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Impact of short and long-range effects on the magnetic interactions in neutral organic radical-based materials

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Abstract

The mutual influence of electronic structure and environment of the constituent units of neutral organic radical-based materials (radical dimers) are analysed by means of wave function calculations (Difference Dedicated Configuration Interaction, DDCI). The focus is put on the magnetic properties modulations of two classes of neutral organic materials by inspecting both short- and long-range effects. The exchange coupling constant J for the high-temperature phase of the 1,3,5-trithia-2,4,6-triazapentalenyl (TTTA) material is calculated to be $J = -95 \text{ cm}^{-1}$ at the DDCI level. The environmental electronic polarization is taken into account self-consistently using the individual polarizabilities of the atoms in a finite block of the crystal lattice (Discrete Reaction Field, DRF) and accounts for less than 5% of the calculated J value in TTTA. Furthermore, taking advantage of the chemical flexibility of the verdazyl radical family, the contribution of strong electron-withdrawing groups is analysed by extracting the J , U , t and K parameters from pairs of substituted verdazyl-based radicals. Our *ab initio* calculations of verdazyl radical pairs suggest that the addition of NO_2 groups produce (i) the variations of the ferromagnetic and antiferromagnetic contributions cancel out, leaving an almost constant exchange coupling constant, *ca.* $J \approx 20 \text{ cm}^{-1}$, and that (ii) enhanced conduction properties can be anticipated. In contrast to inorganic analogues, one may conclude that the magnetic behaviour of neutral organic radical-based materials is mostly governed by the supramolecular arrangement, whereas environmental effects have a lesser impact.

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1 Introduction

Organic radicals are very promising candidates to grow complex multifunctional materials because of their high versatility.[1] They can be used either as simultaneous spin holders and ligands when bound to paramagnetic metal ions,[2–5] or as pure organic radicals to grow multifunctionality from their intrinsic properties.[6–11] These observations have greatly stimulated the interest for nitronyl nitroxides-, phenalenyl-, thiazyl-, selenazyl- and verdazyl-based compounds, all the more after spin-coupled supramolecular networks or spin-crossover phenomena have been suggested in the solid state.[6] However, these radicals have a tendency to spontaneously dimerize, resulting in an undesired quenching of the magnetic properties.[12] Therefore, to be able to design new materials with the desired multifunctionality, it is key to provide a detailed understanding of the microscopic factors that condition their electronic and macroscopic magnetic properties.

The organic materials considered in the present study are quasi one-dimensional structures, constituted by the stacking of dimeric units of $S = 1/2$ organic radicals. The most relevant magnetic interactions found in these systems involve nearest-neighbour blocks along one direction and to a lesser extent, contacts across adjacent chains. At first sight, organic compounds seem easier to describe than their inorganic counterparts, since their magnetic properties are ascribed to a small number of unpaired electrons, which usually occupy one or two mostly π -type molecular orbitals (MOs). However, the main difficulty of organic systems stems from the molecular character of the relevant orbitals, more delocalized as compared to the $3d$ atomic orbitals that govern the magnetic properties of the metal ion-based materials. As a consequence, the spin density is expected to be affected by the local environment of the spin carriers and the long-range polarization of the three dimensional lattice of the material.

The aim of this work is to examine the influence of those short- and long-range contributions that are likely to modify the polarizable singly-occupied MOs (SOMO) of the radicals, and ultimately, the exchange coupling constant (J) and other effective parameters of the electronic structure related to the conduction properties of the material. The macroscopic properties of these radical-based compounds result from a complex interplay between the crystal structure[13–15] and the intramolecular electronic structure.[15, 16] We analyse each of these phenomena independently by (i) performing simulations of the bulk polarization on the crystalline high-temperature phase of 1,3,5-trithia-2,4,6-triazapentalenyl (TTTA) material, and (ii) evaluating the effect of nitro-group substitutions and conformational distortions on the magnetic exchange coupling constant of hypothetical verdazyl-based compounds.

