Theory of Nuclear Quadrupole Interactions of ^{14}N, ^{17}O, and ^{35}Cl Nuclei in *p*-Cl-Ph-CH-N=TEMPO

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Z. Naturforsch. **57a,** 527–531 (2002); received May 17, 2002

Presented at the XVIth International Symposium on Nuclear Quadrupole Interactions, Hiroshima, Japan, September 9–14, 2001.

The nuclear quadrupole coupling constants and asymmetry parameters have been studied for the ^{35}Cl, ^{17}O, and ^{14}N nuclei in the molecular ferromagnet 4-(*p*-chlorobenzylideneamino)-TEMPO (2,2,6,6-tetramethyl-piperidin-1-yloxyl) using elctronic stuctures obtained by the Hartree-Fock procedure for the bare system and systems with trapped muon and muonium. Trends in the sizes of the coupling constants and asymmetry parameters for the various nuclei have been studied, and possible physical explanations have been proposed. For the systems with trapped muon or muonium, very substantial influences of the muon and muonium on the coupling constants and asymmetry parameters for the nuclei close to the trapping sites have been observed. The coupling constants and asymmetry parameters are found to be very different for the various nuclei, for the two cases where muon is trapped near chlorine and muonium near oxygen, indicating that, if experimental data were available to compare with theory, one could make conclusions about which of these two centers is responsible for the observed muon spin rotation frequency associated with the muon magnetic hyperfine interactions in these two trapped systems

Key words: Chemical Ferromagnet; Nuclear Quadrupole Interactions; Hartree-Fock Theory.

1. Introduction

The subject of chemical ferromagnet is of great current interest, especially the origin of their observed ferromagnetism [1, 2] with very low Curie temperatures [1, 3] and the factors [4, 5] that determine the directions of their easy axes. One of the chemical ferromagnets that is the subject of substantial experimental and theoretical investigations is the molecular solid *p*-Cl-Ph-CH=N-TEMPO abbreviation for 4-(*p*-chlorobenzylideneamino)-TEMPO (2,2,6,6-tetramethyl-piperidin-1-yloxyl) (Fig. 1) which has a Curie temperature of 0.4 K from magnetic measurements [1, 3]. Recent muon spin rotation (µSR) measurements [6] have led to a µSR frequency of 3.0 MHz extrapolated to 0 K in the ferromagnetic state. Concurrent electronic structure investigations [7] using first principle Hartree-Fock procedure have shown that the observed µSR frequency could be explained either by a muon trapped near the chlorine atom in this compound or by a trapped muonium near the oxygen of the N-O radical group with the trapped muonium radical system in a singlet state. The easy axis has been determined from this analysis as pointing along the b-axis of the monoclinic lattice. Theory has also shown [5] that this direction of the easy axis can be explained by the magnetic dipole-dipole interactions between the individual molecules (free radicals with spin 1/2).

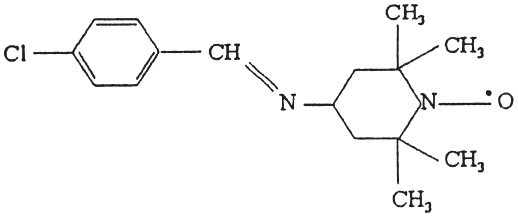

Fig. 1. The *p*-Cl-Ph-CH=N-TEMPO molecule.

Our present investigations of the nuclear quadrupole interactions (NQI) in the *p*-Cl-Ph-CH=N-TEMPO were motivated with three aims in mind. The first is to subject the results of our earlier electronic structure investigations [5, 7] to further test, since NQI parameters are determined by the anisotropy in the charge distribution rather than the spin distribution with determines the magnetic hyperfine properties. The second aim is to study how the charge distribution in the system is influenced by trapping of the muon or muonium leading to changes in the NQI parameters for the various nuclei, the main nuclei of interest here being ^{17}O, ^{14}N, and ^{35}Cl. The third aim is to study differences in the NQI parameters for these three nuclei for the two cases corresponding to the trapping of muon near chlorine and of muonium near oxygen, to assist future experimental measurements to determine which of these two situations is the one responsible for the observed μSR frequency.

