Towards understanding of magnetic interactions within a series of tetrathiafulvalene–π conjugated-verdazyl diradical cation system: a density functional theory study†

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The intramolecular magnetic exchange coupling constants (J) for a series of tetrathiafulvalene (TTF) and verdazyl diradical cations connected by a range of π conjugated linkers have been investigated by means of methodology based on unrestricted density functional theory. The magnetic interaction between radicals is transmitted *via* π–electron conjugation for all considered compounds. The calculation of J yields strong or medium ferromagnetic coupling interactions (in the range of 56 and 300 K) for diradical cations connected by linkers with an even number of carbon atoms that are able to provide a spin polarization pathway, while antiferromagnetic coupling is predicted when linkers with an odd number of carbon atoms are employed. The topological analysis of spin density distributions have been used to reveal the effects of the spin polarization on both linkers and spin carriers. The absence of heteroatoms that impede the spin polarization pathway, and the existence of a unique spin polarization path instead of several possible competitive routes are factors which contribute to large positive J values favoring ferromagnetic interactions between the two terminal π-radicals. The magnitude of J depends strongly on the planarity of the molecular structure of the diradical cation since a more effective orbital overlap between the two π-systems can be achieved. Hence, the dependence of J on the torsion angle (θ) of each spin carrier has been analyzed. In this respect, our findings show that this geometrical distortion reduces largely the calculated J values for ferromagnetic couplings, leading to weak antiferromagnetic interactions for a torsion angle of 90°.

1. Introduction

One of the current trends in materials science lies in the search for multifunctional compounds and within this context, the molecular approach offers unrivaled possibilities for the development of novel combinations of properties, for example, conductivity and ferromagnetism.[1] The most straightforward way to achieve this goal is based on the combination of an organic donor together with a magnetic anion incorporated within the same crystalline lattice. This approach has proven to be successful in many cases resulting in the discovery of several classes of π-d materials with interesting conducting and/or optical and magnetic properties, such as ferromagnetic metals,[2] magnetic superconductors,[3–5] and optically active chiral magnets[6] amongst others. Given these advances, one of the major drawbacks of this strategy resides in the limited interplay between the properties of each of the sublattices, usually resulting in solids displaying two independent properties rather than a combination of them. One step closer towards the realization of truly multifunctional materials with synergistic properties is the design and preparation of single component molecule-based ferromagnetic conductors. In this context, new magnetic materials can be designed combining the synthetic methodologies employed for the preparation of tunable organic compounds,[7,8] together with the magnetic exchange interactions between localized electrons occurring *via* conducting electrons, the so-called double-exchange mechanism which gives rise to room temperature magnetic order in conventional families of magnets such as the iron oxides.[9]

The realization of an organic metallic ferromagnet requires a sufficient conduction path from the organic donor to the a radical unit when the donors are assembled and partially doped.[10] Many organic diradical molecules have been both experimentally synthesized and characterized, while accurate quantum chemical methods have been used to provide the link between macroscopic and microscopic characteristics with great success.[7,8,11] Magnetic coupling mechanisms between radicals have been explained pointing out the intrinsic and environmental effects in the structure and magnetic properties of organic molecular magnets.[11–13] Hence, it was found that magnetic properties can be tuned effectively by the type of

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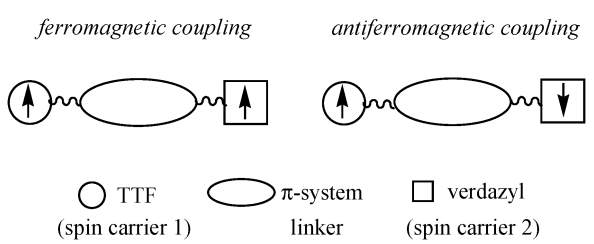
linker connecting both radicals and their respective conformational behavior.

Tetrathiafulvalene (TTF) and its derivatives were originally prepared as strong electron-donor molecules for the development of electrically conducting materials. However, its unique electronic properties have attracted interest towards this molecule from many fields of chemistry.[14] Early works on the preparation of diradicals containing both tetrathiafulvalene and a spin carrier, usually nitrosyl or nitronyl nitroxide groups, linked directly or by a *p*-benzene group were carried out by Sugawara *et al.*[15,16] and Yamaguchi *et al.*[17,18] Following this line, Pilkington *et al.* have developed recently a new synthetic strategy for the preparation of two stable organic heterospin diradicals, TTF and verdazyl, that are linked covalently through two different bridges, namely a cross conjugated pyridine[19] and an alkene π-system,[20] both of which allow communication *via* exchange interactions between the unpaired electrons residing on both TTF and verdazyl moieties. Verdazyl radicals constitute an interesting family of radicals which are sufficiently stable to be characterized magnetically[21] and theoretically.[22]

