Quantitative test of electronic structures of organic ferromagnet systems from first-principles investigations using muon spin rotation data

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The electronic structure of the organic ferromagnet 4-(*p*-chlorobenzylideneamino)-TEMPO is determined by the first-principles unrestricted Hartree-Fock cluster procedure, with and without muon (μ) and muonium (Mu), and its accuracy is tested by investigating μ and Mu trapping sites and corresponding muon hyperfine interaction tensors. The results provide good agreement with the observed muon spin rotation frequency, site assignment, and also easy-axis direction in agreement with that from dipole-dipole interactions between the calculated distributed magnetizations in the molecules.

There is currently great interest[1–5] in understanding of the origin of ferromagnetism, with low Curie temperatures (T_c), in transition-metal-free organic ferromagnets and their associated electron distributions. The system 4-(*p*-chlorobenzylideneamino)-TEMPO [with TEMPO $=(2,2,6,6\text{-tetramethyl-piperidin-1-yloxyl})$], abbreviated as (*p*-Cl-Ph-CH$=$N-TEMPO), is one of a number of TEMPO compounds with different benzene-ring-based ligands of the TEMPO group which have T_c between 0.2 and 0.4 K. The observed ferromagnetism has been ascribed to an indirect exchange[4,5] between the unpaired spin on the NO group in the TEMPO (Fig. 1) of each molecule and those in neighboring molecules, through pathways involving methyl and methylene groups in each molecule. However, because of the extreme weakness of the magnetic interactions between the adjacent molecules, symbolized by the very low T_c, one cannot rule out dipole-dipole interactions[6] between the unpaired spins as at least a partial contributor to the origin of the ferromagnetism.

The present first-principles investigation is aimed at enhancing the understanding of the nature of this ferromagnet, especially obtaining a quantitative and accurate knowledge of the electronic structure of its component molecules. The Hartree-Fock cluster procedure[7] is used for determination of the electron spin distribution in this molecular solid to explain quantitatively the recently obtained[8] experimental zero-field muon spin rotation (μSR) frequency, make assignment of this frequency to trapped μ or Mu sites in this system, and to determine the easy axis direction.[9] However, there is no independent experimental measurement available for the easy axis with which to compare our result obtained from a combination of the hyperfine interaction tensor determined from our calculated electronic wave functions and the experimentally observed μSR frequency. We have therefore also determined the easy axis independently from a study of the magnetic dipole-dipole interaction[10] between the *p*-Cl-PhCH$=$N-TEMPO molecules using magnetic dipole moment distributions from our calculated electronic struc-

ture. Our results verify that the easy axis determined by our dipole-dipole interaction study and analysis of μSR data agree very well with each other. Our investigation also obtains the sites at which μ and Mu can be trapped and which of these sites explains, quantitatively, the observed hyperfine field[8] at the muon, including vibrational effects[11] for the muon, at the trapped μ and Mu sites. These good agreements between theoretical and experimental results provide strong support for the accuracy of the Hartree-Fock cluster procedure for study of electronic structures of organic ferromagnetic systems.

The structure of the single *p*-*Cl*-Ph-CH$=$N-TEMPO molecule and the arrangement[3,4] in pleated sheets of the individual molecules in the molecular solid are shown in Figs. 1 and 2. For our investigation of the electronic structure of this system, we have utilized the first-principles Hartree-Fock-Roothaan variational procedure[12] implemented by the GAUSSIAN 98 set of programs using the (6-31G) basis set,[13] found to be satisfactory for earlier Hartree-Fock cluster investigations of electronic structures and associated properties of a variety of condensed matter systems.[14] The unrestricted Hartree-Fock (UHF) procedure[11,15] was used to incorporate the exchange polarization effect[11,14,15] in systems involving unpaired spin. The trapping of Mu in some other related organic ferromagnets and associated hyperfine interactions was studied earlier[16] by different procedures than the method we have used.

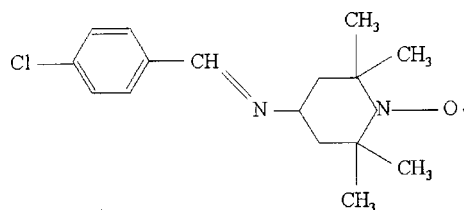For choosing the appropriate cluster for our Hartree-Fock

