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Studies of implanted muons in organic radicals

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Abstract. We have performed semi-empirical molecular dynamics calculations of the electronic and molecular structure of muonium ($=\mu^+e^-$) incorporated into the organic radicals 3-quinoyl nitronyl nitroxide (3-QNNN), para-pyridyl nitronyl nitroxide (p-PYNN), phenyl nitronyl nitroxide (PNN) and para-nitrophenyl nitronyl nitroxide (p-NPNN). These materials are of interest because they show ferromagnetic order at very low temperatures and can be effectively studied using implanted positive muons. Our calculations give evidence for a wide variety of possible muonium binding sites in the conjugated ring systems of the materials as well as in the nitronyl nitroxide group and suggest the formation of local spin triplet as well as singlet states near the muon, a result which is supported by recent experiments.

1. Introduction

There has been considerable interest in a newly discovered class of materials based on the nitronyl nitroxide free radical which, although organic, displays magnetic behaviour. The interest in these materials stems both from the desire to understand how ferromagnetism can occur in a system without d or f electrons (in contrast to usual expectations [1]) and also from the opportunity to tailor properties by making small chemical adjustments, which is possible in organic systems. The first material of this type to be found was the crystal β -phase of para-nitrophenyl nitronyl nitroxide (abbreviated as p-NPNN; see figure 1), which shows bulk ferromagnetism below ~ 0.65 K as demonstrated initially by heat capacity and magnetization measurements [2] and later by muon-spin-rotation (μ SR) measurements [3, 4]. The unpaired spin in this radical [5] is associated with two N–O groups and provides a molecular magnetic moment of order $1 \mu_B$. The shape of the molecule determines the crystal structure which in turn determines the nature of the intermolecular overlap; one must ensure the appropriate overlap of the correct orbitals on neighbouring molecules to produce 3D ferromagnetism (see section 2). For most nitronyl nitroxides, this condition is not satisfied and bulk ferromagnetism is not observed. A large series of different materials which incorporate this nitronyl nitroxide group can be synthesized and, by studying these compounds, one can attempt to understand the rôle played by the rest of the organic molecule in determining the intermolecular orbital overlap, the crystal structure and hence the magnetic properties.

μ SR (for details of the technique and background information, see [6–8]) is a powerful technique which has been extensively applied to organic materials with unusual ground states (for a recent review, see [9]). Measurements on organic ferromagnets in zero magnetic field

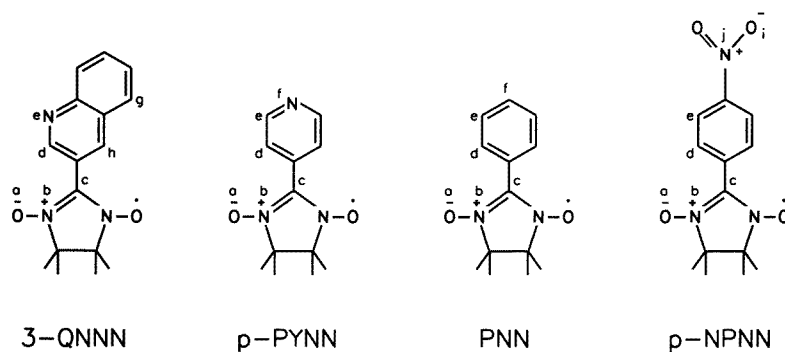


Figure 1. The four radicals studied and the labelling of the potential Mu binding sites. Site c is the α -carbon atom (see section 5.1 in the text).

directly probe the local magnetic field at the muon site and can be easily carried out down to a few tens of mK. The drawback of the technique is that the site and state of the implanted muon are not known. For these organic systems the implanted muon picks up an electron and forms muonium (written $\text{Mu} = \mu^+e^-$) before stopping on a particular molecule (see section 3 and also [7]). The aim of this paper is to determine the extent to which the Mu site and final binding state can be calculated using semi-empirical methods. We have chosen four nitronyl nitroxides on which to perform our semi-empirical simulations: 3-quinolyl nitronyl nitroxide (3-QNNO), para-pyridyl nitronyl nitroxide (p-PYNO), phenyl nitronyl nitroxide (PNO) and para-nitrophenyl nitronyl nitroxide (p-NPNO). In section 2 we review some characteristics of the nitronyl nitroxide radical family, in section 3 we discuss briefly the simulation technique employed and in section 4, section 5 and section 6 we report and discuss the results obtained.

2. The radicals

α -nitronyl nitroxide radicals[†] are stable and usually readily crystallized [10] and have a spin-1/2 ground state. The molecular structures of the particular compounds that we are studying are shown in figure 1. In each material the two N–O groups are joined via a carbon atom (known as the α -carbon atom; see figure 1) and the unpaired electron is delocalized on the whole O–N–C–N–O group. Previous theoretical calculations ([11, 12] and references therein) have indicated that these nitroxides can form stable organic ferromagnets because of the inherently strong spin-polarization (SP) effects present in them (i.e. the large energy difference between corresponding α - and β -orbitals[‡]). It was shown by McConnell ([13] and [14]) that the large positive and negative spin densities (SD) present in certain aromatic free radicals (due to the SP effect) make possible a ferromagnetic (FM) exchange interaction favouring parallel spin angular momentum on neighbouring molecules. This can be attained by stacking radicals in such a way that the atoms of positive SD are exchange coupled most strongly to the atoms of negative SD in neighbouring molecules, an effect that is referred to as the McConnell mechanism.