Figure 1 shows the synthetic material built with TTTA radical units that we used to simulate the response effect induced in the bulk by the singlet–triplet spin-transition and its effect on the exchange coupling constant (J). Following the Heisenberg Hamiltonian model ($\hat{H} = -2J \sum_i \hat{S}_i \cdot \hat{S}_{i+1}$), J can be expressed as the energy difference between the lowest singlet and triplet states ($2J = E_S - E_T$). The electrostatic environmental effects are known to play a major role in inorganic spin networks such as manganites[17], cuprates[18] or spin-crossover iron(II) compounds[19, 20]. Initially, it might be expected that the impact of this phenomenon in neutral organic crystalline materials is not as large as on systems based on paramagnetic transition metal centres. Indeed, in comparison to the later, the TTTA dimers stack in chains that form a less compact packing of the crystalline structure and additionally, the ionic character of such materials is small. These structural and electronic characteristics should lead to comparatively reduced Madelung-like effects

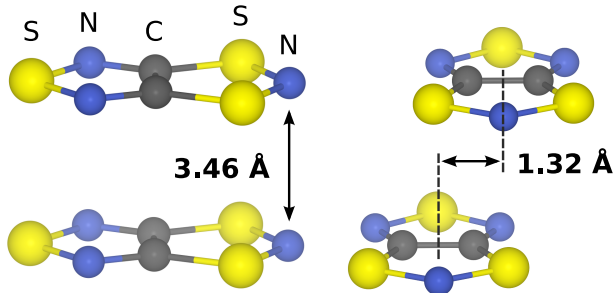


Figure 1: Constitutive unit of 1,3,5-trithia-2,4,6-triazapentalenyl (TTTA) on the high temperature phase. Left: Radical molecules are stacked in chains with an interplanar separation of 3.46 Å. Right: The slippage value between neighbouring radicals is 1.32 Å.

induced in the surroundings. Nevertheless, due to the delocalized character of the spin density, one would expect that the exchange coupling constants are more sensitive to polarization contributions, even though it has never been tested numerically. Thus, we quantify the extent of the electronic response on the environment of the dimer unit and the impact of such fluctuations on its magnetic properties. The electronic polarization of the dimer surroundings is modelled by means of the Discrete Reaction Field (DRF) method,^[21–23] which was successfully applied to account for the polarization effects induced by localized electronic excitations of an inorganic magnetic system.^[24]

Furthermore, the short-range effects caused by the substituent groups of the radicals are analysed by means of hypothetical verdazyl building blocks with some custom chemical modifications. Verdazyl-based materials show high synthetic versatility both at the molecular and crystal

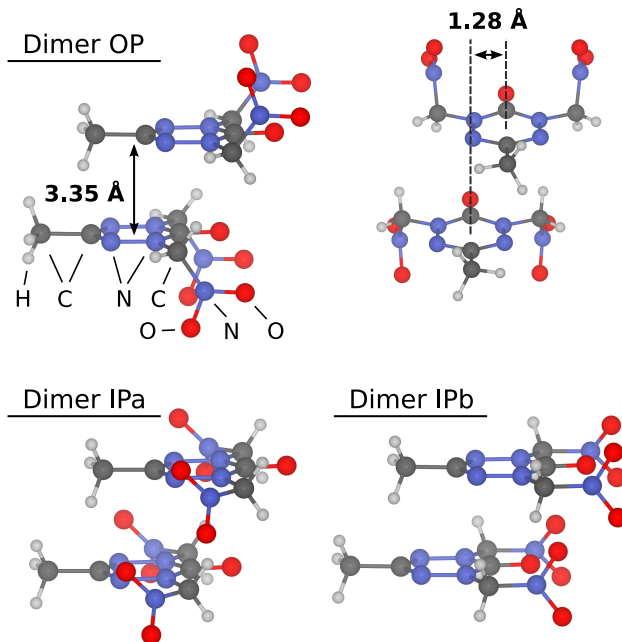


Figure 2: Constitutive unit of the hypothetical verdazyl-based material with NO₂ substituents (dinitro-verdazyl). Top: Dimer structure with the nitro groups oriented out of the molecular plane (Dimer OP). The two radical molecules are separated by 3.35 Å (left) and are slipped by 1.28 Å (right). Bottom: Structures of two other conformers considered in the present work, where the nitro groups are oriented in the molecular plane (Dimers IPa and IPb).

