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Spin Density of a Ferromagnetic Tempo Derivative

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We have determined by polarized neutron diffraction the spin density of a ferromagnetic (Tc=0.28K) tempo derivative: the 4(p-chlorobenzylideneamino)-2,2,6,6-tetramethylpiperidin-1-oxyl, where the nearest and next nearest neighbours N-O sites construct a two-dimensional network parallel to the $(\vec{a}, \vec{b})$ plane. Most of the spin density lies on the N and O atoms of the NO radical and is equally shared between these two atoms. As for the pure tempone, the two carbon atoms neighbouring the nitrogen of the N-O group in the 6-member ring, carry significant spin populations of different signs: −0.074(12) for atom C3 and +0.063(17) for atom C4. This is not consistent with the coupling mechanism proposed previously which implied that the populations of both C3 and C4 should be negative. A tentative explanation for the coupling mechanisms, taking into account the spin density distribution, is discussed.

Keywords: spin densities; polarized neutron diffraction; ferromagnetic free radical

INTRODUCTION

Recently, several tempo derivatives were discovered, which are ferromagnetic, with Curie temperatures ranging between Tc=0.18K and Tc=0.4K[1] when pure tempone remains paramagnetic down to 0.05K [2]. This difference has to be connected with the piling of molecules in the different crystals. In pure tempone, the molecules are considered as isolated, with distances between the oxygen atoms of the nitroxide groups of 4.71 Å and 4.94 Å. In all the above ferromagnetic derivatives, the NO sites construct two-dimensional networks and the oxygen atoms are located on zig zag sheets, the nearest neighbour O---O distances being of the order of 6 Å. This large distances prevent an effect of direct interactions between the N-O sites inside a sheet. However there are methyl and methylene groups intervening between them which can play the role

of ferromagnetic exchange couplers. A mechanism of ferromagnetic interactions inside the sheets has been proposed[3], which implies an alternation of the sign of the spin density when passing from the oxygen of one N-O group to the nitrogen of the next N-O group, as depicted on figure 1. This model has been comforted by ^{1}H-MAS-NMR measurements[4] which showed that the spin densities on methyl and methylene hydrogens are negative.

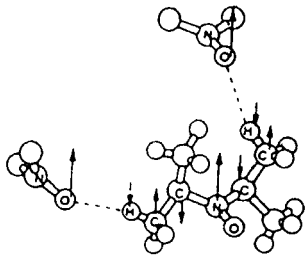

FIGURE 1: Mechanism proposed by ref [1] for ferromagnetic interactions in Cl-TEMPO.

In order to check this model and to gain some comprehension on the magnetic couplings in this series of tempo derivatives, we have investigated by polarized neutron diffraction the spin density of one of these compounds. We have chosen the 4(p-chlorobenzylideneamino)-2,2,6,6-tetramethylpiperidin-1-oxyl (that we shall refer as Cl-TEMPO in the text), a ferromagnetic compound with Tc=0.28K. The chemical structures of the Cl-TEMPO and of the pure tempone, together with the atoms labelling used throughout this paper, are presented on figure 2.

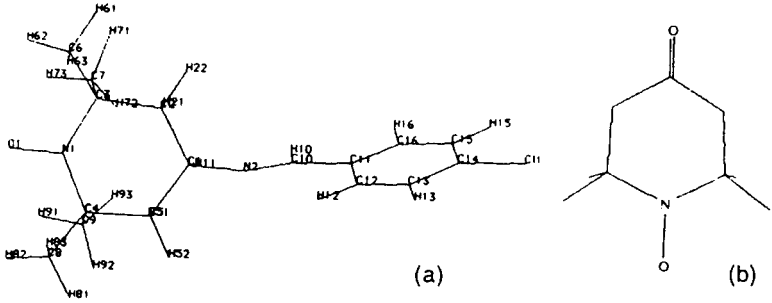

FIGURE 2: Chemical structures: (a) Cl-TEMPO , (b) pure tempone

Polarized neutron diffraction is a very powerful technique to determine the spin density at any point of a molecule. In the case of magnetic molecular materials, the measurements are generally performed in the paramagnetic state: at low temperature, an aligned spin density is induced on a single crystal by a strong magnetic field. This induced spin density has the same periodicity as the crystal cell and scatters the neutrons. Practically, one measures the so-called