Spin-unrestricted INDO calculations carried out on the galvinoxyl radical [15] have been used to express the conditions necessary to establish the FM intermolecular interaction

[†] IUPAC name 2-substituted 4, 4, 5, 5-tetramethyl-4, 5-dihydro-1H-imidazolyl-1-oxyl-3-oxide.

[‡] α and β will be used to denote the spin functions for spin-up and spin-down electrons respectively.

in terms of the combined effect of SP *within* the radical (intramolecular interaction) and a charge-transfer (CT) interaction *between* the radicals (intermolecular interaction). It was found [15] that the intramolecular interaction which favours the FM behaviour should meet the following requirements.

- Stabilization of the α -SOMO (singly occupied molecular orbital) and α -NLUMO (next-lowest unoccupied molecular orbital) relative to the β -NHOMO (next-highest occupied molecular orbital) and β -SOMO respectively.
- Large splittings between the orbital energies for the α - and β -spins in the NHOMO and the NLUMO.

The conditions for the intermolecular FM interactions are as follows.

- Small SOMO–SOMO overlap.
- Large SOMO–NHOMO and/or SOMO–NLUMO overlap.

A radical which crystallizes in such a way as to satisfy these intermolecular requirements is likely to have an electronic state that also satisfies the above intramolecular requirements [15].

Table 1. Summary of crystal data for 3-QNNN, p-PYNN, PNN and p-NPNN.

	3-QNNN	p-PYNN	PNN	p-NPNN β -phase
Chemical formula	C ₁₆ H ₁₈ N ₃ O ₂	C ₁₂ H ₁₆ N ₃ O ₂	C ₁₃ H ₁₇ O ₂	C ₁₃ H ₁₆ N ₃ O ₄
Crystal system	Monoclinic	Monoclinic	Monoclinic	Orthorhombic
Space group	<i>P</i> 2 ₁	<i>C</i> 2/ <i>c</i>	<i>P</i> 2 ₁ / <i>c</i>	<i>F</i> dd2
<i>a</i> (Å)	10.5356(8)	11.166(1)	20.871(33)	10.960(3)
<i>b</i> (Å)	11.0273(7)	11.417(1)	10.150(09)	19.350(3)
<i>c</i> (Å)	6.1267(5)	10.993(1)	12.130(21)	12.347(5)
β (deg)	94.255(6)	108.03(1)	107.15(10)	90
<i>V</i> (Å ³)	709.83(8)	1215.7(2)	2455.4	2618.5
<i>Z</i>	2	4	8	8
Reference	[16]	[17]	[18]	[19]

A brief discussion of the nature of the molecular overlap present in each of the four radicals (figure 1) follows. Table 1 contains relevant crystallographic data.

2.1. 3-QNNN

The dihedral angle in the 3-QNNN molecule between the O–N–C–N–O plane and that of the quinolyl ring is 24.8(1)° [16]. Calculations performed on this family of radicals [17, 20] have shown that the unpaired electron which occupies the SOMO is localized on the nitronyl nitroxide group and has little density on the rest of the molecule. The intermolecular contacts present in the crystal are between the NO groups and quinolyl rings on neighbouring molecules [16]. The 3-QNNN molecules are arranged in a three-dimensional network such that there is little SOMO–SOMO overlap between neighbouring molecules and there is large intermolecular overlap between the SOMO and other frontier orbitals such as the NHOMO and/or the NLUMO [16]. This situation for the orbital overlap satisfies the requirements for FM interaction described above.

2.2. *p*-PYNN

In *p*-PYNN the dihedral angle between the plane of the nitronyl nitroxide group O–N–C–N–O and that of the pyridine ring is $22.8(1)^\circ$ [17]. CNDO calculations [17] have shown that again the SOMO is localized on the nitronyl nitroxide part of each molecule. Since each nitronyl nitroxide group within a chain is adjacent to its neighbour's pyridyl group (in which the SOMO density is very low), the intermolecular SOMO–SOMO overlap is very low while the intermolecular overlap of the SOMO with the other orbitals on neighbouring molecules is very large, thus favouring ferromagnetic interactions.