levels,[25] and are considered as possible targets to generate spin-crossover compounds.[6] Therefore, verdazyl derivatives are ideal candidates to explore the short-range effects induced by the substituents of the verdazyl monomer, turning this class of radicals into a laboratory to inspect magnetic properties in organic materials. The reported crystal structure of these verdazyl-based organic compounds is analogous to that of TTTA. The objective is to evaluate and eventually, control the effects produced by electron withdrawing groups, such as NO₂, attached to the verdazyl radical (see Figure 2). These short-range contributions are to be compared to the traditional ligand field produced by ligands which distort the magnetic orbitals of paramagnetic transition metal ions. Thus, the effective on-site repulsion integral U , hopping integral t and direct exchange K parameters are calculated and compared to address the respective influences of the individual spin carriers and their surroundings. We performed *ab initio* wave function-based calculations upon the low-energy spin states of pairs of radicals (three singlets and one triplet). These electronic structure calculations were carried out by means of the Difference Dedicated CI (DDCI) method, which was described previously in the literature[26, 27] and has provided quantitative estimations of exchange coupling constant in molecular and extended systems.[14, 28]

2 Theoretical Details

The structure of the high-temperature phase of the TTTA compound is suggestive of a regular 1D spin $S = 1/2$ system, the properties of which are mostly governed by the nearest neighbour exchange coupling interaction. X-ray measurements of this crystalline phase reveal an interplanar distance of 3.47 Å and a slippage between neighbouring radicals of 1.32 Å (see Figure 1). A similar slippage amplitude of 1.28 Å is used for the hypothetical verdazyl-based materials to make contact with the experimentally reported TTTA system. Figure 2 shows a schematic representation of such verdazyl dimers.

The presence of two unpaired electrons in a dimer unit anticipates three low-lying singlets and one triplet spin states. The wave functions of these spin states offer useful information related to magnetic and transport properties that can be extracted by application of the effective Hamiltonian theory.[28] This method involves the projection of the lowest eigenstates onto the valence model space and allows for a rigorous quantification of the effective parameters t , U and K . Therefore, to bridge the gap between experimental solid-state observations and theoretical expectations,

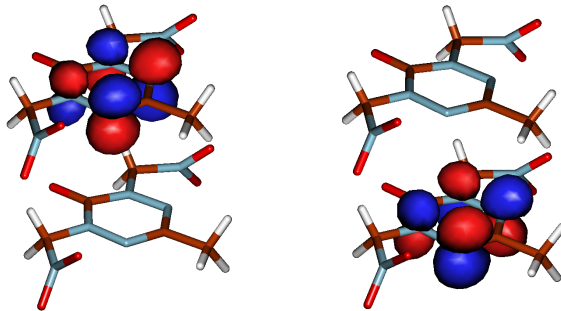


Figure 3: Graphical representation of the two MO that form the active space of the dinitro-verdazyl dimer IPa. The morphology of these two MO is analogue to the ones of the other verdazyl compounds considered in the present work and those of the TTTA.

complete active space self-consistent field (CASSCF)[29] calculations including 2 electrons in 2 molecular orbitals, namely CAS[2,2], were performed upon the dimers using the MOLCAS 7.2 package.[30] As expected for both TTTA and verdazyl-based systems, the magnetic orbitals are the in-phase and out-of-phase linear combinations of the SOMOs, which are shown in **Figure 3** for one of the verdazyl compounds. All our calculations were performed using the same basis set scheme. The carbon, nitrogen and oxygen atoms are described with DZP (14s9p4d)/[3s2p1d] basis sets of the ANO-RCC type.[31] The sulphur atoms of TTTA use a larger TZP (17s12p5d)/[5s4p2d] basis set. The hydrogen atoms hold a minimal (8s)/[1s] basis set.