FIG. 1. *p*-Cl-Ph-CH$=$N-TEMPO molecule. The carbons and the accompanying CH bonds in parts of the benzene and TEMPO ring are not shown to keep the figures clear.
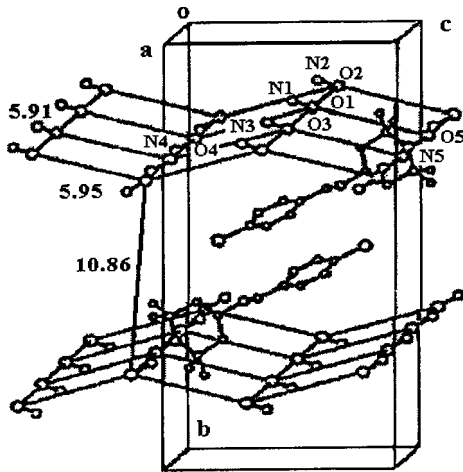
FIG. 2. Crystal structure of p-Cl-Ph-CH=N-TEMPO (Refs. 1 and 2). O1 belongs to the NO bond in the central molecule, and (O2–O5) belong to the NO bonds of the four molecules nearest to the central molecule.

cluster investigation, we have carried out two test calculations, one involving a central molecule ($i=1$) and another involving both the central molecule and another molecule ($i=5$) from the four nearest neighbors of the central molecule (Fig. 2). The results showed that the influence of covalency effects, associated with the neighboring ($i=5$) molecule, on the charge and spin populations on the central molecule was almost negligible. It was therefore felt adequate to take a single central molecule as the cluster. For the trapping sites for μ and Mu in the central molecule, the usual energy optimization procedure in the literature[12,13] was utilized. The positively charged particle μ is expected to bind through Coulomb attraction and polarization effects to the electronegative atoms in the molecule: namely, the radical oxygen and nitrogen, the bridge nitrogen, and chlorine atoms in Fig. 1. For Mu, the likely trapping sites to test are intuitively less clear than for μ, so we have tested the neighborhoods of the various carbon atoms and nitrogen, oxygen, and chlorine atoms in the molecule. Since both Mu and the central molecule carry spin 1/2, both singlet and triplet states of the trapped Mu system have to be considered.

Relaxation effects involving changes in positions[12,13] of neighboring atoms due to the presence of trapped μ or Mu were included in the optimization procedure, convergence tests as a function of the number of neighbors involved in the relaxation, indicating that including the second nearest neighbors of the μ or Mu was sufficient. For μ, of the four sites tested, three—namely, those near the bridge nitrogen—radical oxygen and chlorine were found to provide trapping with binding energies 13.3, 9.54, and 6.26 eV, respectively. The region near the radical nitrogen did not provide trapping, perhaps because of the strong trapping near the radical oxygen which pulled the μ towards itself. As regards the trapping of Mu, only the site near the radical oxygen in a singlet state for the central molecule when the Mu was trapped and the site near bridge nitrogen in a triplet state were found to provide trapping with binding energies of 2.19 and 1.77 eV, respectively.

In trying to identify the trapping site involving μ or Mu which leads to the observed μSR frequency, one might be tempted to consider only the deepest of the five trapping sites found. However, there are two other considerations, the first being that the stronger trapping sites may not be easily approachable for μ or Mu in the solid because those sites may not be well exposed due to steric effects. Second, some of these trapping sites may lead to μSR frequencies larger than the limit of 20 MHz that applies to the technique using pulsed muon sources at KEK-MSL and RIKEN-RAL facilities.[8,17] We have therefore evaluated the μSR frequencies expected from the hyperfine fields for all five trapping sites.

The spin Hamiltonian describing the hyperfine interaction between the muon magnetic moment at a trapped μ or Mu site and the unpaired electrons in the central and other molecules is given by:[11,14]

$$H_S = A\mathbf{I}\cdot\mathbf{S} + \mathbf{I}\cdot\overset{\leftrightarrow}{B}\cdot\mathbf{S}, \tag{1}$$

A and $\overset{\leftrightarrow}{B}$ representing the scalar isotropic Fermi contact and electron nuclear dipolar tensor contributions. The term A and the components B_{ij} of $\overset{\leftrightarrow}{B}$ can be evaluated from available expressions in the literature[11,14] using the UHF electronic wave functions for the central molecule with the trapped μ and Mu and the rest of the molecules, which are bare, without any μ and Mu.