Working towards the realization of molecule-based conducting ferromagnets, we have initiated a series of studies for which stable organic donor molecules comprising verdazyl radicals are grafted onto a TTF framework in which a (cross) conjugated linker connects the π-donor and π-radical units (see Scheme 1). For this class of compounds, the double-exchange mechanism *via* the conducting electrons of the TTF is expected to lead to ferromagnetic alignment of the localized verdazyl radical electrons. These molecule-based systems represent a very promising approach for the development of truly multifunctional compounds. In order to fulfil the potential properties they hold for unique new materials and devices, they must be designed to maximise the interaction between the unpaired electrons. In this article, density functional theory (DFT) calculations using the "broken symmetry" approach[23] are carried out to determine the sign and magnitude of the intramolecular exchange couplings in a series of compounds for which the conjugated linkers between the TTF and the verdazyl radicals have been modified. The results obtained have been analyzed with the help of spin polarization maps and conclusions for rationalizing the size and sign of exchange interactions are drawn for the design of molecules with optimal couplings. Finally, the dependence of the *J* value with respect to the twisting out of the plane defined by the spin carriers and the linkers has also been considered.



Scheme 1 Representation of the units forming the studied systems: two spin carriers (TTF, SC1, and verdazyl, SC2) and the linker (π-conjugated system).

2. Theoretical methodology and computational strategy

The magnetic exchange interaction between two magnetic sites (spin carriers, SCs) 1 and 2 is normally expressed by the phenomenological Heisenberg spin Hamiltonian:

$$\hat{H} = -2J\hat{S}_1\hat{S}_2 \qquad (1)$$

where $\hat{S}_1$ and $\hat{S}_2$ are the respective spin angular momentum operators and J is the effective exchange integral. For a diradical, the lowest energy electronic states are a singlet ($S = 0$) and a triplet ($S = 1$) which are eigenstates of the Heisenberg Hamiltonian. There is a one to one correspondence between the eigenfunctions of the Heisenberg Hamiltonian and those of the exact Hamiltonian from the fact that both Hamiltonians commute with the total spin operators. Therefore, J is directly related to the energy difference between the spin eigenstates and it can be obtained as:

$$E(S = 1) - E(S = 0) = -2J \qquad (2)$$

A positive sign of J indicates a ferromagnetic interaction, whereas a negative sign indicates an antiferromagnetic interaction.

Due to the large number of π-electrons involved in the compounds studied here, the use of multiconfigurational methods which yield pure spin states but are computationally expensive, is not allowed. An alternative treatment is the broken symmetry formalism firstly proposed by Ginsberg[24] and Noodleman,[23,25] and discussed and currently used by others authors (Yamaguchi *et al.*,[26] Bencini,[27,28] Ruiz,[29] Illas,[30] Daul[31]) allows a reliable computation of the magnetic exchange coupling constant using a broken-symmetry (BS) solution for the lowest spin-state. The BS solution is not a pure eigenstate of the Hamiltonian, but a weighted admixture of the singlet and triplet states. Although a proper mapping of the singlet state can be achieved by using spin projection techniques, the presence of the self-interaction error in the commonly employed exchange–correlation potentials overestimates the correction,[32] leading to calculated J values which differ greatly from the experimental results. Therefore, spin projection will not be applied in this work.

The coupling constant can be written as:

$$J = \frac{(E_{BS} - E_T)}{1 + S_{ab}^2} \qquad (3)$$

where S_{ab} is the overlap integral between the two magnetic orbitals a and b. E_{BS} is the energy of the broken-symmetry solution and E_T is the energy of the triplet state. Several equations have been proposed to calculate J depending on the overlap between orbitals a and b or on the value of the averaged spin square momentum operator. Eqn (4) stands for the Ginsberg,[24] Noodleman,[23] and Davidson[33] (GND) formula which is applied when the overlap of the magnetic orbitals is sufficiently small.