2.3. PNN

In the molecule PNN the dihedral angle between the plane of the nitronyl nitroxide fragment and the plane of the phenyl ring in PNN is $\sim 25.0^\circ$ [10]. Susceptibility and magnetization measurements on PNN have shown the presence of weak intermolecular antiferromagnetic (AFM) interactions [21]. The molecular orbitals deduced from UV–visible absorption spectra [22] of PNN imply a weak SP effect and a large energy separation between the α -SOMO (β -SOMO) and the α -NHOMO (β -NHOMO). The magnetic coupling between PNN radicals is therefore dominated by the CT interaction between the α -SOMO in one radical and the β -SOMO on a neighbouring one. Hence the electron transfers without changing its spin direction, preserving the total spin multiplicity and resulting in AFM coupling between the unpaired electrons.

2.4. *p*-NPNN

The nitronyl nitroxide fragment O–N–C–N–O is almost planar, and forms angles of 49.5° and 67.4° with the planes of the phenyl ring and the NO₂ group respectively [10]. The radical forms a two-dimensional network through weak intermolecular contacts between the oxygen atoms in the N–O group and the nitrogen atoms in the NO₂ group of a neighbouring molecule. The FM interaction in *p*-NPNN stems mainly from the SOMO–NHOMO and/or SOMO–NLUMO interactions [20].

3. Method

The computational technique that we have used in this work has been fully described elsewhere [23–25]. It is similar to that of Car and Parrinello [26] in that we update the electronic structure iteratively as the simulation progresses, but differs in that it uses a self-consistent semi-empirical approach to the electronic structure, rather than a full *ab initio* calculation, to simulate the binding of atomic Mu to the radicals. In the calculations we use the INDO semi-empirical parametrization of Hartree–Fock theory [27] to describe the electron wavefunctions. The forces on the atoms are then deduced from the electronic states, and the atoms are relaxed using damped molecular dynamics with iterative determination of the wavefunctions along the atomic trajectory. In spite of the restricted variational freedom of the wavefunction and the neglect of correlation effects, this method is well established as giving reasonable descriptions of the bonding in a wide variety of organic systems. The spin-polarized calculations were done using the unrestricted Hartree–Fock technique, without projecting onto eigenstates of total electron spin.

The calculations were carried out assuming the formation of both electronic singlet and triplet states, which in this context refer to the two resulting electronic spin states of

the muonated radical arising from the interaction between the electron from the Mu atom and the unpaired spin of the molecule (see section 1). The binding energy of Mu and the molecule was determined by taking the difference between the total energy of the new fully relaxed structure (i.e. radical plus Mu) and the sum of the energy for the unperturbed molecule (i.e. before the Mu has been added) and the energy of an isolated Mu atom. This was repeated for both triplet and singlet states in all of the radicals.

It should be noted that in all of these calculations the Mu atom was treated as a light hydrogen atom isotope. This is only a first approximation to a fully quantum mechanical treatment of the muon and as such will not fully capture such features as the zero-point motion of the muon, which would manifest itself through quantities such as the hyperfine coupling constant or the bond lengths and angles between the Mu atom and the relevant atom(s) of the molecule. For a recently developed approach to the full quantum mechanical treatment of the problem, see [28] and [29]. In common with all Hartree–Fock methods, CNDO and INDO calculations do not include correlations among the electrons and this is reflected in the calculated individual energies. The limited flexibility of the basis set inevitably restricts the ability of the electrons to respond to distortions of the molecule; this, combined with the intrinsic limitations of Hartree–Fock theory, causes vibrational frequencies to be overestimated. It also shares with other methods (including *ab initio* approaches) difficulties in predicting the properties of excited states. While CNDO and INDO do not have the accuracy of *ab initio* electronic structure methods, the approach has the advantage of employing a calculation of the electronic structure which is well tested for organic materials and which allows typical organic materials to be treated entirely self-consistently with very modest computational resources. They thus can be easily used to represent the geometries of organic molecules in a very wide variety of chemical environments. The essential features of charge self-consistency and response of atoms to their bonding environment are captured.

In our calculations we assume the molecular structure determined by Sugano *et al* for 3-QNNN [16] and those determined by Awaga *et al* for p-PYNN and PNN [17] and p-NPNN [20]. In all cases the methyl groups on the base of α -nitronyl nitroxide have been substituted for with hydrogen atoms.

4. The SP effect in the unmuonated molecules

We now examine the SP effect in the unmuonated molecules and the SD in both the unmuonated and muonated molecules. For the unmuonated molecules we are interested in confirming that they display the SP effect required for intermolecular FM interactions (see section 2). In addition, in order to examine the magnetic environment of the implanted muon, we analyse the SD distribution for the muonated molecules.

Table 2. Calculated sizes of the energy difference in eV between selected MOs in the unmuonated radicals.