In the ferromagnetic solid, the spins of the central and other molecules all point along the easy axis,[9] whose direction is characterized by the direction cosines (l,m,n) with respect to the X, Y, and Z axes in the monoclinic system, with Z and Y along the c and b axes, respectively, and X in the ab plane, making an angle 14.04° with the a axis. The components H_i ($i=x,y,z$) of the hyperfine field at the muon for a particular site for the trapped μ or Mu can be expressed in terms of the contributions A_k and $B_{k,ij}$ from the various molecules k in the lattice.[7,11,14] For instance, H_x is given by

$$H_x = \left(\frac{2\pi\hbar I}{\mu_N}\right)\left[\sum_k S_k\{l(A_k + B_{k,xx}) + mB_{k,xy} + nB_{k,xz}\}\right], \tag{2}$$

with $k=0$ referring to the contributions from the central molecule and $k\neq0$ from the rest of the molecules. In Eq. (2), μ_N is the muon magnetic moment, $I=1/2$ its spin, S_k is the electronic spin, 1/2 for trapped μ, and 0 and 1 for trapped Mu in singlet and triplet states for the central molecule. For the other molecules, leading to intermolecular contributions, $S_k=1/2$ for the hyperfine field at the muon in both trapped μ and Mu in the central molecule and A is negligible at the muon in the trapped μ or Mu sites in the central molecule. The summations in k in Eq. (2) were carried out over spheres of radii upto 40 Å, centered around the muon, to test convergence, with those molecules, for which the NO groups that mainly carry the unpaired electrons are completely within the sphere of summation being included and others dropped. The convergence, tested by comparing the results for radii 35 and 40 Å for the summation spheres, was found to be better than 0.1%.
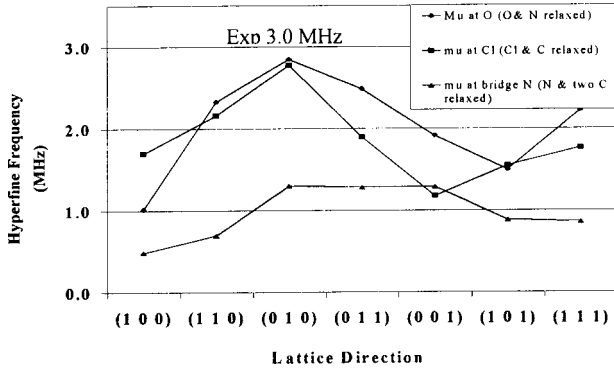
FIG. 3. Plot of the hyperfine frequencies of the muon for two trapped muon and one trapped muonium sites as a function of lattice direction in the (X,Y,Z) reference frame, described in the text.

Because of the lightness of the muon (about 9 times lighter than proton), one has to carry out an average of its properties like the hyperfine field components in Eq. (2) over its vibrational motion[11] using the equation

$$\langle O \rangle = \int \psi_v^2(\mathbf{R}) O(\mathbf{R}) d^3 R, \tag{3}$$

$O(\mathbf{R})$ leading a muon property dependent on its position and $\psi_v(\mathbf{R})$ the vibrational wave function corresponding to the potential experienced by the muon as given by the $\mathbf{R}$-dependent total energy of the cluster system. In principle, one needs to carry out a three-dimensional average in Eq. (3). However, intuitively, in a system like the present one where the Mu or μ is attached to an atom in the periphery of a molecule, one expects the longitudinal vibration to have the most effect. From our investigations, the longitudinal vibration for Mu and μ was found to lead to a less than 3% effect for all five trapped sites, suggesting that vibrational effects were not important.

Of the five μ or Mu trapped centers, two, corresponding to μ near radical O and Mu in the triplet state attached to the bridge N (Fig. 1), were ruled out because the μSR frequencies for them, from the magnitudes of A and B_{ij}, were found to be, respectively, more than 100 and 20 times larger than the experimental value[8] of 3.0 MHz. Figure 3 represents the calculated μSR frequencies, using $\nu = (\mu_N/2\pi I\hbar)(H_x^2 + H_y^2 + H_z^2)^{1/2}$, for the remaining three trapping centers, namely, μ near Cl and bridge N sites and Mu in the singlet state near radical O, for different choices of the direction for the easy axis.

From Fig. 3, the best agreement between the theoretical and experimental[8] μSR frequencies is found for both the Mu in singlet state near the radical oxygen and μ attached to Cl, the μSR frequencies for μ near bridge N being about a factor of 2 smaller than experiment. It would be helpful to have some other technique to distinguish between the two centers that can explain the observed μSR frequency. One possibility is to study the nuclear quadrupole interactions of the ^{35}Cl and ^{17}O nuclei in the presence of μ and Mu using avoided level crossing measurements[18] and compare with theoretical

predictions.[19] However, both these trapping sites lead to the same easy-axis direction close to the (010) or b axis in the monoclinic lattice.