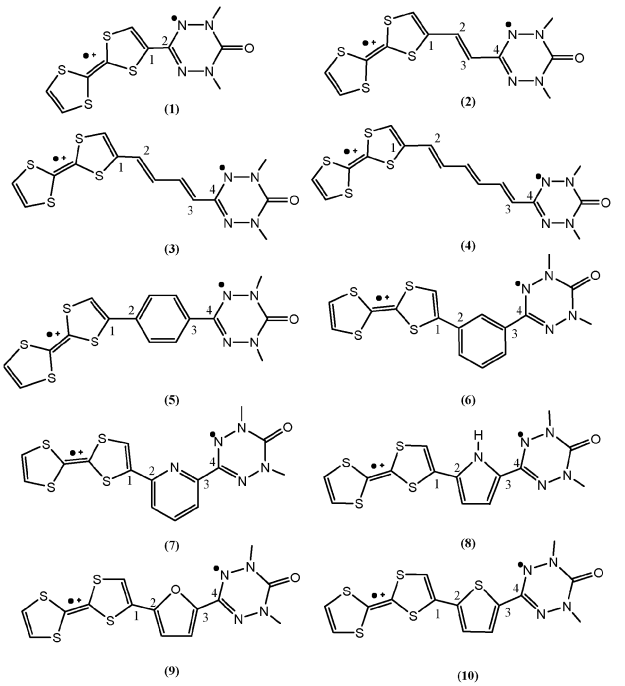
$$J = \frac{(E_{BS} - E_T)}{S_T^2} \qquad (4)$$

Yamaguchi *et al.*[10] proposed an elegant procedure in which the dependence of J upon the overlap is replaced by a

dependence upon the spin contamination of the broken symmetry solution:

$$J = \frac{(E_{BS} - E_T)}{{}^{T}\langle S^2\rangle - {}^{BS}\langle S^2\rangle} \quad (5)$$

All calculations have been carried out by means of the GAUSSIAN03 package.[34] The popular B3LYP exchange–correlation potential approach[35–37] was used in combination with the 6-31G(d,p) basis set[38] for all geometry optimizations. Due to the relevance of the basis set for the determination of accurate J values, single point calculations on the B3LYP/6-31G(d,p) optimized geometries were carried out using the very large 6-311++G(3df,3pd) basis set.[39] All molecules have been fully optimized and analytical frequencies have been carried out to determine its minima character on the potential energy surface. The BS open-shell singlet solution, within the unrestricted formalism, has been calculated using the keyword "guess = mix" and the stability of the obtained BS solution has been ensured by performing a calculation with the keyword "stable". The program MOLEKEL4.0[40] was employed for the graphical representation of the spin polarization.



Scheme 2 TTF-linker-verdazyl diradical cations investigated where the linker is (**1**) no linker, (**2**) ethylene, (**3**) 1,4-butadiene, (**4**) 1,6-hexatriene, (**5**) *p*-phenylene, (**6**) *m*-phenylene, (**7**) 2,6-pyridine, (**8**) 2,5-pyrrole, (**9**) 2,5-furan, and (**10**) 2,5-thiophene. Bridge carbon atoms are numbered.

3. Results and discussion

3.1 Effect of the π-conjugated linker on the value of *J* for TTF–π conjugated-verdazyl diradical cations

The crucial role of the linker between two radicals on the sign and magnitude of the exchange couplings constants is well known.[41,42] In order to understand the magnetic exchange between diradicals composed by TTF and verdazyl groups as spin carriers, a wide set of linkers affording conjugated or cross-conjugated π-electronic systems will be considered here. They can be classified into four groups (see Scheme 2), namely, direct coupling (no linker) between TTF and verdazyl radicals (**1**), π-conjugated linear couplers by one (**2**), two (**3**) and three double bonds (**4**), six-membered conjugated aromatic couplers: *p*-phenylene (**5**), *m*-phenylene (**6**), and 2,6-pyridine (**7**), and finally five membered aromatic couplers: 2,5-pyrrole (**8**), 2,5-furan (**9**), and 2,5-thiophene (**10**). The overlap integrals between the magnetic orbitals for the TTF and verdazyl moieties have been calculated for the fully optimized structures of (**1–10**). Due to the computational cost, the methyl groups attached to the nitrogen atoms in the verdazyl moieties have been replaced by hydrogen atoms. It is well known experimentally that the spin of the TTF moiety is spread out over the sulfur and the central carbon atoms forming a double bond while the spin on the verdazyl moiety is largely localized on the four nitrogen atoms.[43] Table 1 gathers the absolute energies and averaged spin square values for both the open-shell singlet solution and the triplet state together with the J values calculated using eqn (5).

Geometries have been optimized at the B3LYP/6-31G(d,p) level while single point calculations using the larger basis set, 6-311++G(3df,3pd), have been used to calculate J in order to obtain quantitative results. Key geometrical parameters are collected in Table 2, namely the *d*C1–C2 and *d*C3–C4 distances and the torsion angles θ_{SC1} and θ_{SC2} between the planes defined by the linker and the respective spin carrier (see Scheme 3 for the torsion angle definition).

