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Ab Initio Study of Ullman's Nitroxide Biradicals. Exchange Coupling versus Structural Characteristics Analysis

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The exchange coupling of Ullman's nitroxide biradicals, bis[2,2'-(1-oxy-3-oxido-4,4,5,5-tetramethyldihydro-1H-imidazolyl)] (1) and bis[2,2'-(1-oxy-4,4,5,5-tetramethyldihydro-1H-imidazolyl)] (2), has been determined by performing *ab initio* calculations followed by a specific configuration interaction on model compounds where the methyl groups have been substituted by hydrogen atoms, C1 and C2, respectively. The analysis of the dependence of the coupling on the conformation angle between each nitroxide moiety shows that even in the perpendicular structure the singlet state is found below the triplet. The calculated singlet–triplet gaps for the experimental value of the twist angle, -364 cm^{-1} for C1 and -175 cm^{-1} for C2, are in very good agreement with recent experimental results for 1 and 2.

1. Introduction

In recent years a wide program of characterization of the structure and magnetic properties of compounds containing coupled paramagnetic metal ions and stable organic radicals such as nitroxides^{1–4} has been developed. Many different coupling mechanisms have been observed, ranging from strong antiferromagnetic⁵ to ferromagnetic.^{3,6}

Among the nitroxides, the nitronyl and iminonitroxides^{7,8} exhibit interesting properties in relation to their delocalized structure and have been extensively used to design high-spin molecular-based species. In this respect, dinitroxides have not received much attention because intramolecular interactions are generally antiferromagnetic,⁹ leading to complexes having a low-multiplicity ground state. Nevertheless they provide interesting samples of medium-size biradicals which can be investigated with sophisticated *ab initio* methods, in order to get deeper information on the exchange coupling mechanism.

Very recently¹⁰ a thorough comparative study of the structural and magnetic properties of bis(nitronyl) and bis(imino) nitroxides, i.e. bis[2,2'-(1-oxy-3-oxido-4,4,5,5-tetramethyldihydro-1H-imidazolyl)] (compound 1) and bis[2,2'-(1-oxy-4,4,5,5-tetramethyldihydro-1H-imidazolyl)] (compound 2), respectively, first synthesized by Ullman et al.,¹¹ has been reported. A singlet ground state was found for both compounds in solution and in the solid state. The singlet–triplet (S–T) gaps were found at -311 and -194 cm^{-1} in bis(nitronyl) and bis(imino) nitroxides, respectively. Furthermore, in each molecule the two π -systems are not coplanar but present almost equal deviation angles ($\alpha = 55^\circ$ for 1, $\alpha = 54^\circ$ for 2).

The aim of the present work is to get a deeper insight on the influence of conformational and/or structural parameters on the sign and magnitude of their magnetic properties by performing *ab initio* calculations. The singlet–triplet energy differences in these exchange magnetic coupling problems are so small that a quantitative evaluation of the gaps is a real challenge that two independent determinations of the energy can not overcome, since the error on each state is of a higher order of magnitude, and specific methods are needed. We have recently proposed

a general strategy for the calculation of energy differences,¹² specially suited for biradical S–T gaps, as shown in dihalide-bridged dinuclear copper complexes.¹³ After a recall of the method, we report the study of the influence of the conformational angle on the exchange coupling on Ullman's nitroxide biradicals.

2. Method of Evaluation of the Singlet–Triplet Gap

Small organic biradicals have been the subject of many theoretical works¹⁴ performed with *ab initio* methods including a high level of correlation. The impossibility of treating systems with a great number of electrons such as metal complexes at the same level of accuracy has led to the development of specific methods for the study of the magnetic behavior of polynuclear metal compounds with unpaired electrons. Early works^{15,16} presented semiquantitative approaches to this problem through a MO analysis, leading to an interpretation of the singlet–triplet energy difference in terms of the HOMO–LUMO separation or of the overlap between magnetic orbitals. Although successful qualitative predictions have been made from those methods, nonempirical calculations including the effects of electron correlation are necessary in order to reach reliable estimations.