As regards the two high-frequency μSR signals associated with μ trapped near the radical oxygen and Mu in the triplet state near the bridge nitrogen, there is some evidence for their presence from the missing fraction in our experiment,[8,17] although one cannot be sure about the occurrence of two frequencies. Our missing fraction is rather low, suggesting that the high-frequency signals not observed would have rather small amplitudes and would be very difficult to observe in longitudianl field repolarization measurements.[2]

We have tested this conclusion for the easy axis, from μSR data, by an independent method involving the dipole-dipole interaction between the distributed magnetic moments on the individual molecules in the solid. In earlier work[10] on similar chemical ferromagnets as the TEMPO system under study here, investigations of the easy-axis direction have been carried out assuming that the dipole-dipole interaction occurs between magnetic moments localized on a single atom in each molecule. Our results for the electronic structure of the present system, combined with the Mulliken approximation[20] for the spin populations on the atoms, shows that the spin distribution is in fact somewhat delocalized, with the radical O and N atoms carrying $0.74\mu_B$ and $0.31\mu_B$, respectively, the balance of $-0.05\mu_B$ being distributed over the rest of the atoms. Using the energy expression

$$E_{\text{dip-dip}} = \sum_{i=1}^{n} \boldsymbol{\mu}_{ci} \cdot \sum_{d \neq c} \sum_{j=1}^{n} \left\{ \frac{\boldsymbol{\mu}_{dj}}{R_{ci,dj}^3} - \frac{3\mathbf{R}_{ci,dj}(\boldsymbol{\mu}_{dj} \cdot \mathbf{R}_{ci,dj})}{R_{ci,dj}^5} \right\}, \tag{4}$$

for the dipole-dipole interaction in the ferromagnetic state between a particular (central) molecule and the others in the solid, where $\boldsymbol{\mu}_{ci}$ represents the magnetic moment on atom i in the central molecule and $\boldsymbol{\mu}_{dj}$ that on atom j in the molecule d in the solid, the values of n in the summations over i and j being just 2, for the radical N and O in each molecule. In the ferromagnetic state, the magnetic moments $\boldsymbol{\mu}_{ci}$ and $\boldsymbol{\mu}_{dj}$ on all the atoms point in the same direction: namely, the easy axis.[9]

To determine the direction of the easy axis we have to obtain its polar and azimuthal angles θ and φ in the coordinate system (X,Y,Z) described earlier in connection with the direction of the hyperfine fields at the muon in the trapped μ and Mu sites. We have therefore minimized $E_{\text{dip-dip}}$ with respect to θ and φ. For this purpose, the summations over the molecules d in Eq. (4) were carried out, for the O and N atoms ($i=1,2$) on the central molecule c, over spheres of 40 Å radii, centered on the two atoms, similar to the procedure used in the evaluation of the intermolecular contributions to the components of the hyperfine tensors $\vec{B}$ at the muons. The minimum in $E_{\text{dip-dip}}$ was found to be in the direction $\theta = \varphi = 90°$, which is along the b axis, in agreement with the analysis of the hyperfine fields at the muon positions. The accuracy of θ and φ obtained from $E_{\text{dip-dip}}$ has been estimated at better than 1% from the following considerations. The convergence of the summations over the 40 Å spheres used

in Eq. (4) was found to be better than 0.1%. The confidence limit due to the use of point dipoles at radical N and O in Eq. (4) was expected to be comparable to that found for the similar summation in the case of the components of $\vec{B}$ at the muons, where the results using the entire calculated magnetic moment distributions from our electronic structure investigations discussed earlier agreed within 1% of that using two point dipoles at radical O and N atoms as in Eq. (4). It would be interesting to test the nature of this agreement between these two types of summation in the case of systems where the magnetic moment distribution is more diffuse than in the present TEMPO system.

The good agreement between the easy-axis directions by the two procedures involving minimization of $E_{\text{dip-dip}}$ and the comparison between the theoretical and experimental μSR frequencies provides confidence in the accuracies of both procedures. This good agreement also suggests that in the organic ferromagnets, the mechanism involving spin-orbit interactions[9] is not as significant in influencing the easy-axis direction as the dipole-dipole interaction mechanism, which is not unexpected since there are no iron-group atoms with strong spin-orbit interactions.

Finally, the good agreement found in this work between the measured μSR frequency and theory testifies to the accuracy of the calculated electronic wave functions. It would therefore be interesting in the future to use the electronic structure results from first-principles cluster methods to examine quantitatively the predicted Curie temperatures for the onset of ferromagnetism from both indirect exchange[4,5] and dipolar[6] mechanisms to test their relative importance in this class of organic ferromagnet systems involving weak intermolecular interactions. The results of such an investigation will also throw light on the mechanisms for the origin of the ferromagnetism or antiferromagnetism in materials of great current interest involving localized clusters of transition-metal atoms widely separated from each other by organic molecular systems.[3,21]

[1] L. P. Le, A. Keren, G. M. Luke, W. D. Wu, Y. J. Uemura, M. Tamura, M. Ishikawa, and M. Kinoshita, Chem. Phys. Lett. **206**, 405 (1993).