2. Procedure

The electronic charge distribution, needed for the evaluation of the NQI parameters for the ^{14}N and ^{17}O nuclei of interest in the present investigation, was obtained from the electronic structure results calculated by the Hartree-Fock-Roothaan variational procedure [8] for the individual molecules (Fig. 1) in the molecular solid *p*-Cl-Ph-CH=N-TEMPO, as discussed in our earlier work [7] in this molecule dealing with magnetic hyperfine effects associated with trapped muon (μ) and muonium (Mu). Using the calculated occupied state electronic wavefunctions [7], the contributions to the electric field gradient tensor components from within the molecule containing the nucleus under study, the intramolecular contribution, are obtained using the expression [8]

$$V_{ij} = -e \sum_{\mu} \left\langle \psi_\mu \left| \frac{3 r_i r_j - r^2 \delta_{ij}}{r^5} \right| \psi_\mu \right\rangle + e \sum_{N} \frac{z_N (3 R_{iN} R_{jN} - R_N^2 \delta_{ij})}{R_N^5}, \qquad (1)$$

where $r_i\,(r_j)$ are the X, Y and Z components of the position vector $\boldsymbol{r}$ of an electron with respect to the nucleus under study and $R_i\,(R_j)$ are the corresponding components of the position vectors $\boldsymbol{R}_N$ of the various nuclear charges in the molecule. The electronic wavefunctions ψ_μ refer to the occupied states of the electrons in the molecule. Since the individual molecules carry spin 1/2 in the absence and presence of a muon, the Unrestricted Hartree-Fock Procedure [9] has been used before for the electronic structure investigation. The difference between the wavefunctions of paired spin states referring to spins parallel or anti-parallel to the unpaired spin of the valence states in the individual molecules is not so important in the present investigation because the sums of the contributions from opposite spins occurs in (1) in contrast to the difference characterizing exchange core polarization effects for magnetic hyperfine interactions. For the singlet state involving trapped Mu, there is no unpaired spin valence state and hence no difference between the wavefunctions for paired spin states with opposite spin and the Restricted Hartree-Fock approximation [5] has to be used.

For the intermolecular contributions to the electric field gradients at the nculei, we have followed a similar procedure as that adopted in our earlier work [5, 7] on the magnetic hyperfine interactions at the muon in trapped μ and Mu sites. Thus

$$V_{ij}\ (\text{Intermolecular}) = \sum_{n \neq 0} V_{ij}\,(n), \qquad (2)$$

where the summation over n refers to the molecules surrounding the central molecule (corresponding to $n = 0$) which contains the ^{14}N, ^{17}O, and ^{35}Cl nuclei for which the NQI parameters are being calculated. For testing the convergence in the sum over n, we have carried out the summation over spheres of different radii centered around the nuclei in the central molecule. For magnetic dipole hyperfine interaction investigations [5, 7], a radius of 40 Å was found to be appropriate and is expected to apply for our NQI investigation, since it involves similar dependences over electronic and nuclear coordinates.

The EFG calculations at the nuclei in the central molecule with trapped muon and muonium at the five sites where trapping has been found [5, 7] were calculated by the same procedure as for the system with no muon or muonium trapping using (1) and (2) and electronic wavefunctions ψ_μ obtained for trapping at different sites. Our major interest is of course in checking which of the two centers [5, 7], μ trapped near chlorine or trapped Mu in singlet state is the appropriate one to associate with the observed μSR signal, by comparing the calculated NQI parameters for these two centers with the experimental parameters which may become available in the future. However, it will also be useful to examine the NQI parameters associated with the bridge nitrogen to see if they indeed disagree with experimentally measured values and one can completely rule out the trapped μ near the bridge nitrogen as a candidate for the observed μSR signal as has been found from earlier analysis of magnetic hyperfine interactions [5, 7]. We are also interested in the other two centers namely, μ trapped near the radical oxygen and Mu in triplet state trapped near the bridge nitrogen to study the natures of the changes in the NQI parameters of ^{17}O in radical oxygen and ^{14}N in bridge nitrogen with those obtained when Mu is trapped near the radical oxygen and μ is trapped near bridge nitrogen. This will enhance the physical understanding of the nature of the electron distributions for all five trapped μ and Mu systems.

