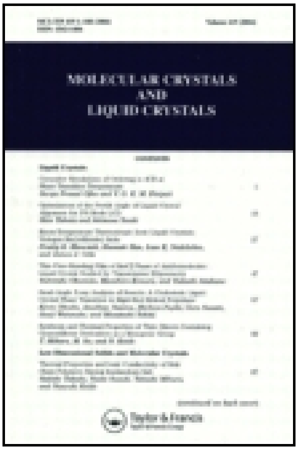

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Does the McConnell-I Model Really Work? An ab Initio Study of the Magnetic Character of Some Intermolecular Contacts

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Does the McConnell-I Model Really Work? An ab Initio Study of the Magnetic Character of Some Intermolecular Contacts

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The performance of the first model proposed by McConnell to rationalize the nature of the magnetic interactions in purely organic molecular crystals (the McConnell-I model) has been analyzed using ab initio methods. As a first step, we analyzed the form of deriving the basic formula of the McConnell-I model from a general Heisenberg spin Hamiltonian. We reached the conclusion that it is not possible in general, although the two show some resemblance. When the same procedure is applied to the well known example of the [2.2]paracyclophanes, we found that the agreement with the experiment comes from the fortuitous cancellation of terms which is not likely to hold in general. We then studied the high-low spin energy difference for the H_2NO dimer and the methyl-allyl radicals for different relative orientations of the two monomers using CASSCF calculations and the 6–31G(d) basis set. It is found that there are regions in which McConnell-I model does not reproduce the ab initio results. So, we can conclude that the McConnell-I does not work in general.

Keywords: molecular magnetism; McConnell-I model; ferromagnetism; ab initio computations

INTRODUCTION

Experimentally, the presence of magnetism in a molecular crystal and its dimensionality depends on the way the crystal packs, that is, on the distance and relative spatial orientation of the molecules which constitute the crystal.[1] The rationalization of this dependence is a key step towards the controlled obtention of better molecular magnets, that is, towards the design of molecular magnets. The other needed ingredient is to know how to control the packing of the molecular radicals within the crystal.

The most widely used tool to rationalize the presence of magnetism in purely organic crystals is the McConnell-I model,[2a] so called because is the first of the two models[2b] proposed by the same author. This McConnell-I model is a qualitative model based on a Heisenberg spin Hamiltonian and predicts the presence of intermolecular ferromagnetic interactions only when the crystal presents short intermolecular contacts between atoms bearing considerable spin population of opposite sign.[2a] Accordingly, the magnetic behavior of a molecular crystal can be rationalized by computing the atomic spin population on the atoms of the radicals, a property available from experimental[3] or computational[4] studies.

In spite that the validity of the McConnell-I model has never been demonstrated in a rigorous way, that validity has been generally accepted based on two types of evidence: a) the observed relative stability of the singlet/quintet states in the pseudo-ortho, pseudo-meta, and pseudo-para [2.2]paracyclophanes,[5] which follows the McConnell-I predictions, and b) the results from ab initio computations on simple model systems.[6] However, some experimental magneto-structural relationships are difficult to explain by a straightforward application of the McConnell-I model, raising doubts on its validity and range of applicability. This has prompted us to start a systematic study on the validity of the McConnell-I model, trying to answer to the following question: does it really work?.

ANALYTICAL APPROACH

To find an answer to the previous question we first carried out an statistical analysis of the crystal packing of 47 α-nitronyl nitroxides (α-NN) crystals presenting dominant ferro and antiferromagnetic interactions (characterized by looking at their χT vs. T plots in the 273-4 K range).[7] According to the McConnell-I model, short NO···ON contacts in the plane for N-O···O angles in the +90 to -90° range are associated to strong antiferromagnetic interactions, because these groups localize a large part of the positive atomic spin population. Therefore, these class of contacts should be only present within the crystals presenting dominant antiferromagnetic interactions. This is not what our statistical analysis[7] showed: one can find short NO···ON contacts of the previous type within the ferromagnetic and antiferromagnetic subsets with similar probability. In fact, the distribution in the space of the NO···ON contacts is nearly identical for the ferro and antiferromagnetic subsets of crystals. This is not a proof that the McConnell-I model is failing, as there are more groups in each molecule capable of magnetic interactions, and the magnetic character is the consequence of the combined set of interactions. However, the previous result clearly indicates that many structure-magnetism relationships done up to now have no statistical support: the simplified use of the McConnell-I model just looking at the NO···ON contacts is not a valid procedure. Similar conclusions are reached when the C-H···ON contacts are analyzed.[7b]