2.1 Incorporation of the DRF model on TTTA

Most of the electronic correlation effects of the dimer unit and the polarization of its environment were treated on top of the zeroth-order CASSCF wave functions. While the latter corresponds to a long-range electrostatic phenomenon of the material, the former are related to short-range contributions of the dimer itself. Hence, the low-energy spectroscopy of a single dimer unit, that forms the quantum region or cluster, were determined (*i*) in the gas-phase, and (*ii*) in the presence of a polarizable environment consisting of 320 induced dipoles centred on the lattice positions and extending over $\sim 13 \text{ \AA}$ around the dimer. The electronic response effects on the extra-cluster region are simulated by means of the DRF method, as implemented in the DRF90 code.[32] This method offers a rigorous treatment of the electronic polarization of the embedding through the inclusion of a set of atomic polarizabilities in the lattice sites. We set the polarizabilities of the surrounding atoms to $\alpha_S = 2.904 \text{ \AA}^3$, $\alpha_N = 1.098 \text{ \AA}^3$ and $\alpha_C = 1.530 \text{ \AA}^3$ for sulphur, nitrogen and carbon, respectively.[33] The electronic density of the dimer unit at some given level of calculation and the DRF embedding are combined in the computational model self-consistently. Electronic correlation effects were subsequently incorporated using either a perturbational treatment (second-order perturbation theory, CASPT2)[34] as implemented in the MOLCAS 7.2 package,[30] or the variational Difference Dedicated CI (DDCI)[26] framework by using the CASDI code.[35] For the present study we mostly used the DDCI-1 and DDCI-3 levels of calculation (often referred in the literature as CAS+S and DDCI, respectively).

The theoretical description of both types of contributions (environment polarization and electronic correlation) has been already developed by integrating the DRF at the CASSCF level followed by a CASPT2 step.[24] We use exactly the same approach on the high-temperature phase of the TTTA compound to quantify the electric response of the environment to a given spin state. We performed the CASPT2 calculations with *no* imaginary shift factor and an IPEA value of 0.00 hartree.[36] This original choice of the zeroth order Hamiltonian has been shown to give more accurate results for magnetic coupling parameters than the modified Hamiltonian with an IPEA factor of 0.25 hartree. [37] All electrons but the core ones were correlated. However, the CASPT2 approach has a main drawback that arises from the contracted character of its wave function. The internally contracted reference of CASPT2 makes the relative importance of the configurations in the reference wave function to be uncorrected by the electron correlation treatment, which leads in general to a significant underestimation of the coupling. The DDCI method overcomes this limitation thanks to its decontracted character. Therefore, we also implemented a pure variational self-consistent treatment of the environment polarization by integrating the DRF model at the DDCI level.

Within the DDCI framework, the key and critical element is the definition of a common set of MOs to simultaneously describe singlet and triplet states. It is common practice to use average MOs of the CAS[2,2]SCF singlet and triplet states. However, other schemes have also been proposed, showing the sensitivity of the resulting J values to the set of MOs.[38] To suppress the arbitrariness of this choice, it is possible to apply the iterative DDCI (iDDCI- n) scheme introduced by García *et al.*[39] This procedure goes through the definition of the density matrices of the singlet and triplet states from the DDCI wave functions and builds the corresponding average density matrix. The latter is then diagonalized, producing a subsequent set of natural MOs. This scheme is iterated until convergence onto the singlet–triplet energy difference. We performed these iDDCI calculations on TTTA to stress the importance of improved MOs based on correlation effects as compared to some previous studies.[40]

The DRF method was incorporated self-consistently in the iDDCI calculations of TTTA spin states. State specific induced dipoles in the embedding were determined through DDCI-1 calculations for the singlet and triplet, separately. The resulting MOs and dipoles were used in a DDCI-3 calculation to calculate the magnetic coupling parameter in a polarized environment. Hence, in our implementation of DRF, the singlet–triplet energy difference value is not the result of a DDCI calculation using a single set of orbitals for both spin-states. It is known that the DDCI method is not meant to be applied in this fashion, but the aim of the present approach is to benefit from a variational treatment of electronic correlation in combination with DRF while keeping a bearable computational cost. The acronyms DDCI-1 and DDCI-3 for DRF calculations were maintained on purpose to mark the level of correlation of the calculations and make contact with the gas-phase results.