"flipping ratio", the ratio between the intensities I_+ and I_- at the peak of each Bragg reflection, where + and - correspond to the spin states of the incoming neutrons:

$$R(hkl) = \frac{I_+}{I_-} = \left| \frac{F_N(hkl) + F_M(hkl)}{F_N(hkl) - F_M(hkl)} \right|^2 \quad (1)$$

where $F_N(hkl)$ and $F_M(hkl)$ are the nuclear and the magnetic structure factors of the crystal, that is the Fourier components of the periodic nuclear density and the Fourier components of the periodic spin density. If the nuclear crystal structure (positions and vibration parameters of all the atoms) is well known, the measurement of the flipping ratios R(hkl) allows the determination of the magnetic structure factors and then the reconstruction of the spin density.

As the crystal structure of Cl-TEMPO has been determined by X-ray diffraction at room temperature[5], only the "heavy" atoms (all the atoms except the hydrogens) were accurately located, and their position and vibration parameters were determined at room temperature only. We have then performed another diffraction experiment, with unpolarized neutrons to locate all the atoms, including hydrogens, at low temperature, in order to refine the crystal structure in the same conditions as the spin density investigation.

NEUTRON DIFFRACTION

The crystal structure experiments were performed on the unpolarized neutron lifting counter diffractometer D15 of the Institut Laue Langevin-Grenoble (λ=1.173Å, T=4.5K) on two crystals: crystal **1** (6x2x2 mm^3) mounted with the $\vec{a}$ axis vertical, and crystal **2** (3.5x2.5x1 mm^3), mounted with axis $\vec{b}$ vertical. Altogether the integrated intensities of 1209 (crystal **1**, $\sin\theta/\lambda$ up to 0.65$Å^{-1}$) and of 897 (crystal **2**, $\sin\theta/\lambda$ up to 0.74 $Å^{-1}$) independent reflections were measured. The monoclinic space group $P2_1/c$ is preserved between room temperature and 4.5K. The lattice constants, at T=4.5K, are: a=5.736(9)Å, b=23.946(11)Å, c=11.322(10)Å and β=104.36(9)°. The position parameters and the anisotropic thermal parameters Uij of all the atoms were refined at low temperature, together with the extinction coefficients g of each of the two crystals, using the programme ORXFLS[6]. The refinement went quite well with $wR(F^2)$=5.50%, χ^2=1.51.

The structure is displayed in figures 3 and 4. As shown in figure 4, the NO sites construct two-dimensional networks and the oxygen atoms are located on zig zag planes, parallel to the $(\vec{a},\vec{c})$ plane. Compared to room temperature, the distances and bond angles inside the molecule have changed very little. What has changed is the intermolecular distances. The nearest neighbour O---O distances which were 5.91 Å and 5.95 Å at room temperature are now 5.74 Å and 5.87 Å at low temperature. The intersheet O---O distance (roughly along $\vec{b}$) grows during the cooling from 10.86 Å to 13.26 Å.

Inside the zig zag plane, contacts exist between molecules along the $\vec{a}$ direction. As shown in figure 5, these contacts connect atom O1 from molecule

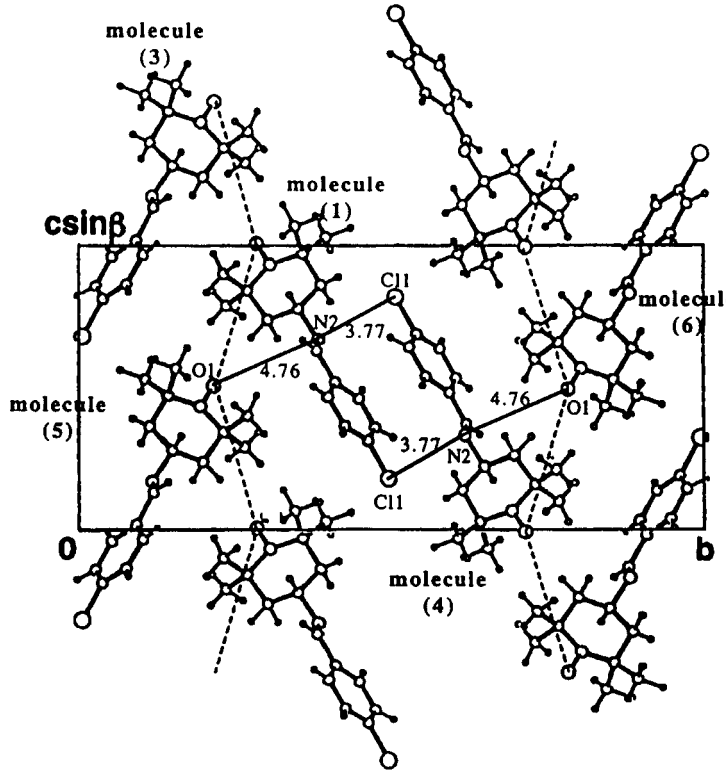

FIGURE 3: Crystal structure of Cl-TEMPO projected along the $\bar{a}$ axis of the unit cell