Among the methods leading to quantitative estimates of these energy gaps, Noodleman¹⁷ has developed a formalism in the unrestricted Hartree–Fock context where the exchange coupling constant is evaluated through the energy difference between the highest spin multiplet and the broken symmetry state. This model has been applied to polynuclear sulfur-bridged iron complexes¹⁸ or to dinuclear copper complexes.¹⁹

On the other hand, *ab initio* direct calculations based on a perturbative development up to second order of the configuration interaction (CI) problem have been proposed some years ago²⁰ and applied to different copper dimers.²¹ This method, based on Anderson's²² formalism, explicitly considers the main physical contributions to the S–T energy difference from the magnetic centers and the ligands or the substituents, without important computational effort. Although in general good agreement with experience is found, some important effects are neglected due to the truncation of the perturbation expansion at second order. On the basis of the same theory of effective

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Hamiltonians and following an earlier suggestion of Broer and Maaskant,²³ we have recently proposed a variational procedure that allows us to overcome these difficulties and gives quite good agreement with experimental results in $[\text{Cu}_2\text{X}_6]^{2-}$,¹³ which can be considered a special case of a more general proposal.¹² The generalization of this method to magnetic interactions in polynuclear systems has shown good agreement with full configuration interaction (FCI) calculation in model Li clusters.²⁴ The procedure will now be briefly recalled.

Biradicals can be considered as a particular case of the more general problem involving two electrons in two active molecular orbitals. With $S_z = 0$, the complete active space (CAS) is defined by four determinants, generating four states. If φ and φ^* are the active MOs, the three singlet and triplet states can be expressed at the zeroth order:

$$|^1\psi_1^0\rangle = \lambda|\dots p\bar{p}\dots\varphi\bar{\varphi}\rangle - \mu|\dots p\bar{p}\dots\varphi^*\bar{\varphi}^*\rangle$$

$$|^1\psi_2^0\rangle = \mu|\dots p\bar{p}\dots\varphi\bar{\varphi}\rangle + \lambda|\dots p\bar{p}\dots\varphi^*\bar{\varphi}^*\rangle$$

$$|^1\psi_3^0\rangle = 2^{-1/2}[|\dots p\bar{p}\dots\varphi\bar{\varphi}^*\rangle + |\dots p\bar{p}\dots\varphi^*\bar{\varphi}\rangle]$$

$$|^3\psi^0\rangle = 2^{-1/2}[|\dots p\bar{p}\dots\varphi\bar{\varphi}^*\rangle - |\dots p\bar{p}\dots\varphi^*\bar{\varphi}\rangle]$$

In a weakly interacting system with two unpaired electrons, the MOs φ and φ^* are nearly degenerate and the weights of the ground state, λ , and the diexcited state, μ , are almost equal. Two localized magnetic orbitals can be obtained from a simple rotation of φ and φ^* . If the molecule is a dimer, two 'magnetic' orbitals, each one almost localized in each monomeric unit, can be defined by performing a simple $\pi/4$ rotation:

$$a, b = 2^{-1/2}(\varphi \pm \varphi^*)$$

giving two states $|^1\psi^0\rangle$ and $|^3\psi^0\rangle$ essentially described through neutral forms in the valence bond framework, since the weight of the ionic contributions is small

$$|^1\psi_1^0\rangle \cong |^1\psi^0\rangle = 2^{-1/2}[|\dots p\bar{p}\dots a\bar{b}\rangle + |\dots p\bar{p}\dots b\bar{a}\rangle] = 2^{-1/2}[|\Phi_1\rangle + |\Phi_2\rangle]$$

$$|^3\psi^0\rangle = 2^{-1/2}[|\dots p\bar{p}\dots a\bar{b}\rangle - |\dots p\bar{p}\dots b\bar{a}\rangle] = 2^{-1/2}[|\Phi_1\rangle - |\Phi_2\rangle]$$

whereas the remaining singlet states have essentially ionic character

$$|^1\psi_2^0\rangle \cong 2^{-1/2}[|\dots p\bar{p}\dots a\bar{a}\rangle + |\dots p\bar{p}\dots b\bar{b}\rangle]$$

$$|^1\psi_3^0\rangle = 2^{-1/2}[|\dots p\bar{p}\dots a\bar{a}\rangle - |\dots p\bar{p}\dots b\bar{b}\rangle]$$

The two neutral degenerate determinants $|\Phi_1\rangle = |\dots p\bar{p}\dots a\bar{b}\rangle$ and $|\Phi_2\rangle = |\dots p\bar{p}\dots b\bar{a}\rangle$ generate a model space S , and by using the many-body perturbation theory, a 2×2 effective Hamiltonian may be built on that model space. Up to second order, the elements of this effective Hamiltonian may be written

$$\langle\Phi_i|H^{\text{eff}(2)}|\Phi_j\rangle = \langle\Phi_i|H|\Phi_j\rangle + \sum_{\Phi_\alpha \notin S} \frac{\langle\Phi_i|H|\Phi_\alpha\rangle\langle\Phi_\alpha|H|\Phi_j\rangle}{E_j^0 - E_\alpha^0}$$

where $|\Phi_i\rangle$ and $|\Phi_j\rangle$ are $|\Phi_1\rangle$ or $|\Phi_2\rangle$ and $|\Phi_\alpha\rangle$ are all the determinants interacting with them. Since $|\Phi_1\rangle$ and $|\Phi_2\rangle$ are