2.2 Nitro-addition on hypothetical verdazyl

The effect of the intramolecular electronic structure (*i.e.* short-range effects) was studied for a hypothetical series of NO₂ substituted verdazyl compounds. Our inspection of these dinitro-verdazyl systems was limited to the on-top packing, guided by recent theoretical studies.[14] Different orientations of the substituent groups can be anticipated, in particular in the presence of bulky substituents such as the NO₂ groups. Therefore, we investigated three conformations for the reference verdazyl radical and its NO₂ di-substituted analogue, which are depicted in **Figure 2**. One dimer with the NO₂ groups in out-of-plane positions with respect to the verdazyl ring (OP) and two other conformers that have the nitro groups following an in-plane orientation (IPa and IPb). The energies and wave functions of the four lowest spin states (*i.e.* three singlets and one triplet states) were calculated for each conformer using the DDCI procedure. The effective Hamiltonian theory[28] gives access to the ferromagnetic (K) and the antiferromagnetic ($-2t^2/U$) contributions to the total coupling. The understanding of their respective variations offers a strategy to ever increase the control over the magnetic behaviour of organic assemblies. Due to the large computational cost of the iDDCI calculations, the verdazyl-based systems were studied at the DDCI-3 level using averaged singlet and triplet CASSCF orbitals.

3 Results and Discussion

3.1 Long-range effects on TTTA

The effects of the bulk polarization were investigated on the high-temperature phase of the TTTA material using CASPT2 and various DDCI calculations with the DRF model. Table 1 summarizes our estimates of the exchange coupling constant J using the Heisenberg Hamiltonian formulation $\hat{H} = -2J\hat{S}_1 \cdot \hat{S}_2$. Let us remind that $2J$ is the singlet–triplet energy difference. The resulting J value at the CASPT2 level suggests that the environment polarization effects are rather limited and account for a 5 % change of the exchange coupling constant for this material. The largest induced dipoles in the environment have a value of 4×10^{-3} D. Therefore, the small response induced in the surroundings of the dimer confirms that such neutral organic radical material can be depicted as interacting $S = 1/2$ units, neglecting the polarizability of the environment. This result contrasts with conclusions drawn for inorganic materials, and more evidently for ionic crystals.

Table 1: Exchange coupling constant of the TTTA compound calculated in gas phase and with the DRF embedding.

Method	Gas Phase	DRF	
	J (cm ⁻¹)	J (cm ⁻¹)	Variation (%)
DDCI-3	-63		
iDDCI-1	-45	-51	-13.3
iDDCI-1(3) ^a		-95	3.1
iDDCI-3	-98		
CASPT2	-80	-84	-5.0

^a full DDCI-3 calculation using the iDDCI-1 MOs and including the DRF environment.

The response effects obtained at the iDDCI-1 level produce a change on J of 6 cm⁻¹, a slightly larger relative variation of 13.3 % as compared to the CASPT2 result. However, this larger effect is due to the shortcomings of the iDDCI-1 wave function, which only incorporates part of the electronic correlation and hence, underestimates the TTTA antiferromagnetic character. Compared to our CASPT2 result ($J = -80$ cm⁻¹), the situation is significantly better in the gas phase at the iDDCI-3 level ($J = -98$ cm⁻¹), obtaining a closer agreement with the experimental measurement by Fujita *et al.* ($J = -220$ cm⁻¹)[8] and the computational estimation by Clarke *et al.* ($J = -136$ cm⁻¹)[41]. Furthermore, once more electron correlation is incorporated variationally to the system with the polarizable environment by performing a full DDCI-3 calculation using the iDDCI-1 MOs with the DRF (iDDCI-1(3) in Table 1), the relative effect of the environment is reduced from 13.3 % down to 3.1 %. This observation is consistent with the CASPT2 calculations and confirms that the larger DRF variation observed at the iDDCI-1 level cannot be uniquely attributed to an environmental effect, because it can also be recovered by incorporating more electronic correlation. These results with DRF as well as the large variation observed in the gas phase between the DDCI-3 ($J = -63$ cm⁻¹) and iDDCI-3 ($J = -98$ cm⁻¹) confirm the tremendous importance of the MOs in the description of magnetic systems holding delocalized spin densities.[38, 42] Their flexibility as compared to mostly atomic-like d orbitals of paramagnetic ions is here clearly evidenced.