	3-QNNN	p-PYNN	PNN	p-NPNN
α -SOMO– β -NHOMO	0.17	0.92	2.12	1.92
α -NLUMO– β -SOMO	0.85	1.68	1.79	1.51
α -NHOMO– α -NLUMO	12.52	13.13	13.84	12.91
β -NHOMO– β -NLUMO	12.30	12.86	12.31	12.53

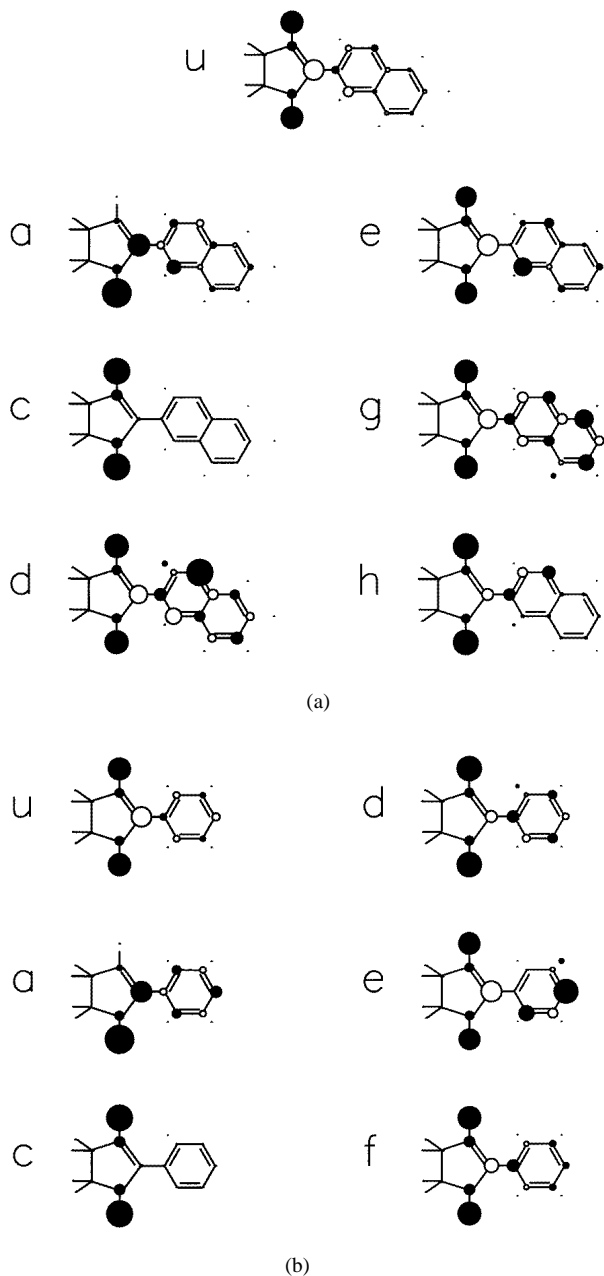


Figure 2. Spin density for the unmuonated molecule (labelled u) and for triplet states of the muonated sites referred to by letters in figure 1. The empty and filled circles denote negative and positive spin density respectively. The radius of the circle is proportional to the magnitude of the spin density. The molecule is (a) 3-QNNN, (b) p-PYNN, (c) PNN and (d) p-NPNN.

As discussed above, it has been established that as intramolecular conditions necessary to establish FM interaction in a crystal, the energies of the α -SOMO and α -NLUMO must come close to those of the β -NHOMO and β -SOMO respectively, and that there should be

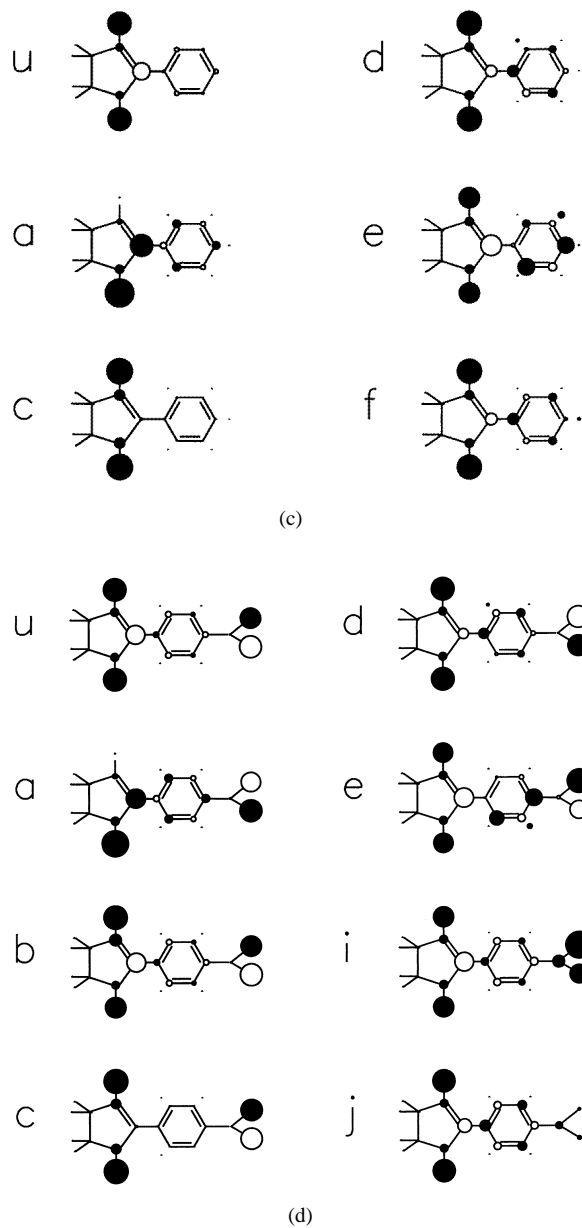


Figure 2. (Continued)

large energy splittings between the orbital energies for the α - and β -spins in the NHOMO and NLUMO (table 2).