In a step forward, we studied the analytical derivation of the McConnell-I basic formula in the context of the Heisenberg spin theory.[8] The McConnell-I model is based on the application of the following spin Hamiltonian:

$$\hat{H}^{AB} = -\hat{\mathbf{S}}^{A} \cdot \hat{\mathbf{S}}^{B} \sum_{i\in A, j\in B} J_{ij}^{AB} \rho_i^A \rho_j^B \qquad (1)$$

in which J_{ij}^{AB} are two-centre exchange integrals, and ρ_i^A, ρ_j^B are spin densities on atoms i, j of fragments A and B. The $\hat{S}^A, \hat{S}^B$ are the total spin operators for fragments A, B. The previous expression is an approximation of the general expression of a Heisenberg spin Hamiltonian, whose formula is

$$\hat{H}^S = Q - \sum_{i,j} J_{ij}\left(2\hat{S}_i \cdot \hat{S}_j + \tfrac{1}{2}\hat{I}_{ij}\right) \tag{2}$$

in which Q is just a Coulomb shift (which is taken in many cases as zero) and $\hat{I}_{ij}$ the identity spin operator (in some cases not included). A first comparison of the properties of these two Hamiltonians can be done by looking at the energy difference between the triplet and singlet states generated from the interaction of two doublet fragments (it can be done for any high and low spin states generated from any spin fragments with the same results). In the exact Heisenberg case, the expression for the energy difference between the singlet and the triplet states is:

$$E^S - E^T = \sum_{i,j} J_{ij} \Delta P_{ij} \tag{3}$$

where the ΔP_{ij} is defined as

$$\Delta P_{ij} = P_{ij}^S - P_{ij}^T \tag{4}$$

being J_{ij} the exchange integrals, and P_{ij}^S and P_{ij}^T the singlet and triplet exchange density matrices obtained from singlet and triplet eigenvectors using any ab initio method. Using the McConnell-I Hamiltonian, the same energy difference is

$$E^S - E^T = \sum_{i \in A, j \in B} J_{ij}^{AB} \rho_i^A \rho_j^B \tag{5}$$

being ρ_i^A and ρ_i^B the atomic spin populations in the atoms i and j of centers A and B, respectively. Comparing equations (3) and (5), it is clear that the McConnell-I model is valid only if we make the association

$$\Delta P_{ij} \Leftrightarrow \rho_i^A \rho_j^B \quad (6)$$

However, there is no theoretical justification for this. Clearly $\rho_i^A \rho_j^B$ is the product of the difference of spin densities evaluated from a two doublet fragment, while ΔP_{ij} is the difference of singlet and triplet two-particle density matrices evaluated from two different supermolecule computations (one for the triplet and one for the singlet), that is, they are mathematically two type of objects. *There is no obvious reason why these two quantities should be related each other than heuristically.*

We have done a strict quantitative test of the Heisenberg and McConnell-I Hamiltonians computing the quintet-singlet energy difference for the ortho-, meta- and para- [2.2]paracyclophanes. What we found in this case is that the McConnell-I model works because of fortuitous cancellations: the agreement arises because the signs of $\rho_i^A \rho_j^B$ and ΔP_{ij} are the same and many J_{ij} are zero. However, many of the J_{ij} are zero because the perfect alignment of the C atoms in the [2.2]paracyclophanes, a fact that is not generally applicable to other systems. *Therefore, there is no reason to expect this situation to hold in general, that is, we have shown that there is no general reason for the McConnell-I model to work*.

