topology, as indicated in Figure 2, and consequently on the magnitude and number of the relevant exchange interactions. Thus, in the linear conformation there are two relevant magnetic interactions only that occur in almost a straight line, resulting in a quasi-1D magnetic chain. On the contrary, a helical conformation implies a distribution of the radical centers along the interior of the helix, resulting in a larger number of nearest magnetic neighbors, leading to a quasi-3D magnetic system. Moreover, the helical conformation introduces a privileged direction for magnetic interactions to transmit.

The perfect 1D polymer may be seen as a limiting model for this growing linear polyradical. To check whether the appearance of a secondary structure is an effect of an infinite polymeric structure, decaradicals (10 magnetic sites) molecular units have been optimized. Cartesian coordinates of the optimized structures are in section 4 of the Supporting Information. For derivatives from both polymers **1** and **2**, the helix shape remained intact, indicating that it is a stable local minimum, and the ground state keeps being the high-spin state (section 4.3 on the Supporting Information). On the contrary, local minima for the linear derivatives were not located, although a clear tendency to compact the secondary structure is observed. This indicates that if the polyradical is large enough, the interruption of the magnetic path at the extremes does not destroy either the adopted secondary structure or the local magnetic interactions occurring in the interior. Very importantly, this conclusion shows that materials based on 1D-like polyradicals do not necessarily require precursors obtained through polymerization processes, but rather oligomers long enough for a secondary structure to form and stabilize the radical centers.

4. CONCLUSIONS

This work presents a theoretical study of the structural, electronic structure features, and magnetic properties of two 1D-like polyradicals based on odd alternant hydrocarbons and presenting the radical centers in the backbone of the π-conjugated polymer, connected through a 1,3-phenylene unit.

The present results show that, as predicted by Yoshizawa et al.,[37] structural flexibility plays a crucial role allowing two linear (**1a**, **2a**) and helical (**1b**, **2b**) conformations. As a result of the π−π interactions, the helical conformation is preferred in all cases, and dispersion terms appear to be crucial. Additionally, the existence of a helix as a secondary structure promotes stabilization of the radical centers by steric hindrance, and one can safely argue that additional steric protection of the radical

centers could be achieved using PTM derivatives, although this may require controlling the interplay between steric congestion and structural freedom.

For the polymers under scrutiny, the particular topology of the π-system in the repeating unit ensures a high-spin ground state,[15−18] as fully confirmed by the present state of the art calculations. In fact, the energy of the ferromagnetic ground state is well below the most stable antiferromagnetic phase, implying that the ferromagnetic behavior will be maintained even at room temperature. Therefore, the predicted magnetic properties are robust, and the values of the magnetic coupling constants are remarkably large (∼300 cm^{-1}) compared to the typical exchange interaction found in coordination complexes,[46] rarely exceeding 100 cm^{-1}. Moreover, the preferred helical conformation introduces a more complex magnetic topology, which resembles to a 2D cylindrical network. This certainly has an impact on the expected macroscopic properties of the material, especially when compared to the linear conformation.

Finally, relying on the successful synthesis of a robust $S = 3/2$ ground-state triradical[7] from a discrete precursor with three potential radical sites, one could extrapolate the argument to precursors with a larger but constant number of potential radical sites for obtaining well-defined polyradicals. Attempts in this directions have been pursued, but imposing a conformational restriction for making the system totally planar (section 4.3 and ref 93 in ref 5). This strategy led to unsuccessful results, which could be explained by the impossibility for adopting a secondary structure. As indicated by the investigated decaradical, the key point would be to work with precursors long enough to ensure the appearance of a secondary structure, stabilizing the radical centers. In this way one would avoid the implicit drawbacks of a polymerization process in which it is only possible to obtain a distribution of molecules around an average molecular mass, and topological defects are difficult to prevent. From a synthetic point of view, working with a defined precursor provides a simple starting point to improve the optimization of the chemical process to generate the polyradicals quantitatively. Given that the synthesis of the molecular precursor is affordable, it would be possible to obtain polyradicals with a constant number of radical sites, very stable ferromagnetic ground state, large magnetic interactions, and secondary structure-induced anisotropy. To finalize, note that by applying an external magnetic field, one could think of aligning and separating the discrete units which may open the way to purely organic magnetic devices.

■ ASSOCIATED CONTENT

ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.5b11739.

> The following information can be found: primitive cell coordinates of optimized polymers structures for the ferromagnetic solution; energy expressions, computed absolute energies and definition of magnetic solutions required for the extraction of magnetic exchange interactions; density of states and band structure diagrams for FM and AFM solutions of polymer **2b**; optimized geometries (high-spin solution) of the different decaradicals derived from polymers **1b** and **2b** and calculated energetic differences for the decaradical derived from polymer **2b**; and SOMO and spin density for the helical decaradical derived from **2b** (PDF)

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Notes

The authors declare no competing financial interest.

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