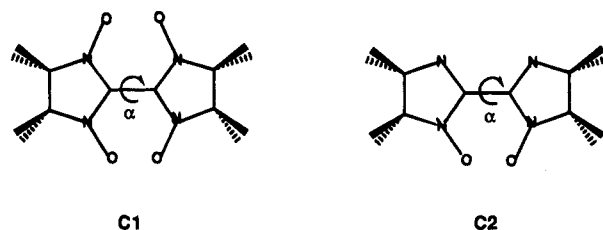


Figure 1. Molecular structures of C1 and C2.

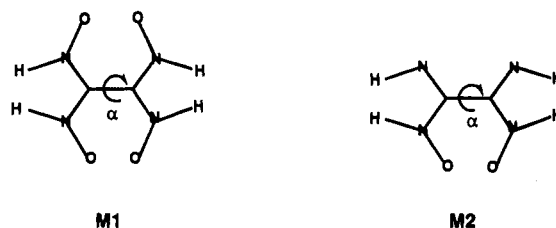


Figure 2. Structure of M1 and M2.

degenerate, only the extradiagonal matrix element $\langle\Phi_1|H^{\text{eff}(2)}|\Phi_2\rangle$ introduces differences between the two roots of $H^{\text{eff}(2)}$. The determinants not belonging to the model space are easily generated,²⁰ and this subspace may be summarized in a list which has as well a transcription through the original delocalized MOs.¹³ By taking a generator as the vacuum state, this list consists in single or double substitutions with only one or two inactive orbitals as holes or particles

$$| \rangle = |\Phi_i \in \text{CAS}\rangle$$

single substitutions $p \rightarrow i$

double substitutions $\varphi^2 \rightarrow ij$

$pq \rightarrow \varphi^{*2}$

$\varphi p \rightarrow \varphi^* i$

where p and q labels are used for holes (including φ) and i and j labels are used for particles (including φ^*).

The list may split into two lists, if the irreducible representations (IRs) of the singlet and the triplet are not the same.¹³ It must be pointed out that the size of the CI space is small, since it grows only as the square of the MO set dimension.

The next step of the procedure consists in performing a diagonalization of this subspace of single and double excitations to obtain the S-T gap as the difference between the first two roots of this variational CI if both states belong to the same IR or the difference between the first eigenvalue of the diagonalization of the subspace belonging to each IR.

3. Results

3.1. Computational Details. Both Ullman's nitroxide biradicals have been modeled by substituting methyl groups by hydrogen atoms and keeping the experimental distances and angles given in ref 10. Thereafter, we will refer to these models as C1 and C2, for compounds 1 and 2, respectively (Figure 1). In order to analyze the effect of external substituents on the magnetic interaction, two simpler models have also been used in the calculations where the methylenic groups have been replaced by hydrogen atoms, referenced as M1 and M2, respectively (Figure 2).

Two different basis sets have been used in the calculations. The first basis set is a valence double- ζ (DZ) basis for all atoms.

TABLE 1: Size of the Differential CI Spaces (Number of Determinants) in the DZ and DZP Basis Sets for Singlet and Triplet States in Models M1, M2, C1, and C2

basis set	M1		C1		M2	C2
	¹ A ₁	³ A ₂	¹ A ₁	³ A ₂	^{1,3} A	^{1,3} A
DZ	5 124	5 122	10 678	10 674	12 971	31 175
DZP	10 646	10 644	21 568	21 564	31 903	

The second one is a valence double- ζ plus polarization (DZP) basis set, obtained by adding one polarization function to the precedent one for second-row atoms as well as for hydrogen, with exponents $\zeta_{3d} = 0.85$ for carbon and nitrogen and $\zeta_{2p} = 0.8$ for hydrogen. Core potentials have been used for second-row atoms.²⁵

All the CI calculations have been performed from the molecular orbitals of an open shell RHF (OSRHF) calculation of the triplet state.²⁶ In order to show the independence of the result on the MO set, a Nesbet²⁷ calculation has also been carried out for C1 with the DZP basis set.