1 to methyl atoms H72 and H93 of molecule 2 at distances 2.62 Å and 2.49 Å respectively. Other O•••H contacts are at larger distances. In the same zig zag plane, along the $\bar{c}$ direction, contacts connect atom O1 from molecule 1 to methyl atoms H61 and H63 of molecule 3 at distances 2.37 Å and 3.40 Å respectively. One has to note also the existence between these two molecules of a contact between O1 of molecule 1 and methylene hydrogen H22 at a distance of 2.74 Å (see figure 5). The distance between the O1 atom of molecule 1 and the imino nitrogen N2 of molecule 3 is only 4.76 Å, as shown in figure 3. Finally, along the $\bar{b}$ axis a contact exists, which is also represented in figure 3, between the terminal Cl of molecule 1 and the imino nitrogen N2 of molecule 4 at a distance of 3.77 Å.

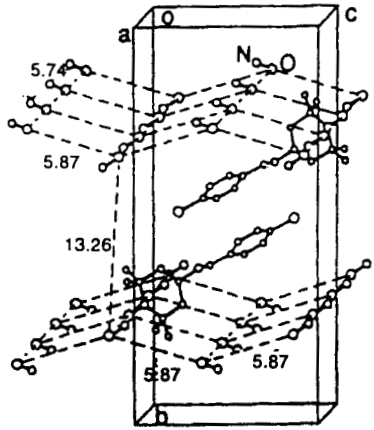

FIGURE 4: Zig zag sheets of the NO groups in the crystal structure of Cl-TEMPO.

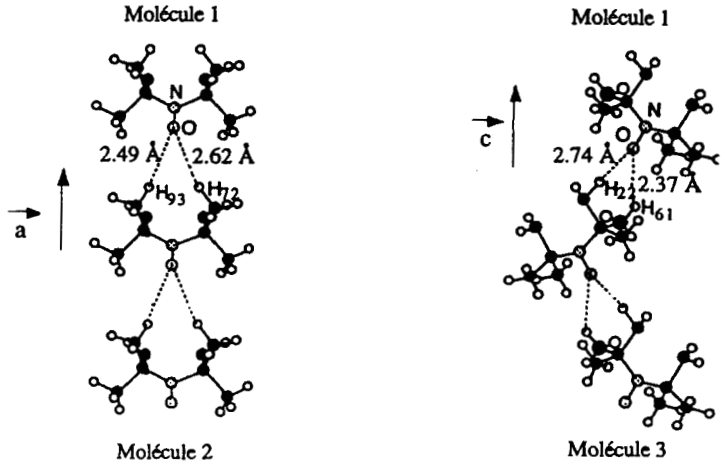

FIGURE 5: Contacts between molecule 1 and molecules 2 and 3.

The spin density experiment was performed on the polarized neutron lifting counter diffractometer D3 of the ILL-Grenoble (T=1.5K, λ=0.843Å, H=4.5T). We have mounted crystal **1** on the diffractometer, with the ā axis vertical and parallel to the applied field. We have measured the flipping ratios of

246 independent reflections up to $\sin\theta/\lambda=0.50$ Å^{-1}. Precise nuclear structure factors were calculated from the refined low temperature crystal structure. The magnetic structure factors F_M's were determined from expression (1).

To reconstruct the spin density from the F_M's, we have modelled this density and we have refined the parameters of the model which best fit the experimental data[7]. A Hartree-Fock type magnetic wave function $|\psi_i\rangle$ is constructed from standard Slater orbitals at each magnetic site: $|\psi_i\rangle=S\alpha_{ij}|\varphi_j\rangle$. To allow both positive and negative spin populations, the spin density is expanded as:

$$s(r) = \sum_{\text{atom } i} S_i \langle\psi_i|\psi_i\rangle \qquad (2)$$

The individual atomic populations S_i, the coefficients α_{ij} and the radial exponents ζ of the Slater functions of each orbital are the parameters of the model.