From the last two rows of table 2 we see that for all four radicals there is a large energy splitting between the orbital energies for the α - and β -spins in the NHOMO and NLUMO. We find that the energy separation between the levels is around 13 eV in all cases, which is of the same order of magnitude as that found from spin-unrestricted calculations performed on the galvinoxyl radical [15]. As for the first condition, namely that the α -SOMO should

be stabilized relative to the β -NHOMO and likewise the α -NLUMO to the β -SOMO, we see that this is in fact the case for all radicals.

5. Spin density

The calculated SD for each unmuonated molecule and that for the muonated species (assuming the sites marked in figure 1) are shown in figure 2. We discuss these results in detail in this section.

5.1. Unmuonated molecules

In each case the distribution of SD within the nitronyl nitroxide group in the unmuonated molecules is such that the positive SD is mainly distributed over the N–O groups, while a large negative SD appears on the central carbon atom (referred to as the α -carbon atom) as can be seen qualitatively in figure 2. This large negative SD on the α -carbon atom of the nitronyl nitroxide group is analogous to that found on the central carbon atom in both the $\text{CH}(\text{CH}_2)_2$ (allyl) [12] and $\text{CH}(\text{HNO})_2$ radicals [30]. SD is also found on the phenyl (or substituted phenyl) ring of each radical with alternating sign around the ring. This is consistent with the enhanced SP effect discussed in section 4. Equivalent alternating patterns of SD populations have been found for p-NPNN and for other para- and meta-substituted nitronyl nitroxides with electron withdrawing groups (CN, CO_2H , etc) or electron donating groups (such as NH_2 , OH, OCH_3 , etc) by performing INDO–UHF calculations [31].

The alternating SD on the phenyl ring of PNN has been observed experimentally by neutron diffraction experiments [18], although it is very weak and on the limit of detectability. Alternating SD is not found in similar experiments on p-NPNN [10] and must be either not present in that material or present but significantly smaller in magnitude than in PNN. This is believed to be due to the larger dihedral angle between the plane of the nitronyl nitroxide group and the plane of the nitrophenyl ring in p-NPNN as compared with PNN which alters the mixing of orbitals, and results in smaller polarization [10].

5.2. Muonated molecules

5.2.1. *3-QNNN*. For Mu sites a and c (on the nitronyl nitroxide group) we see (figure 1 and figure 2(a)) that the SD is either positive or close to zero on the nitrogen and oxygen atoms. On the α -carbon atom it is negative for site c but positive for site a in contrast with the spin distribution on this group for the unmuonated molecule. The SD has a substantially lower population on the phenyl and quinolyl rings but here we retain the characteristic alternation of SD signs.

For Mu sites d, g, e and h, the SD on the nitronyl nitroxide group is the same as that found for the unmuonated molecule, i.e. positive on nitrogen and oxygen atoms and negative on the α -carbon atom. For sites d, g and h, the sign of the SD alternates all the way around both rings, with negative SD on the carbon atom to which the Mu atom is attached (see again figure 2(a)). For site e, though, we see that the SD is positive on the nitrogen atom to which the Mu atom is bonded. It is positive as well for the two neighbouring carbon atoms and elsewhere it alternates in sign as it does for the other muonated and unmuonated 3-QNNN molecules.

5.2.2. *p-PYNN and PNN*. We discuss first the results for p-PYNN. For Mu sites a and c (i.e. the Mu sites on the nitronyl nitroxide; see figure 1) we find only positive SD on

the nitronyl nitroxide atoms. This can be seen in figure 2(b) and is analogous to the SD distribution seen for the equivalent sites in 3-QNNN. On the phenyl ring the SD population is much reduced compared to that on the nitronyl nitroxide group, but as with 3-QNNN it alternates in sign around the ring.

For the Mu sites on the phenyl ring (sites d, e and f; see figure 1) the SD on the bridge remains the same as in the unmuonated case, i.e. positive on the oxygens and nitrogens and negative on the α -carbon atom. As with 3-QNNN, the atom to which the Mu is attached has negative SD if it is a carbon atom while it has positive SD if it is a nitrogen atom (site f); in this case the two surrounding carbon atoms again have positive SD. This difference might be due to the electron withdrawing nature of the nitrogen atom since the SD is negative on the corresponding carbon atom in PNN when Mu adds on site f. PNN shows the same qualitative behaviour as described for sites a, b, c, d and e in p-PYNN with only a slight variation in the magnitude of the SD on the different atoms (see figure 2(c)).