3.2 Short-range effects on verdazyl-based compounds

Dynamical correlation effects, such as instantaneous charge redistributions in the vicinity of the spin carrier, are known to potentially deeply modify the exchange coupling constants in dinuclear metal-ion based complexes and materials.[5, 28, 43] Similar effects can be induced in organic biradicals by properly substituting some side groups in the vicinity of the magnetic orbitals. However, it is not completely settled yet whether the magnetic coupling in these organic systems is governed by the same mechanisms as the well-studied inorganic compounds.[44–47] Therefore, we present here a model study that establishes how charge redistributions around the magnetic unit affect the electronic structure parameters of the biracial system. For this purpose, we calculate the exchange coupling constant at the DDCI-3 level for the proposed verdazyl-based systems (see Figure 2) Subsequently, the effective on-site repulsion integral (U), hopping integral (t) and direct exchange (K) are extracted using the effective Hamiltonian theory and the information available in the three low-lying singlets and one triplet wave functions.

The results for the three studied conformations of the non-substituted verdazyl compound (1,3,5-trimethyl-oxoverdazyl) are gathered in the top part of Table 2. The corresponding values for the NO₂ di-substituted analogues (1,5-di(nitromethyl)-3-methyl-oxoverdazyl) are reported in the bottom part of Table 2. The three conformations of the 1,3,5-trimethyl-oxoverdazyl compound differ by the rotation of the methyl groups. Thus, one can expect negligible changes of the magnetic behaviour or of any of the effective parameters under consideration. In fact, this is exactly what is observed for the three conformers. However, there is a small variation of the ferromagnetic character along the structures, more significantly on the IPb conformer, which stresses the inherent variability of the exchange coupling constant with respect to small structural changes on this kind of organic materials.

Table 2: DDCI-3 level values of the exchange coupling constant J , effective on-site repulsion integral U , hopping integral t and direct exchange K parameters for the verdazyl-based compounds (Figure 2).

1,3,5-trimethyl-oxoverdazyl			
	OP	IPa	IPb
J (cm ⁻¹)	19	20	23
U (cm ⁻¹)	30 696	30 657	30 342
t (cm ⁻¹)	55	54	64
K (cm ⁻¹)	18	18	20
1,5-di(nitromethyl)-3-methyl-oxoverdazyl			
	OP	IPa	IPb
J (cm ⁻¹)	18	15	25
U (cm ⁻¹)	30 575	×	×
t (cm ⁻¹)	895	×	×
K (cm ⁻¹)	68	×	×

Let us now concentrate on the OP conformer and the chemical modification induced by the presence of nitro groups in the vicinity of the spin density. The main idea behind this chemical change

is to increase t , maintaining U constant and to eventually enhance the antiferromagnetic contribution which is governed by the t^2/U ratio. The strong electron-withdrawing character of the nitro groups should favour the effective electron transfer between the two radical monomers, thus increasing $|t|$, while it should not cause any major change on the U value since the nitro groups are not directly bound to the verdazyl ring. The on-site repulsion U is indeed not affected by the chemical substitution (see Table 2) and remains *ca.* $30\,600\text{ cm}^{-1}$. In contrast, the $|t|$ value experiences a marked increase. The electron-attracting nitro groups produce a charge depletion in the nitrogen-rich part of the radical that facilitates the electron hopping. Therefore, the absolute value of the antiferromagnetic contribution to the exchange coupling is increased. On the other hand, the ferromagnetic K component increases in the presence of the NO_2 groups. Despite the noticeable modulations produced on the different parameters, the antiferromagnetic and ferromagnetic variations cancel out leaving a quasi constant J value. This indicates that the substitution of the verdazyl ring with NO_2 groups can increase the electron transport, which is guided by t , without destroying the magnetic properties of the system.