We have refined the parameters of this orbital model, for all the carbon, chlorine, nitrogen and oxygen atoms of the molecule as well as the methyl and methylene hydrogen atoms of the piperidine ring. On the nitrogen and the oxygen atoms of the nitroxide group, the magnetic orbital was expanded in functions of $|2p_x\rangle$, $|2p_y\rangle$ and $|2p_z\rangle$. The radial exponents ζ were refined to $\zeta_N=2.36(9)$ and $\zeta_O=2.40(9)$ atomic units. For the other atoms, they were approximated to their spherical contribution, and their radial exponents ζ were taken in literature[8]. Table I displays the individual atomic populations S_i. The agreement between the observed and calculated data is quite good, with a χ^2 factor of 2.14. Figure 6 represents the spin density reconstructed by this method and projected along the local z axis of site N1.

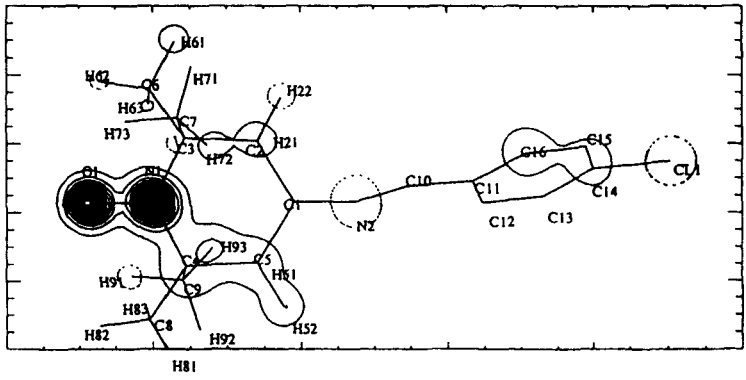

FIGURE 6: Spin density reconstructed by orbital modelling and projected along the z axis of N1 (contour step : 0.05 μ_B/Å^2).

TABLE I: Spin populations (normalized to unity) obtained from the orbital model refinement

atom	spin population	atom	spin population
O 1	0.396 (14)	C 6	-0.054 (16)
N 1	0.388 (19)	H 61	0.038 (12)
C 1	0.007 (11)	H 62	-0.019 (12)
C 2	0.006 (16)	H 63	0.038 (13)
H 21	0.038 (13)	C 7	0.021 (19)
H 22	-0.032 (13)	H 71	-0.014 (12)
C 3	-0.074 (12)	H 72	0.055 (14)
C 4	0.069 (17)	H73	0.010 (14)
C 5	0.039 (17)	N 2	-0.068 (14)
H 51	0.017 (14)	C 10	0.021 (18)
H 52	0.046 (14)	C 11	-0.016 (17)
C 8	0.003 (17)	C 12	-0.015 (16)
H 81	0.011 (12)	C 13	-0.008 (13)
H 82	-0.012 (12)	C 14	0.041 (13)
H 83	-0.002 (15)	C 15	0.019 (16)
C 9	0.012 (17)	C 16	0.064 (17)
H 91	-0.029 (15)	Cl 1	-0.058 (13)
H 92	-0.001 (13)		
H 93	0.052 (14)		

As expected, most of the density is concentrated on the nitroxide group. The two carbon atoms which are neighbouring the nitroxide group carry a significant spin population of opposed signs: -0.075(12) for C3 and +0.070(17) for C4. On the rest of the molecule the alternation of the signs is almost perfect. The largest spin densities are carried by the imino N2 atom: -0.069(14) and the terminal chlorine atom: -0.059(13). For most of the hydrogen atoms, the spin population remains of the order of the uncertainty. The values found for some of them (0.055(14) for H72, 0.052(14) for H93) are significant. They are much higher than the common value of -0.00070(3) found for the methyl and methylene hydrogen by the ^{1}H-MAS-NMR technique[4], but these latter measurements were performed between 170K and 290K, that is at temperatures where the methyl hydrogen are rapidly rotating

and do not reflect the spin density at low temperature when these atoms are fixed.

DISCUSSION

As in many other nitroxide radicals[9,10], most of the spin density (80% here) has been found on the NO group and a much smaller amount (20%) is delocalized on the other atoms of the molecule: on the piperidine ring, but also on the aryl part. We shall examine successively these different densities and compare them to those measured on other simple tempo compounds.