5.2.3. *p*-NPNN. For Mu site a (placed on the nitronyl nitroxide group) we see (figure 2(d)) that the population of SD on the nitronyl nitroxide group itself and on the phenyl ring resembles that found for the equivalent sites in the muonated 3-QNNN, p-PYNN and PNN molecules. This means that there is a positive SD on all atoms (i.e. the oxygen and nitrogen atoms and the α -carbon atom) belonging to the nitronyl nitroxide group and a substantially reduced SD population on the phenyl ring which alternates in sign. We find that the SD on NO₂ is distributed mainly on the oxygen atoms in contrast to the results found by Yamaguchi *et al* [31] with INDO-UHF calculations in which the SD on both oxygen atoms is negative and substantially reduced. In our case the electronic self-consistency procedure breaks the symmetry and we therefore get a positive SD on one oxygen and negative SD on the other. There is a much reduced SD on the nitrogen atom which is comparable with the value in reference [31].

Mu sites b and c, also on the nitronyl nitroxide group, differ from site a in that the SD on site c is negative. Because of this we see that, for Mu site b, the SD on the phenyl ring alternates in sign but in an opposite sense to the case of Mu site a. For Mu site c the SD is practically zero on site c as well as on the atoms of the phenyl group; nevertheless the SD alternates in sign around the ring as it did for site b. The SD population on the NO₂ group is positive on one oxygen atom and negative on the other while it is much reduced on the nitrogen atom.

The Mu sites on the phenyl ring (sites d and e in figure 2(d)) show again a qualitative behaviour analogous to that found for the equivalent Mu sites in the molecules 3-QNNN, p-PYNN and PNN (that is, in the nitronyl nitroxide group there are positive, positive and negative SD on the nitrogen, oxygen and carbon atoms respectively). For the distribution around the phenyl ring we see the characteristic alternation of SD signs and also that the carbon atom to which the Mu atom is attached in both cases has negative SD. For the population on the NO₂ group the SD is again positive on one oxygen atom, negative on the other and negligible on the nitrogen atom (as it was with the unmuonated molecule and sites a, b and c). The sign of the SD on the nitrogen atom is determined by the sign on the carbon atom to which it is bound on the phenyl ring.

For Mu placed on the NO₂ group, sites i and j, the distribution of spin density on the nitronyl nitroxide group and on the phenyl ring is equivalent to that found for the four unmuonated molecules. The SD is positive for all of the atoms in the NO₂ group (NO₂ acts as an electron withdrawing group [31]).

Table 3. The calculated binding energy (eV) of Mu sites for each molecule, with the most stable listed first.

	3-QNNN	p-PYNN	PNN	p-NPNN
Triplet c	-5.71	Singlet c -6.53	Triplet c -5.99	Triplet c -5.71
Triplet h	-5.44	Triplet c -5.71	Triplet d -4.63	Triplet d -4.63
Triplet d	-4.63	Triplet d -4.63	Triplet f -4.63	Triplet i -4.63
Triplet g	-4.35	Triplet f -4.63	Triplet a -4.08	Triplet j -4.63
Triplet a	-4.08	Singlet d -4.35	Singlet a -4.08	Singlet i -4.63
Singlet a	-4.08	Singlet a -3.81	Triplet e -2.99	Singlet j -4.35
Triplet e	-3.81	Triplet a -3.81	Singlet f 0.00	Triplet a -4.08
Singlet b	-2.18	Singlet e -3.81	Singlet e + 1.09	Singlet a -3.54
Singlet e	-1.90	Triplet e -3.27		Triplet e -3.27
Singlet h	-0.82	Singlet f -1.09		Singlet b -1.91
Singlet g	+0.54			Triplet b -1.36
				Singlet e + 1.09

6. Binding energy

The calculated binding energy for the sites considered in each molecule is shown in table 3. These semi-empirical results suggest that the most energetically favoured binding sites for the Mu are spin triplets. At the majority of the sites considered, the spin triplet was favoured over the singlet, and at a few sites the spin singlet was not even a bound state. The stability of the triplet sites is consistent with the observation that states of higher multiplicity are found at lower energies when electrons of parallel spins are kept apart by the antisymmetry principle (Hund's rule) [27, 32]. Nevertheless this does not always apply; in many cases the energetic ordering of the terms arising from a given molecular configuration depends on the balance between the Coulomb attraction energy (electron–nucleus) and the Pauli-principle repulsion energy between electrons of like spin. Recent longitudinal-field μ SR measurements on p-NPNN have confirmed that although a major fraction of the implanted muons are in an electronic spin-singlet configuration they can also be found in a degenerate spin state, believed to be a triplet rather than a doublet state [4]. It is thus believed that in muon-implantation experiments *both* spin-singlet and spin-triplet states can be formed in p-NPNN. This implies that the muon may implant in more than one state and not necessarily in only the state which is lowest in energy. A similar situation occurs with a number of other materials [7].