In general, the sign of the exchange coupling does not depend on the basis set but J values calculated with the large basis set reduce its magnitude between 18 and 101 K for (**5**) and (**9**), respectively, while (**1**) and (**8**) increase the J value. Therefore, the results of J obtained with the 6-31G(d,p) can be considered as qualitative results. Our calculated J value for the direct coupling (without linker) between the TTF unit and the verdazyl diradical cation (**1**) yields a very weak antiferromagnetic interaction ($J = -25$ K). This result is in agreement with previous experimental studies by Sugawara *et al.*[15,16,44] on similar systems, namely a TTF or pyrrole unit directly linked to a nitronyl nitroxide radical, where an antiferromagnetic coupling between unpaired electrons was proved, although triplet signals were observed by ESR from a thermally populated low lying excited triplet state. Theoretical calculations at the PM3/UHF computing level on the planar structure afforded positive J values, while experimentally it was estimated to be about -100 K.[15] This disagreement was attributed to the strong dependence of the J value on the dihedral angle between the spin carriers.

The gas-phase geometry optimization for compounds (**2**), (**3**) and (**4**) yields planar structures with strong ferromagnetic interactions. Interestingly, the enlargement of the chain for compounds (**2**), (**3**), and (**4**) leads to an increment in the calculated J, with values of 152, 192, and 234 K, respectively. Hence, this trend indicates a better transmission of the spin polarization along the π-conjugated system for larger –C=C–

Table 1 B3LYP/6-31G(d,p) and B3LYP/6-311++G(3df,3pd) absolute energies (a.u), $\langle S^2 \rangle$ and intramolecular exchange coupling constants for TTF-verdazyl diradicals (**1–10**) calculated using eqn (5)

		B3LYP/6-31G(d)			B3LYP/6-311++G(3df,3pd)		
		BS singlet	Triplet	J/K	BS singlet	Triplet	J/K
(**1**)	E	−2194.51675	−2194.51673	−5	−2194.85194	−2194.85182	−25
	$\langle S^2 \rangle$	0.99	2.03		1.00	2.03	
(**2**)	E	−2271.92696	−2271.92782	185	−2272.28581	−2272.28651	152
	$\langle S^2 \rangle$	1.02	2.04		1.03	2.04	
(**3**)	E	−2349.34090	−2349.34210	256	−2349.72263	−2349.72352	192
	$\langle S^2 \rangle$	1.02	2.05		1.04	2.05	
(**4**)	E	−2426.75541	−2426.75697	331	−2427.15986	−2427.16096	234
	$\langle S^2 \rangle$	1.02	2.06		1.03	2.06	
(**5**)	E	−2425.58660	−2425.58695	75	−2425.98646	−2425.98672	56
	$\langle S^2 \rangle$	1.01	2.03		1.03	2.03	
(**6**)	E	−2425.58643	−2425.58613	−61	−2425.98615	−2425.98608	−15
	$\langle S^2 \rangle$	0.99	2.03		1.02	2.03	
(**7**)	E	−2441.62200	−2441.62159	−86	−2442.02859	−2442.02847	−27
	$\langle S^2 \rangle$	0.98	2.03		1.02	2.03	
(**8**)	E	−2403.51619	−2403.51721	222	−2403.91381	−2403.91518	300
	$\langle S^2 \rangle$	1.02	2.03		1.03	2.03	
(**9**)	E	−2423.36076	−2423.36174	212	−2423.76876	−2423.76927	111
	$\langle S^2 \rangle$	1.03	2.04		1.03	2.04	
(**10**)	E	−2746.33798	−2746.33859	131	−2746.75290	−2746.75327	82
	$\langle S^2 \rangle$	1.02	2.04		1.03	2.04	

chains, leading to a stabilization of the triplet state. This state is the preferred one according to the spin alternation rule.[45–47] Using the same linkers and nitronyl nitroxide as spin carriers Datta *et al.*[41] also found a stabilization of the triplet state, which led to a decrease of the calculated J values, since the coupling between the studied bis-nitronyl nitroxide diradicals was antiferromagnetic. Recently, compound (**2**) has been synthesized and magnetic measurements yielded a negative Curie Weiss constant characteristic of antiferromagnetic coupling,[19] which is in contrast with the calculated result of J for the planar structure. Unfortunately, the X-ray structure has not been obtained to date and as a consequence, the geometrical structure is unknown. In order to explain this difference, the dependence of J with respect to the torsion angles θ_{SC1} and θ_{SC2} between the linker and the spin carriers will be investigated in detail in section 3.3.