[2] S. J. Blundell, P. A. Pattenden, F. L. Pratt, R. M. Valladares, T. Sugano, and W. Hayes, Europhys. Lett. **31**, 573 (1995).

[3] See, for example, D. Gatteschi, P. Carretta, and A. Lascialfari, Physica B **289-290**, 94 (2000) and references therein.

[4] M. Yasui, H. Yoshikawa, H. Yamamoto, T. Ishida, T. Nogami, and F. Iwasaki, Mol. Cryst. Liq. Cryst. Sci. Technol., Sect. A **279**, 77 (1996).

[5] T. Nogami, T. Ishida, M. Yasui, F. Iwasaki, N. Takeda, M. Ishikawa, T. Kawakami, and K. Yamaguchi, Bull. Chem. Soc. Jpn. **69**, 1841 (1996).

[6] See, for example, R. Bersohn and T. P. Das, Phys. Rev. **130**, 2070 (1961) and references therein.

[7] A brief report about the muon and muonium sites in the present system is presented in Proceedings of the VIII μSR Conference, Les Diablerets, 1999 [Junho Jeong, Tina M. Briere, N. Sahoo, T. P. Das, Seiko Ohira, K. Nishiyama, and K. Nagamine, Physica B **289-290**, 132 (2000)].

[8] Takayuki Ishida, S. Ohira, Tomoaki Ise, Kensuke Nakayama, Isao Watanabe, Takashi Nogami, and Kanetada Nagamine, Chem. Phys. Lett. **330**, 110 (2000).

[9] Charles Kittel, *Introduction to Solid State Physics*, 2nd ed. (Wiley, New York, 1956), p. 428.

[10] Tohru Kawamoto and Naoshi Suzuki, J. Phys. Soc. Jpn. **63**, 3158 (1994).

[11] N. Sahoo, S. K. Mishra, K. C. Mishra, A. Coker, T. P. Das, C. K. Mitra, and L. C. Snyder, Phys. Rev. Lett. **50**, 913 (1983); N. Sahoo, S. B. Sulaiman, K. C. Mishra, and T. P. Das, Phys. Rev. B **39**, 13 389 (1989).

[12] A. Szabo and N. S. Ostlund, *Modern Quantum Chemistry* (McGraw-Hill, New York, 1982); *Electronic Properties of Solids Using Cluster Methods*, edited by T. A. Kaplan and S. D. Mahanti (Plenum Press, New York, 1995).

[13] M. J. Frisch *et al.*, Computer code GAUSSIAN 98, revision A.6, Gaussian Inc., Pittsburgh, PA, 1998.

[14] See, for example, Refs. 16, 72, and 75–82 in article by T. P. Das, in *Electronic Properties of Solids Using Cluster Methods* (Ref. 12), pp. 1–28.

[15] R. E. Watson and A. J. Freeman, in *Hyperfine Interaction*, edited by A. J. Freeman and R. B. Fraenkel (Academic Press, New York, 1967); G. D. Gaspari, Wei-Mei Shyu, and T. P. Das, Phys. Rev. **134**, A853 (1964).

[16] M. I. J. Probert and A. J. Fisher, J. Phys.: Condens. Matter **9**, 3241 (1997); **9**, 3635 (1997); R. M. Valladeres, A. J. Fisher, S. J. Blundell, and W. Hayes, *ibid.* **10**, 10 701 (1998).

[17] S. Ohira, Master's thesis, University of Tokyo, 1997.

[18] R. F. Kiefl, Hyperfine Interact. **32**, 707 (1996).

[19] Junho Jeong, Tina M. Briere, N. Sahoo, T. P. Das, S. Ohira, K. Nishiyama, and K. Nagamine, Z Naturforsch. A (to be published).

[20] R. S. Mulliken, J. Chem. Phys. **23**, 1833 (1955).

[21] S. J. Blundell, F. L. Pratt, T. Lancaster, I. M. Marshall, C. A. Steer, W. Hayes, T. Sugano, A. Caneschi, D. Gatteschi, J. F. Letard, and S. L. Heath, in Proceedings of the Ninth International Conference on μSR, Williamsburg, Virginia, 2002 [Physica B (to be published)].