The results of our calculations of binding energies, summarized in table 3, imply the following.

- The most favoured binding site for the Mu atom in all of the radicals is site c, i.e. the α -carbon atom joining the two N–O groups in the nitronyl nitroxide group. It forms a local spin triplet in all cases except in p-PYNN where it forms a local spin singlet.
- The next most favoured site is site d (see figure 1) giving a triplet state in the ortho-muonated molecules (except in the case of 3-QNNN where it is preceded by a lower-energy state at site h (see figure 1) which corresponds to the other ortho-substitution). For site d we find that the triplet-state binding energy has the same value in all four molecules, namely -4.63 eV.
- Triplet sites in the para-muonated substituted (i.e. p-PYNN or p-NPNN) or unsubstituted (i.e. PNN) phenyl ring have the same binding energy of -4.63 eV; these are sites i and j in the molecule p-NPNN and site f in the molecules p-PYNN and PNN.
- Site a, situated on the oxygen atom of the nitronyl nitroxide group (see figure 1), is

equally favoured as a singlet and as a triplet in all molecules except p-NPNN where a triplet state is preferred over a singlet state by an energy difference of 0.54 eV.

Thus we find that the Mu atom will bind preferentially in a triplet state on the α -carbon atom of the nitronyl nitroxide group or in descending order of preference in an ortho-, para- and finally meta-substitution where sometimes it is actually unbound (i.e. as a singlet in PNN and p-NPNN).

It is important to note that our calculations have been performed with a single isolated molecule. It is known that the overall magnetic properties of these materials are strongly influenced by their crystal arrangement. Nevertheless, although it is possible that in the solid state the steric effects force the Mu atom into a given state, we have chosen to allow full structural relaxation of the molecules in the presence of the Mu atom since it is expected that the details of the Mu binding site will be more strongly determined by the very local molecular environment than by effects of the crystal structure [33]. Thus we do not include the constraining effect of the neighbouring molecules in the crystal structure (which would be hard to reliably model anyway) but do allow the Mu atom to be free to distort the individual molecule in order to accommodate itself. Hence for the unmuonated molecules our calculated dihedral angles between the nitronyl nitroxide and the plane of the α -substituent are reduced to values close to zero, in contrast to the values of 20–50° found in the solid state.

In the simulations certain sites (b, c and d) were found to be unstable, with the result that the Mu atom migrated to a different, more stable, site. For these sites a consistent pattern emerged.

- Triplets for 3-QNNN, PNN and p-PYNN starting at site b moved to site c.
- Singlets for PNN and p-PYNN starting at b moved to a.
- Singlets for 3-QNNN, p-NPNN and PNN starting at c moved to b.
- Singlets for 3-QNNN, p-NPNN and PNN starting at d moved to a.

If the preferred site were considerably more bound than any other site, only one site would contribute to the observed signal in the μ SR experiments. Our semi-empirical results however suggest that the difference in binding energies between the most preferred site and the others is at most of the order of ~ 1 eV and that the probability of having more than one site occupied is considerable. This possibility of more than one available site would be significantly enhanced if the zero-point motion of the muon were included. The experiments on p-NPNN indicate that at least two final states (singlet and triplet) are actually observed [4]. The semi-empirical results presented here for p-PYNN and p-NPNN can be compared with those obtained from *ab initio* density functional calculations [33, 34]; though they differ in the prediction of the preferred muon site, they also show that singlet formation is possible and that it is likely that more than one site may be occupied.

In table 4 we give an estimate of the vibrational frequency for selected Mu bonds

Table 4. Estimated values for the vibrational frequencies in eV of selected bonds and corresponding zero-point energy values in eV, for the different types of Mu bonds encountered.

Bond	Vibrational frequency	Zero-point energy
O–Mu	1.38	0.69
C–Mu	1.05	0.53
N–Mu	1.15	0.58

as well as the corresponding values of the zero-point energy. These were obtained from the vibrational frequencies reported for the equivalent hydrogen bonds by scaling by the appropriate factor (i.e. $\sqrt{m_p/m_\mu}$). On zero-point-energy grounds, the favoured type of Mu bond would be that corresponding to the smallest zero-point energy, i.e. Mu bound to a carbon atom (see table 4), and this is in fact what we obtain for all of the molecules; the lowest-energy sites consistently correspond to C–Mu bonds. As can be seen from table 4, the magnitude of the zero-point energy is comparable to the energetic difference between the most favoured site and the next-closest one for all of the radicals (see table 3). We believe that the predictions of the approach would be improved if the zero-point motion of the muon were included.

We have stressed throughout the paper that the magnetic behaviour exhibited by these materials is very sensitive to the intermolecular arrangement of the crystal but our calculations have been limited to a single isolated molecule. A future avenue of research is to include more than one molecule in necessarily more computationally demanding calculations, and use the information obtained from the present work in the selection of the trial sites. This could be performed with a modified version of the code that includes periodic boundary conditions.