The optimized geometry of compounds (**5**) and (**6**) does not afford a planar structure, the steric repulsion between the hydrogen atoms of the TTF moiety and the linker results in a θ_{SC1} value of $\sim 32^\circ$ (see Table 2). Therefore, the observed decrease in the J value, 56 and −15 K for (**5**) and (**6**) can be attributed to the reduced delocalization of π-electrons due to the lack of planarity. In compound (**7**), the presence of the pyridyl nitrogen atom instead of the phenyl C–H largely reduces the steric repulsion and restores the planarity of the system, increasing slightly the J value to −27 K. Compound (**7**) has also been synthesized and the measured EPR spectra suggest the presence of a triplet state.[20] However, the calculated value of J (−27 K) indicates the possibility that the observed triplet is due to a thermal population of the excited triplet state which has been observed in other cases of antiferromagnetically coupled diradicals.[12,48] Finally, compounds (**8**), (**9**), and (**10**) are connected *via* a five-membered linker and yield ferromagnetic couplings of 300, 111 and 82 K, respectively. Steric repulsions between the hydrogen atom of TTF moiety and the hydrogen atom of the pyrrole and the sulfur atom of the thiophene lead again to deviations from planarity. However, due to the smaller size of the five-membered ring than for the six-membered rings, the torsion angle is less pronounced ($\sim 14^\circ$) and the calculated J values are of larger magnitude.

Table 2 Selected geometrical parameters for B3LYP/6-31G(d,p) optimized geometries at the triplet state and the broken-symmetry open shell singlet solution

	Triplet			Open-shell singlet		
	dC1C2	dC3C4	θ_{SC1}	dC1C2	dC3C4	θ_{SC1}
(**1**)	1.467	1.467	0	1.468	1.468	0
(**2**)	1.442	1.457	0	1.445	1.460	0
(**3**)	1.434	1.453	0	1.438	1.457	0
(**4**)	1.438	1.453	0	1.436	1.456	0
(**5**)	1.468	1.485	−32.2	1.468	1.484	−32.7
(**6**)	1.469	1.485	−32.6	1.465	1.482	−31.0
(**7**)	1.477	1.490	0	1.476	1.489	0
(**8**)	1.430	1.454	−14.1	1.431	1.459	−17.9
(**9**)	1.430	1.455	0	1.431	1.458	0
(**10**)	1.439	1.460	15.8	1.442	1.463	16.4

In summary, all compounds present two unpaired electrons which are strongly coupled *via* the (cross) conjugated linker. Analysis of the sign of J shows ferromagnetic interactions for compounds with linkers presenting an even number of carbon atoms, *i.e.* systems (**2–5**), and (**8–10**), while medium antiferromagnetic interactions are calculated for linkers with an odd number of carbon atoms (**6**) and (**7**).

3.2 Towards a rationalization of the ferro/antiferro behavior using the topology of the spin density distribution

The use of the spin alternation rule[45,46] based on Hund's rule can be very helpful for understanding the preference for a certain state of a given diradical linked by a conjugated electronic system. However, there are certain factors that

make it difficult to predict the sign of J following the spin alternation rule, such as the presence of heteroatoms, the coexistence of two competitive spin polarization pathways, or the non-planarity between the π-conjugated systems. These three factors play a key role in contributing to the magnetic exchange interactions of the diradical cations (**1–10**). In this respect, their effect on the spin polarization has been analyzed and will be discussed. The spin density distributions for all diradicals in their optimized structure and ground states are plotted in Fig. 1.

For all spin density plots, the unpaired electrons are mainly localized on both TTF and verdazyl moieties. Interestingly, the TTF presents a strong spin delocalization among all heavy atoms due to the remarkable conjugation of its π-system, implying that the carbon atom attached to the linker (C1) presents a weak spin polarization. On the other hand, the unpaired electron of the verdazyl group is delocalized among the four nitrogen atoms and the C4 suffers a strong spin polarization of the opposite sign. Therefore, both spin carriers interact with the conjugated linker in different ways and strengths. The absence of a linker in compound (**1**) produces competing spin polarization and delocalization effects at the C1 atom. The lower energy of the broken symmetry singlet solution indicates that spin delocalization on the C1–C2 bond prevails on spin polarization. The group of diradicals connected by a chain of double bonds, compounds (**2–4**), nicely follows the spin alternation rule. It is worth noting the considerable spin polarization of the π-systems of the linkers formed by –C≡C– units, supporting the large J values reported in Table 1. Furthermore, the position of the radical carriers attached to a six-membered ring determines the sign of J. Hence, *para*- or *meta*-substitutions lead to ferromagnetic and antiferromagnetic coupling for diradicals (**5**) and (**6**), respectively. A comparison of the data for compounds (**6**) and (**7**) shows that the replacement of a C–H fragment by a nitrogen atom restores the planarity of the system, thus favoring delocalization of the π-electrons. Attachment of the TTF and verdazyl radicals to the 1- and 3-positions of the five-membered ring of the linkers opens up the possibility for two competitive coupling pathways involving a different number of atoms (3 or 4), that is further complicated by the effect of the heteroatoms. Although groups like –NH, O, and S contain two π electrons and follow the spin alternation rule, the larger electronegativity of the heteroatom hinders the spin polarization as can be observed in Fig. 1 for (**8**), (**9**) and (**10**).