On the NO group, the spin density has been found equally shared between the oxygen and the nitrogen atoms (ratio 50/50). On pure tempone[10] where the molecules are quite isolated and the Curie law is followed down to very low temperature, the ratio was close: 47/53, favouring slightly the nitrogen site, while on tempol[10], where the oxygen of the NO group is strongly involved in magnetic interactions through an hydrogen bond, the spin density on the oxygen atom is markedly depleted and the ratio of spin populations between the oxygen and the nitrogen was reduced to 39/61. We can consider this ratio as a raw indication of the magnetic interactions passing through the oxygen of the NO radical, and the experimental ratio of 50/50 suggests a rather small, but not negligible level for these interactions. This localized spin density has been found to correspond to a molecular wave function built from 2p orbitals of the nitrogen and the oxygen atoms.

On the piperidine ring, the largest spin densities on the atoms other than the NO group, lie on the carbon atoms neighbouring directly this NO group. The spin populations have been found unambiguously of opposite signs. This result leads us to discuss the coupling mechanism proposed by Nogami et al[3]. This mechanism, inside the zigzag sheets, would couple molecules 1, 2 and 3. According to this model, the signs of the spin populations on the N, C, C, H and O atoms should alternate as a result of the hyperconjugation, with a negative sign on the hydrogen atoms, as depicted in figure 1. However, the experimental spin density does not show this sign alternation, and in particular, the difference of signs on C3 and C4 indicates that the coupling scheme is certainly more complex than the rather simple model which has been proposed. Let us remind that in tempone, the parent compound for which, as for Cl-TEMPO, these two carbon atoms are not constrained to be identical by the crystal symmetry, the spin populations were also found to be of different signs: -0.056(20) and 0.027(23).

What can then be said on the coupling paths? Along the $\vec{a}$ direction, between molecule 1 and molecule 2 (figure 5), we can see on table I that the two hydrogen atoms H72 and H93, at contact distances of 2.62 Å and 2.49 Å from atom O1 carry rather large spin populations: 0.056(14) and 0.053(14). Even if the signs do not correspond to the proposed model, it is clear that these atoms participate to the coupling.

Along the $\vec{c}$ direction, between molecule 1 and molecule 3 (figure 5), there are two methyl hydrogen atoms, bound to carbon C6, which are in contact with atom O1 and which carry a noticeable spin density: H61 at a distance 2.37 Å carries a spin population of 0.038(12) and H63, at a distance 3.40 Å carries 0.038(13). Besides that, the methylene atom H22, bound to carbon C2, is at a

distance 2.74 Å of atom O1 and has a spin population of -0.032(13). It is therefore natural to think that these hydrogen atoms and the carbons to which they are connected are implied in the magnetic interactions.

Along the $\bar{b}$ direction, there are appreciable densities on the imino nitrogen N2 (-0.069(14)) and the chlorine Cl1 (-0.058(13)). Therefore, an intermolecular magnetic interaction seems to induce the spin densities on N2 and Cl1. As shown in figure 3, molecules 1, 4, 5 and 6 are linked by magnetic interaction paths along the $\bar{b}$ direction: O1 (molecule 5)---N2 (molecule 1)---Cl1 (molecule 4) and Cl1 (molecule 1)---N2 (molecule 4)---O1 (molecule 6). The intermolecular atomic distances O1--N2 and N2--Cl1 are 4.76Å and 3.77Å, respectively. Thus N1O1 radical (molecule 5) may induce the negative spin density on N2 (molecule 1), which in turn would induce the negative spin density on Cl1 through a π-electron conjugation. Thus, the magnetic interaction paths among molecules 1, 4, 5 and 6 would cause the ferromagnetic coupling between the adjacent zigzag sheets of NO radical sites which are separated along the $\bar{b}$direction.

The polarized neutron investigation on the ferromagnetic nitroxide radical Cl-TEMPO has clearly shown that 80% of the spin density is localized on the NO group of the radical, equally shared on the nitrogen and the oxygen atoms and that 20% of this density is delocalized on the other atoms of the molecule. The analysis of this delocalized part allowed to see that the scheme of the magnetic interactions between adjacent molecules is not simple but implies different pathways. In particular the role of some methyl and methylene hydrogen atoms has been evidenced.

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