7. Conclusions

In this paper we model muon implantation in several nitronyl nitroxides by treating the muon as a classical particle akin to a light proton, calculating the electronic structure of the muonated molecule, and using the energy and forces thereby obtained to damp the system and hence to obtain the minimum-energy configuration. With this method we are able to establish the preferred muon binding sites in the four recently synthesized organic magnets: 3-QNNN, p-NPNN, p-PYNN and PNN. We find that the lowest-energy bonding configurations of muonium and the radicals which constitute these materials include triplet as well as singlet states, raising the possibility that both will be observed, consistently with experiment. We find also that muonium bonds preferentially to the nitronyl nitroxide bridge.

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References

- [1] Heisenberg W 1928 *Z. Phys.* **49** 613
- [2] Tamura M, Nakazawa Y, Shiomi D, Nozawa K, Hosokoshi Y, Ishikawa M, Takahashi M and Kinoshita M 1991 *Chem. Phys. Lett.* **186** 401
- [3] Le L P, Keren A, Luke G M, Wu W D, Uemura Y J, Tamura M, Ishikawa M and Kinoshita M 1993 *Chem. Phys. Lett.* **206** 405
- [4] Blundell S J, Pattenden P A, Pratt F L, Valladares R M, Sugano T and Hayes W 1995 *Europhys. Lett.* **31** 573
- [5] Okumura M, Yamaguchi K, Nakano M and Mori W 1993 *Chem. Phys. Lett.* **207** 1
- [6] Dalmas de Réotier P and Yaouanc A 1997 *J. Phys. C: Solid State Phys.* **9** 9113
- [7] Cox S F J 1987 *J. Phys. C: Solid State Phys.* **20** 3187
- [8] Schenck A 1985 *Muon Spin Rotation Spectroscopy* (Bristol: Hilger)
- [9] Blundell S J 1997 *Appl. Magn. Reson.* **13** 155

- [10] Zheludev A, Bonnet M, Ressouche E, Schweizer J, Wan M and Wang H 1994 *J. Magn. Magn. Mater.* **135** 147
- [11] Yamaguchi K, Fueno T, Nakasuji K and Murata I 1986 *Chem. Lett.* 629
- [12] Yamaguchi K and Fueno T 1989 *Chem. Phys. Lett.* **159** 465
- [13] McConnell H 1958 *J. Chem. Phys.* **28** 1188
- [14] McConnell H 1963 *J. Chem. Phys.* **39** 1910
- [15] Awaga K, Sugano T and Kinoshita M 1987 *Chem. Phys. Lett.* **141** 540
- [16] Sugano T, Tamura M, Kinoshita M, Sakai Y and Ohashi Y 1992 *Chem. Phys. Lett.* **200** 235
- [17] Awaga K, Inabe T and Maruyama Y 1992 *Chem. Phys. Lett.* **190** 349
- [18] Ressouche E, Zheludev A, Boucherle J X, Gillon B, Rey P and Schweizer J 1993 *Mol. Cryst. Liq. Cryst.* **13-26** 232
- [19] Kinoshita M 1993 *Synth. Met.* **55-57** 3285
- [20] Awaga K, Inabe T, Nagashima U and Maruyama Y 1989 *J. Chem. Soc. Chem. Commun.* 1617
- [21] Awaga K and Maruyama Y 1989 *Chem. Phys. Lett.* **158** 556
- [22] Awaga K and Maruyama Y 1989 *J. Chem. Phys.* **91** 2743
- [23] Wallace D S 1989 *DPhil Thesis* University of Oxford
- [24] Wallace D S, Stoneham A M, Hayes W, Fisher A J and Harker A H 1991 *J. Phys.: Condens. Matter* **3** 3879
- [25] Wallace D S, Stoneham A M, Hayes W, Fisher A J and Testa A 1991 *J. Phys.: Condens. Matter* **3** 3905
- [26] Car R and Parrinello M 1985 *Phys. Rev. Lett.* **55** 2471
- [27] Pople J A and Beveridge D L 1970 *Approximate Molecular Orbital Theory* (New York: McGraw-Hill)
- [28] Valladares R M, Fisher A J and Hayes W 1995 *Chem. Phys. Lett.* **242** 1
- [29] Fisher A J and Valladares R M 1996 *Protons and Muons in Material Science* ed E A Davis and S F J Cox (New York: Taylor & Francis) p 299
- [30] Yamaguchi K, Okumura M, Maki J, Noro T, Namimoto H, Nakano M, Fueno T and Nakasuji K 1992 *Chem. Phys. Lett.* **190** 353
- [31] Yamaguchi K, Okumura M and Nakano M 1992 *Chem. Phys. Lett.* **191** 237
- [32] Levine I N 1983 *Quantum Chemistry* (Boston, MA: Allyn and Bacon)
- [33] Probert M I J and Fisher A J 1997 *J. Phys.: Condens. Matter* **9** 3635
- [34] Valladares R M, Probert M I J and Fisher A J 1996 *Mater. Sci. Eng. B* **37** 247