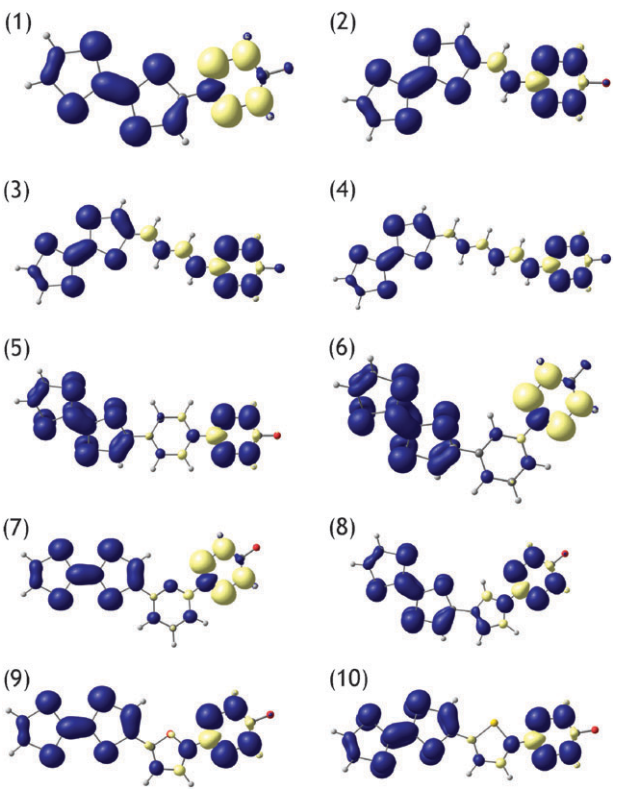
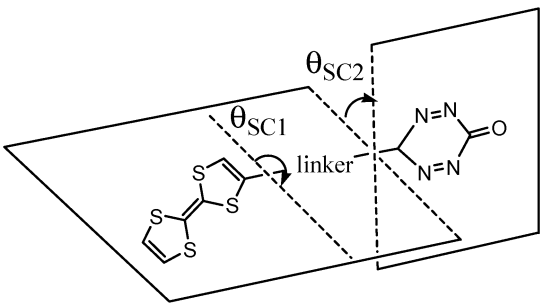


Fig. 1 Plots of spin density distributions for diradicals (**1–10**) (Isocontour value 0.002; blue for alpha spin and yellow for beta spin).

3.3 Analysis of the dependence of J with the TTF and verdazyl torsion angles

The previously considered J values correspond to fully optimized molecular structures in a gas-phase environment. However, crystallization can impose geometry constraints due to packing effects which can severely modify the studied intramolecular magnetic exchange values, as has been demonstrated experimentally for similar diradicals.[49,50] In this respect, the torsion angles between the planes formed by the spin carriers and the linkers are difficult to control given that they are largely dependent on the final solid-state structure. In this section, J is calculated along the twisting movement of the spin carriers as given by the scan of θ_{SC1} and θ_{SC2} dihedral angles (see Scheme 3), from 0 to 90° considering increments of 15° for each diradical. Hence, these curves represent the evolution from a planar structure where the two radicals belong to the same π-system, to a structure where one unpaired electron remains in the π-system and the other lies on the σ-plane, yielding an exchange coupling interaction *via* orthogonal σ–π systems. In Fig. 2 the values of J calculated using eqn (5) for a given θ_{SC1} and θ_{SC2} are plotted, also the energetic barriers to afford a value of 90° of θ_{SC1} and θ_{SC2} angles are listed in Table 3.

Qualitatively, the correlation of the J values with the torsion angles depends of the sign of the interaction at $\theta_{SC1} = \theta_{SC2} = 0°$. Ferromagnetic compounds (**2–5**) and (**8–10**) follow a decreasing trend for J upon twisting of either θ_{SC1} or θ_{SC2}. This decrement is smooth at the beginning, $0° < \theta_{SC1}, \theta_{SC2} < 45°$, but sharp for the $45° < \theta_{SC1}, \theta_{SC2} < 90°$ interval, leading to antiferromagnetic interactions for a σ–π diradical



Scheme 3 Schematic representation of torsion angles θ_{SC1} and θ_{SC2}.