For compound **1**, an evaluation of the influence of the twist angle α between the π -systems of both cycles on the S–T gap has been performed by using the DZ basis set on both M1 and C1 and the DZP basis set on M1. Several values have been considered for α : 0, 25, 55, 75, and 90°. A single calculation with DZP basis set has been performed on model C1 with the experimental value of the twist angle $\alpha = 55^\circ$.

For compound **2**, the influence of the twist angle has also been considered on M2 with DZ and DZP basis sets, with $\alpha = 0, 40, 55, 70, 90, 125$, and 180°. A single calculation with the experimental value of α has been carried out on C2 with the DZ basis set. The lack of symmetry in compound **2** avoids the calculation with the DZP basis in this molecule, since the size of the memory required for the molecular integrals in the IC program is about 400 Mb.

The symmetry point groups of C1 and C2 are D_2 and C_1 , respectively. In C1, the singlet state ¹A₁ and the triplet state ³A₂ belong to different IRs and the list of determinants splits into two lists, one for each symmetry, while in C2 there is only one list, since both states belong to the A IR. The CI spaces for M1 and M2 present the same characteristics. The sizes of the different CI spaces are collected in Table 1.

3.2. Bis(nitronyl) Nitroxide. Figure 3 shows the variation of the S–T gap in front of the α angle for C1 with the DZ basis set and for the model M1 with both DZ and DZP basis sets. As expected, all the calculations show that the singlet state is considerably stabilized in the planar structure. As discussed in the experimental work of Alies et al.,¹⁰ the conjugation of the π -systems in this structure would enhance the antiferromagnetic behavior, while their orthogonality would maximize ferromagnetic character.

Nevertheless, even in the perpendicular structure the singlet is found below the triplet as yet observed for the twisted ethylene.²⁸ It must be noticed the strong similarity between the two cases, i.e. the twisted ethylene and the bisnitroxides in their perpendicular conformations: in each nitroxide moiety, the singly occupied orbital is of π^* symmetry, leading to a very small SCF exchange integral between the two singly occupied orbitals. In such a case, as discussed previously,^{28b} rather small spin polarization effects can give rise to a violation of Hund's rule. Furthermore, a large negative spin density has been found at the bridge carbon atom in the nitronyl nitroxide monoradical.²⁹

Another interesting point which emerges from the results reported in Figure 3 is that the influence of the substituents external to the region of the interaction between the radical

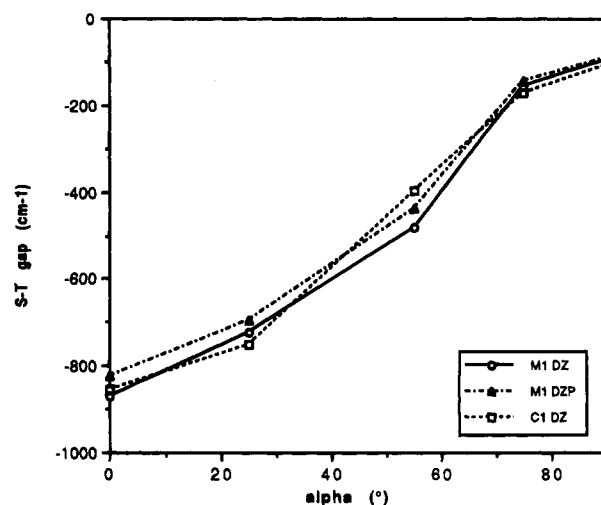


Figure 3. Dependence of the singlet–triplet gap on the conformational angle α in the bis(nitronyl) nitroxide C1 and the model compound M1, in the DZ and DZP basis sets. The S–T gap (in cm^{-1}) is calculated as the singlet energy minus the triplet energy.

fragments, i.e. the methylene groups of each monomer, is not significant in the magnitude of the S–T gap and in its behavior in front of the α angle, since the qualitative behavior of M1 and C1 is quite comparable. A similar effect was already pointed out in binuclear copper dimers.^{13b} For the experimental value of the angle, the S–T gaps calculated in either M1 or C1 are in good qualitative agreement with the reported experimental value of -311 cm^{-1} , since the calculated values range from -482 to -398 cm^{-1} .

The inclusion of polarization in the atomic basis set systematically lowers the S–T difference and decreases the antiferromagnetic character. This effect in M1 is smaller than 10% for the different values of the twist angle, and for the experimental value $\alpha = 55^\circ$ the difference between the calculated S–T gap for M1 in both basis sets is around 40 cm^{-1} . In C1, due to the size of the molecular set when including polarization, 198 MOs requiring 200 Mb of RAM memory in the CI calculation, only the experimental α angle has been considered with the DZP basis set. The calculated gap for model C1 with this basis set is -365 cm^{-1} , in quite good agreement with the value reported in the experimental work,¹⁰ evaluated from a Heisenberg Hamiltonian. The trend previously observed in model M1 when including polarization in the atomic basis set is also found here, since the gap decreases about 30 cm^{-1} .