The two conformers with in-plane NO_2 groups, IPa and IPb, deserve particular attention. In this case, unique effective t , K and U parameters cannot be defined based on our simple model of the dimer. In fact, the dimers we worked with have no inversion centre (Figure 2), meaning different Coulomb potentials on the monomers and thus, specific effective parameters for each of them. This circumstance causes a large splitting in energy between the two ionic singlet states, which is schematically represented in Figure 4. The effect of the in-plane NO_2 groups compared to the out-of-plane case is large for the ionic states and enforces the non-equivalence of the two verdazyl monomers in the embedded dimer representation of the material. This splitting is also observed for the IPb conformer, even though its effect is smaller due to the weaker through-space interactions of the NO_2 groups. Nevertheless, in the crystalline environment all the radical units are equivalent in the lattice and this differentiation does not occur. Therefore, the model composed just by one biradical shows to be capable of describing properly each monomer as long as there are not strong inter-monomeric interactions along the radical chain. In contrast with the OP conformer, the biradical model becomes inappropriate for the conformers IPa and IPb, where the proximity of the electron-withdrawing groups affords for through-space transfers, which polarize the SOMOs and empower the non-equivalence between the two monomers.

We performed some exploratory calculations of the IPa nitro substituted compound with a larger model to confirm the dependence of the Coulomb potential difference with the system size. Two additional monomers were added to the dimer, enlarging the system to a tetramer of verdazyl radicals. The four monomers are stacked with an equal separation and slippage between all adjacent monomers, using the same values as in the model of the biradical. The two extreme monomers had one additional H atom added to their structure to obtain an artificial closed shell electronic configuration, which combined with the use of minimal basis sets resulted in a cheap basic representation of the immediate surroundings of the central dimer. CAS[2,2]SCF calculations were performed converging onto a set of active orbitals localized on the inner part of the tetramer, in analogy with the previous calculations done for dimer model (see Figure 3). The results show a significant reduction of the energy splitting between the ionic states, decreasing from $8 \times 10^3\text{ cm}^{-1}$ to $4 \times 10^3\text{ cm}^{-1}$. Thus, once highly polarizing interactions exist (*e.g.* by close NO_2 groups), it becomes imperative to explicitly include all the polar sources affecting the magnetic centres of interest. In the case of the verdazyl conformers with in-plane NO_2 groups, not only the nitro groups of the monomer itself have to be incorporated, but also the ones found on all of its first-neighbours

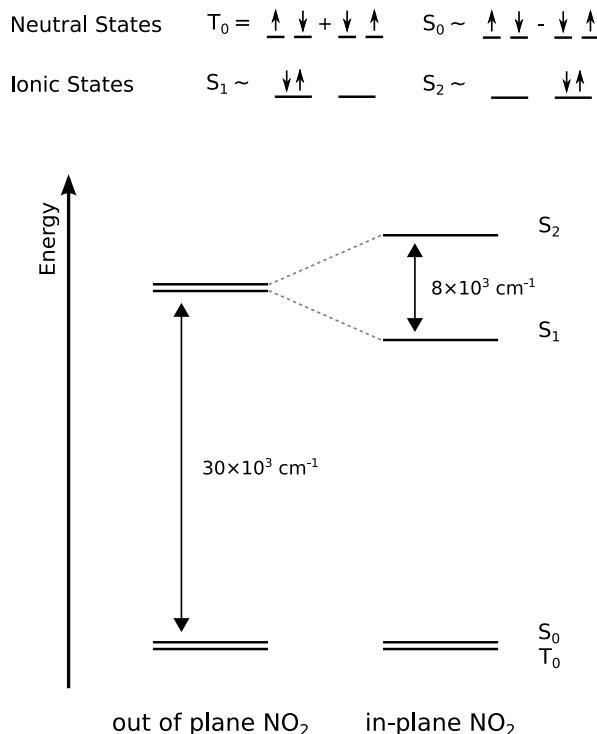


Figure 4: Schematic representation of the energy splitting between the high-lying singlet states for the IPa conformer compared to the OP conformer.

in the chain. Unfortunately, these effects propagate through the crystal, making their description by such small models rather difficult.