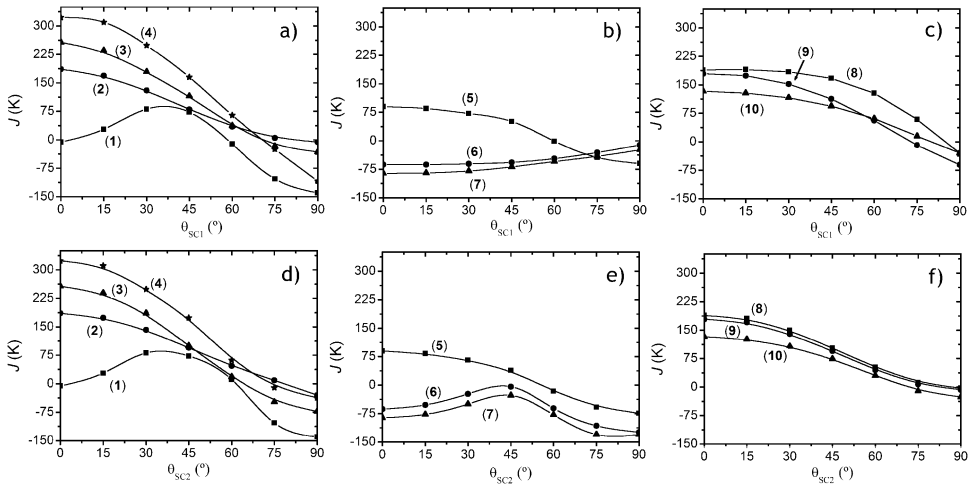


Fig. 2 B3LYP/6-31G(d,p) calculated J values for (**1–10**) diradicals upon torsion of TTF and verdazyl groups (θ_{SC1} and θ_{SC2}).

configuration. Therefore a spin crossover process from the triplet state to the singlet state occurs in the course of the twisting of either spin carrier. Antiferromagnetic compounds (**1**), (**6**), and (**7**) show an opposite trend for small rotations (from 0 to 45°) of either spin carriers, which leads to an increment of the J values. Surprisingly, different trends are found for the large torsions (between 45 and 90°) of the TTF unit or the verdazyl group. Hence, while the torsion of the TTF unit shows a continuation of the increasing trend of J values, for the verdazyl group, the J goes down drastically. This behavior can be explained considering the changes in the electronic structure upon θ_{SC1}, θ_{SC2} torsion. In this respect, small twisting angles lead mainly to a loss of conjugation in the π-system which produces systematically a decrease of the absolute J value for both ferro- and antiferromagnetic interactions. On the other hand, large twisting angles introduce spin polarization coupling between the diradicals *via* the σ electronic system of the linker.

At a torsion angle of 90° of either spin carrier, the spin of the unpaired electron in the π-orbital polarizes the spin of the paired electrons in the orthogonal σ-orbitals and *vice versa*. In all compounds, the spin coupling through the σ-system of the linker leads to a destabilization of the triplet state when compared with the singlet state.

Interestingly, large torsions of the spin carriers of (**6**) and (**7**) diradicals show opposite trends (see Fig. 2b and e). This fact can be understood if the Mulliken analysis of the atomic spin density is considered (see Table 4). Clearly, the C1 atom presents a much smaller value of spin polarization, 0.030 (**6**) and 0.015 (**7**), than the C4 atom, 0.164 (**6**) and 0.150 (**7**), indicating a less effective polarization of the linker by the TTF unit than the verdazyl group and, therefore, a much reduced polarization for the σ system of linker in the σ–π diradical configuration upon torsion of the TTF group (θ_{SC1} = 90°, θ_{SC2} = 0°). Considering the energetic cost for each spin carrier to twist out of the plane given by the conjugated linker, it is clear that the TTF moiety is easier to rotate than the verdazyl radical (see Table 3). In this respect, the verdazyl radical presents a larger preference for a planar conformation which is also due to the smaller steric repulsion compared to the TTF or nitronyl nitroxide groups.