In order to test the influence on the results of the set of MOs used to build the CI space, the last calculation on C1 has also been performed starting from a Nesbet half electron calculation. The result, -364 cm^{-1} , confirms that the gap is in practice independent of the choice of the MOs, as was already pointed out.¹²

3.3. Bis(imino) Nitroxide. In the structure determination of compound **2**, it was found¹⁰ that one of the two independent molecules in the symmetric unit exhibited statistical disorder involving the oxygen atom of the NO groups, suggesting that an appropriate model should be that of half-occupancy of oxygen atoms, leading to an averaged determination of the structure reflected in short NO bond distances. The geometrical parameters considered in the present work are those corresponding to the unit not affected by the disorder.

The decrease of the symmetry in compound **2** has limited the analysis of the influence of the twist between π -systems on the S–T gap to the model M2. In this case, for $\alpha = 0$ and $\alpha = 180^\circ$, both conformers are not equivalent, the first one corresponding to a *cis* position of the NO groups, and the second

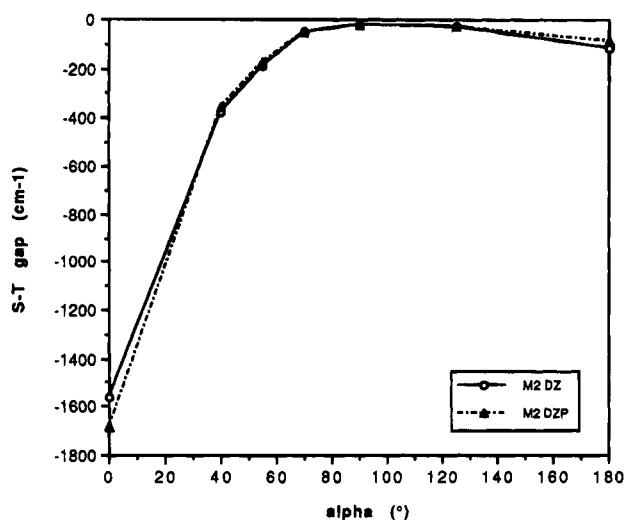


Figure 4. Dependence of the singlet-triplet gap on the conformational angle α in the model compound **M2** for the bis(imino) nitroxide **C2**, in the DZ and DZP basis sets. The S-T gap (in cm^{-1}) is calculated as the singlet energy minus the triplet energy.

one to a *trans* position. The results are shown in Figure 4. As in **M1**, the strongest antiferromagnetic character corresponds to planar structures, although in this case the different distance between magnetic groups, almost concentrated in the oxygen atoms, leads to different through-space interactions. The S-T gap is much smaller in the *trans* conformer. The smallest magnitude of the S-T separation happens as expected for $\alpha = 90^\circ$. As in **M1** and **C1**, the inclusion of polarization functions in the basis set slightly decreases the S-T gap, although in this case the influence is quite small. For the experimental twist angle, $\alpha = 55^\circ$, the calculated gap is -188 cm^{-1} with the DZ basis set and -175 cm^{-1} with the DZP basis set, in very good agreement with the experimental value, -194 cm^{-1} .

For **C2**, a DZ calculation has been performed on the experimental geometry with $\alpha = 55^\circ$. The calculated gap is -209 cm^{-1} , in quite good agreement with experience. As in the first molecule, the influence of the external substituents is not strongly significant on the magnitude of the gap, with a difference of only 20 cm^{-1} . The calculation with the DZP basis set was not possible with our present memory and disk capabilities, but with the trend shown in **M1**, **M2**, and **C1**, a value very close to the experimental gap may be expected.

4. Conclusions

The present work shows that, even in the perpendicular structure, the Ullman's nitroxide biradicals exhibit a singlet ground state, as already observed in the twisted ethylene. The violation of Hund's rule can be explained by the dynamical spin polarization of the σ -system under the exchange field of the two unpaired electrons.²⁸

As already observed in previous exchange coupling calculations,^{13b} the role of the substituents external to the spin interaction region is not crucial for the magnitude of the gap.

The specific CI used in the present work, based on the theory of effective Hamiltonians and including all the second-order differential effects, allows the accurate and inexpensive determination of the small energy differences involved in the exchange coupling. The calculated S-T gaps in the Ullman's nitroxides are in very good agreement with the experimental results.

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