Nevertheless, the evaluation of the exchange coupling constant on the model including one dimer unit is still possible, as J can be calculated from the two low-lying neutral states. The values obtained at the DDCI-3 level with a minimal CAS[2,2] (Table 2) show that the exchange coupling constant is not significantly affected by the orientation of the NO_2 groups. Accordingly, based on the outcome of the nitro-addition on the OP structure, one could draw the conclusion that the effect of the nitro groups on the ferromagnetic and antiferromagnetic components also cancel out for the IPa and IPb conformers. However, studies performed on the Ullman’s biradicals showed the key role of spin-polarization for this type of materials.[47–50] Precisely, through analysis based on a valence-bond description of those biradicals, Angeli *et al.* concluded that the most appropriate picture of each radical site is attained by considering three strongly interacting electrons, rather than one unpaired electron.[51] All the interacting electrons must be treated equally by the reference Hamiltonian resulting from the CASSCF calculation, meaning that the formal SOMOs and the more polarizable lower-lying MOs should be all included into the active space. Thus, two verdazyl-localized π -type MOs and two non-bonding MOs, which account for the nitrogen lone pairs on the verdazyl ring, were added to the active space, resulting in a CAS[10,6].

Table 3 shows a comparison of the qualitative effect that the enlargement of the active space has on the J values obtained for the different verdazyl conformers. The CAS[2,2] results exhibit no change in the exchange coupling constant between the out-of-plane and the in-plane conformers, as previously observed for the DDCI-3 calculations. On the other hand, once the short-range interactions are included by enlarging the active space, the rotation of the NO_2 groups largely

Table 3: Effect of the size of the active space to the exchange coupling constants (cm^{-1}) of the out-of-plane (OP) and in-plane (IPa) verdazyl conformers after the nitro-addition calculated at the CASSCF level.

	OP	IPa
CASSCF	J (cm^{-1})	J (cm^{-1})
CAS[2,2]	3263	3112
CAS[10,6]	-38	314

affects the magnetic centre of the dimer. It even produces a dramatic change of its magnetic character, varying from anti-ferromagnetic, for the OP conformer, to ferromagnetic, for the IPa. Therefore, to reveal the sensibility of the unpaired electrons to their closer environment, it is necessary to work with more complex models that incorporate their short-range interactions. We expect the same qualitative behaviour from DDCI-3 calculations based on the CAS[10,6], as the shortcoming of the CAS[2,2] calculation is on its reference wave function and consistent results were obtained for the Ulmman’s biradicals with a bigger CAS.[51] Unfortunately, the size of the problem to be solved in our case is unmanageable at this time. The phenomenon which is here evidenced is reminiscent of the well-known ligand field splitting in transition metal complexes. Short-range contributions arising from the coordination sphere are likely to deeply modify the magnetic channels.

4 Conclusions

In this paper, we examined the respective roles of short- and long-range effects in the rationalization of magnetic properties of neutral organic radical-based materials. *Ab initio* calculations (DDCI and CASPT2) including the dynamical response of the environment (DRF) were carried out on dimer units of the reported high-temperature phase of the TTTA compound (Figure 1), and a series of hypothetical nitro-substituted verdazyl materials (Figure 2). The long-range effects on TTTA have been analysed by means of an original development that integrates the DDCI calculations and the DRF model self-consistently. Despite the intrinsic delocalized character of the spin densities, the polarization of the environment does not manifest itself, even at the best level of calculations. The gas-phase and embedded dimer cluster calculations differ by less than 5 % (Table 1). On the other hand, the iterative DDCI procedure (iDDCI) which takes into account the MOs relaxation when correlation effects are turned on produces a larger change in the J value, a reflection of the sensitivity of the delocalized spin densities to correlation effects. The importance of these short-range effects were finally estimated by the nitro-addition of hypothetical verdazyl-based dimers and by varying the conformation of the nitro position. Despite the absence of magnetic properties modifications, the t/U ratio which governs the conduction properties is significantly enhanced upon addition of the nitro group (Table 2). Furthermore, an unexpected sensitivity to the substituent positions is found (Figure 4 and Table 3), a result which questions again the relevance of a Heisenberg picture for such flexible materials. The through-space contribution arising from bulky and electro-active substituents such as the nitro groups cannot be eliminated. Thus, the standard 2 electron / 2 orbital description of the ferro- and antiferromagnetic contributions to the exchange coupling constant is possibly inappropriate for this kind of materials.

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