To summarize, although some of the diradical compounds studied in this work show a strong ferromagnetic coupling at the equilibrium geometry, the torsion angles θ_{SC1} and θ_{SC2} decrease the value of the magnetic exchange interaction considerably. The energy barrier for this torsion has been calculated to be less than 10 kcal mol^{-1}. Therefore, the experimental results[20] measured for compound (**2**) can be explained either by intermolecular coupling or a distortion of one spin carrier with a θ_{SC1} or θ_{SC2} torsion angle close to 90°. In order to design compounds with strong ferromagnetic coupling, the energetic barriers for the torsion of the TTF

Table 3 B3LYP/6-31G(d,p) relative energies to the minimum in kcal mol^{-1}, for (**1–10**) diradicals upon torsion of TTF (θ_{SC1}) and verdazyl (θ_{SC2})

	ΔE (θ_{SC1} = 0°, θ_{SC2} = 0°)	ΔE (θ_{SC1} = 90°, θ_{SC2} = 0°)	ΔE (θ_{SC1} = 0°, θ_{SC2} = 90°)
(**1**)	0	7.36	7.36
(**2**)	0	7.79	9.63
(**3**)	0	5.80	9.87
(**4**)	0	7.19	10.16
(**5**)	0.72	2.42	8.02
(**6**)	0.62	8.75	7.16
(**7**)	0	2.92	5.09
(**8**)	0.09	4.80	9.84
(**9**)	0	6.33	6.96
(**10**)	0.04	7.81	7.87

Table 4 Mulliken spin populations of the atoms connecting the spin couplers and the linker for diradicals (**1–10**) in the corresponding ground state calculated at B3LYP/6-31(d,p) level

	C1	C2	C3	C4
(**1**)	0.085	−0.003	—	0.155
(**2**)	0.055	−0.097	0.117	−0.169
(**3**)	0.036	−0.064	0.141	−0.172
(**4**)	0.018	−0.036	0.169	−0.176
(**5**)	0.031	−0.027	0.057	−0.170
(**6**)	0.030	−0.023	−0.038	0.164
(**7**)	0.015	−0.003	−0.033	0.150
(**8**)	0.043	−0.007	0.020	−0.170
(**9**)	0.029	−0.037	0.084	−0.167
(**10**)	0.027	−0.041	0.083	−0.169

(mainly) and the verdazyl group should be increased in order to force the molecule to adopt a planar conformation, thus maximizing the spin coupling effects.

4. Conclusion

The intramolecular magnetic exchange coupling constants for a series of TTF and verdazyl diradical cations connected by a set of conjugated linkers have been investigated using density functional theory. The magnetic interactions are mainly transmitted through π–electron conjugation for all diradical cations. Strong ferromagnetic coupling is anticipated for linkers providing a spin polarization pathway with an even number of atoms with calculated J values ranging from 56 K (**5**) to 300 K (**8**). We have also observed that the linkers formed by linear chains of C=C bonds, and 2,5-pyrrole give the largest J values. The obtained values of J can be explained by: (i) the adoption of a planar structure which allows better orbital overlap between the two π-systems; (ii) the absence of heteroatoms that may interrupt the spin polarization pathway and (iii) the existence of a unique spin polarization path instead of more than one possible route. The effects of the spin polarization and spin delocalization mechanisms on both spin carriers and linkers have been rationalized by means of the topological analysis of spin density distributions. Due to the different nature of the spin carriers, their conjugation with the π-system and the spin polarization of the linker takes place in different ways. The TTF radical cation forms a more conjugated C1–C2 bond than the corresponding C3–C4 bond in the verdazyl radical as suggested by shorter bond distances. On the other hand, the verdazyl radical polarizes the linker more efficiently than the TTF radical cation due to the larger spin density on C4 atom when compared to the C1 atom. Finally, we should note that the energy barrier for the torsion of the TTF or verdazyl moiety is rather small, less than 10 kcal mol^{-1} for value of torsion angle of 90°. This geometrical distortion reduces drastically the calculated J value for a ferromagnetic coupling. A rotation of 75° of one of the spin carriers implies that intramolecular couplings will be antiferromagnetic for all compounds due to the polarization of the σ orbitals of the linker by the π-orbital containing the unpaired electron. This behavior will have an important effect, since intermolecular forces and the lattice energy will play an important role in determining the final configuration of the molecules in the solid state.

To conclude, this study shows that the concept of a spin polarized donor can be extended to TTF systems bearing verdazyl radicals. It is highly feasible that some of the radicals described here will afford a triplet ground state upon one-electron oxidation. The clear advantage of studying TTF donors appended with verdazyl radicals lies in the fact that they are straightforward to prepare and are stable when exposed to air and moisture. If a columnar stacking of these donors is realized when the compounds are partially doped, such a self-assembled material could afford molecule-based conducting ferromagnets. Work along these lines is currently in progress and will be reported in due course.

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