AB INITIO COMPUTATIONS OF SOME SIMPLE SYSTEMS

To further test the validity of the McConnell-I model we studied the high spin-low spin energy difference for various orientations of two simple dimers, the H_2NO dimer and the methyl-allyl system. The first one was selected because it is a simple prototype for the study of the magnetic interactions between two nitronyl groups. Therefore, the conclusions obtained in this study are of interest to understand the magnetic interactions in the α-nitronyl nitroxide crystals. The second dimer, was selected because is one of the model systems taken previously to proof the validity of the McConnell-I model.[6]

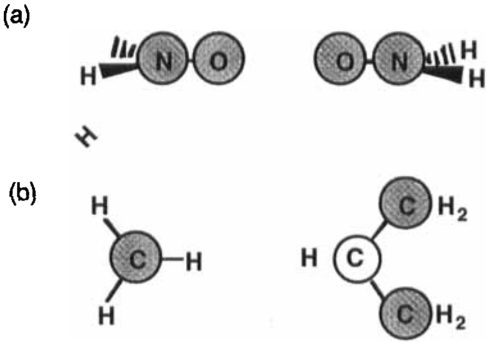

FIGURE 1. Spin densities for the isolated fragments of (a) the H_2NO dimer, and (b) the methyl and allyl radicals (shaded atoms: positive spin density, unshaded atoms: negative)

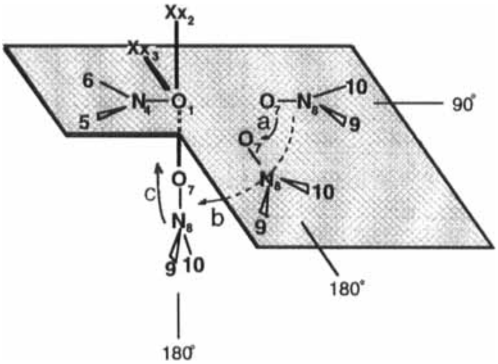

FIGURE 2. Scans carried out with the H_2NO dimer. The two extreme configurations are marked as 90 and 180 degrees.

Ab initio computations at the CASSCF and other levels with very extended basis sets (the smallest one was a 6-31+G(d) basis) give for the isolated fragments the spin distribution shown in Figure 1 (in a diagrammatic qualitative form).

We evaluated the singlet-triplet energy difference of the H_2NO dimer along the two directions of the space indicated in Figure 2: one scan is done keeping all the atoms in the same plane (the shaded plane of Figure 2); the second scan is in the C_s plane of the fixed fragment (the left one in Figure 2) perpendicular to the shaded plane. In both cases the shortest contact is the O···O distance, kept frozen at 3Å for this study. We selected these geometrical arrangements because they are characteristic of many NO···ON orientations found in some α-nitronyl nitroxide crystals. According to the McConnell-I model, in all the points of the scans one overlaps atoms bearing atomic spin density of the same sign. Therefore, such model predicts that the most stable spin state should be always the singlet (the antiferromagnetic one).

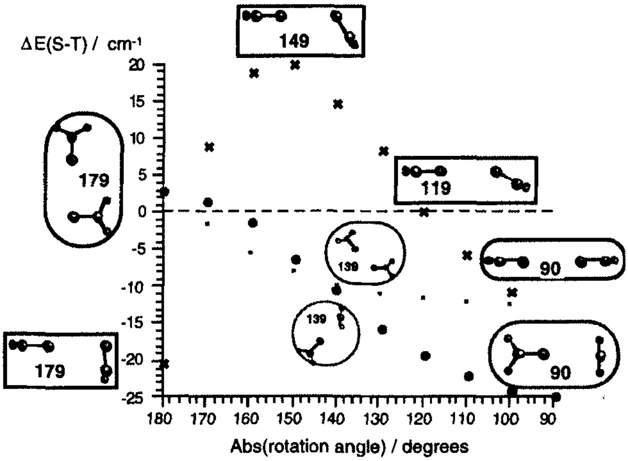

FIGURE 3. Variation of the singlet-triplet energy difference in the two scans performed on the H_2NO dimer (see text).

We computed the singlet triplet energy difference using the CASSCF method and the 6-31+G(d) basis set. The CAS space was a small (2,2) composed of two orbitals and two electrons (the two unpaired electrons of the two fragments and the π orbitals in which they are located). The singlet-triplet energy difference obtained in these computations is shown in Figure 3, along with the angle and geometrical conformation of the dimers in some points of the curve. The scan within the shaded plane is always antiferromagnetic (the ground state is the singlet), in good agreement with the McConnell-I predictions. However, this is not the case for the scan along the plane perpendicular to the shaded one. Here *one finds a region in which the dimer behaves ferromagnetically, against the McConnell-I predictions* (the angles in the range from around 119° to 175°).

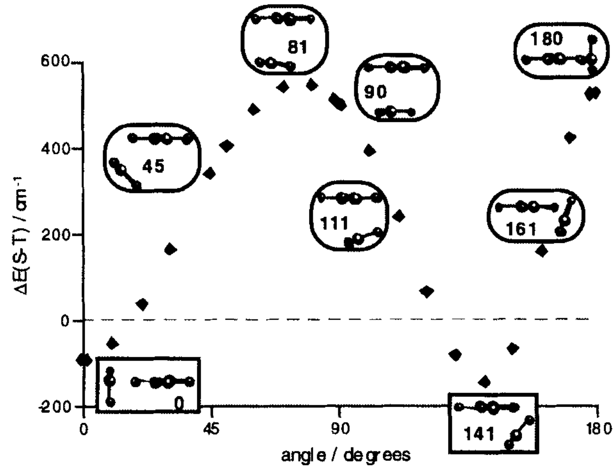

FIGURE 4. Variation of the singlet-triplet energy difference with the H-C_{allyl}···C_{methyl} angle for the methyl-allyl dimer (see text).

To test if the failure of the McConnell-I model predictions was just a exceptional behavior in the H_2NO dimer, we carried out a similar study on the methyl-allyl dimer. In this system we evaluated the singlet-triplet energy difference as the carbon methyl (C_{methyl}) rotates around the central C atom of the allyl (C_{allyl}) fragment, forcing the C_{methyl} to lye in the C_s plane perpendicular to the C-C-C plane of the allyl (see Figure 4 for some snapshots). The angle of the variation is the H-C_{allyl}...C_{methyl} angle. At 0° C_{methyl} is in the C-C-C plane of the allyl, and sitting on the H end of the C_{2v} axis which passes through the central allyl carbon and the H atom attached to it. At 90° the methyl and allyl are in parallel planes, with the C_{methyl} atom on top of the C_{allyl} carbon. At 180° C_{methyl} is in the C-C-C allyl plane, sitting on the C_{2v} axis, but on the C end of this axis. The $C_{allyl}...C_{methyl}$ distance was kept fixed at 3Å. All computations were carried out using the CASSCF method and the 6.31G(d) basis set. The CAS space was a (4,4), which includes all the π orbitals and electrons of the isolated methyl and allyl fragments in the active space.

According to the McConnell-I model the ferromagnetic state (the triplet) should be the ground state when $H\text{-}C_{allyl}\cdots C_{methyl} = 90°$, in good agreement with what say the ab initio results. However, the state stability should not change for small variations of the $H\text{-}C_{allyl}\cdots C_{methyl}$ angle when the distance is kept constant. Figure 4 says that this is not the case: as the angle goes to 180° the singlet becomes more stable, being the most stable state around 141°. Therefore, once more the McConnell-I model fails to explain the magnetic character in some regions of the potential energy surface.

One can argue that the regions in which the McConnell-I model has failed are out of the original proposal of McConnell, who designed its model for π-π interactions. However, as we saw before,[8] its apparent success in the π-π case comes from a fortuitous cancellation of terms associated to the high symmetry of the problem, a situation that will not hold in general. We have found enough reasons here as to stop thinking that the McConnell-I model is a good and general procedure to carry out the analysis of the magnetic properties of a molecular crystal.

Acknowledgments

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