3. Results and Discussion

We present first our results for the NQI parameters for the ^{14}N, ^{17}O, and ^{35}Cl nuclei in *p*-Cl-Ph-CH=N-TEMPO without any trapped μ and Mu. Table 1 shows our results for the principal components of the EFG tensor, the nuclear quadrupole coupling constants (e^2qQ) and asymmetry parameters (η) for the four nuclear sites of interest in the present work. The nuclear quadrupole moments used for ^{14}N, ^{17}O, and ^{35}Cl are respectively 0.0193, 0.0258 and 0.0822 barns [10]. The results include intra-molecular and inter-molecular contributions. However, for all four nuclear sites that we have studied, the inter-molecular contributions to e^2qQ have been found to be less than 0.1% and to η less than 0.2%. In particular, in the case of the radical oxygen site, the ^{17}O nuclear quadrupole coupling constant from purely intra-molecular contributions is 15.309 MHz as compared to 15.314 MHz from Table 1 including inter-molecular contributions. The corresponding results for η are respectively 0.4837 (Table 1) and 0.4845 with and without inter-molecular contributions included.

The trends in the e^2qQ and η among the four nuclear sites in Table 1 can be understood from an examination of both the corresponding nuclear quadrupole moments [10] and the principal EFG tensor components. Thus for e^2qQ, the larger value for the ^{35}Cl nucleus as compared to the ^{17}O and ^{14}N nuclei can be understood by the much larger value of Q [10] and also the principal EFG components. The larger values for the latter have to do with both the differences in symmetry and the sizes between the chlorine and the other two atoms. Thus the chlorine atom being a larger atom, the valence orbitals involve 3p orbitals which are less shielded than the 2p orbitals in oxygen and nitrogen leading to larger expectation values $\left\langle \frac{1}{r^3} \right\rangle$ for the chlorine orbitals than for the other two atoms [11]. Secondly; Fig. 1, the Cl atom is at one end of the molecule in contrast to the radical and bridge nitrogen atoms and also has less double-bond character because of the greater mismatch in its size with its neighboring carbon than between oxygen and its nearest neighbor, the radical nitrogen and the bridge nitrogen and its nearest neighbor carbon atom. The combination of these latter factors leads to greater departures from spherical symmetry for the chlorine atom and hence larger field gradient. The smaller double bond character expected for chlorine also leads to the weaker departure of the charge distribution from axial symmetry and hence much smaller η in Table 1 .

Table 1. Nuclear quadrupole coupling constants and asymmetry parameters for the ^{14}N, ^{17}O, and ^{35}Cl nuclei in *p*-Cl-Ph-CH=N-TEMPO in ferromagnetic state.

Nuclear site	V_{zz}	V_{yy}	V_{xx}	e^2qQ (MHz)	η
Radical ^{14}N	1.061	–0.746	–0.315	4.807	0.408
Radical ^{17}O	2.526	–1.875	–0.651	15.314	0.484
Bridge ^{14}N	1.097	–0.767	–0.331	4.971	0.397
^{35}Cl	3.654	–1.891	–1.763	70.280	0.035

The smaller but significant differences between ^{17}O and ^{14}N in e^2qQ in Table 1 are also understandable from some of the similar considerations as for ^{35}Cl. Thus the ^{17}O nucleus has a quadrupole moment about 30% higher [10] than the ^{14}N nucleus, in the right direction for the larger e^2qQ. However, the bulk of the difference arise from symmetry considerations, the oxygen atom being like chlorine at one end of the molecule. The double bond characters are comparable and larger than for the Cl atom both as expected from the similar sizes of the N and O atoms and their neighbors, Fig. 1, and from the Mulliken populations [12] we have obtained from our calculated electronic structures. The larger double bond characters lead to the substantially larger asymmetry parameters found (Table 1) for the ^{14}N and ^{17}O sites. It would be very helpful to have measured values of the e^2qQ and η for the ^{35}Cl, ^{14}N, and ^{17}O nuclei to compare with the results in Table 1 and have a more quantitative test of our calculated [5, 7] electronic distributions.

In Table 2, we have tabulated our results for the NQI parameters for the nuclei in the atoms which bind the μ or Mu at all the five trapping situations found in our earlier work [5, 7], namely μ bound to radical O, bridge N and Cl (Fig. 1) and singlet Mu bound to the radical O

Table 2. Nuclear quadrupole coupling constants and asymmetry parameters in *p*-Cl-Ph-CH=N-TEMPO in presence of trapped Mu and μ in ferromagnetic state for the ^{14}N, ^{17}O, and ^{35}Cl nuclei nearest and next nearest to the trapping sites.

Nuclear site	e^2qQ (MHz)	η
Radical ^{14}N[a]	7.970	0.658
Radical ^{17}O[a]	13.577	0.964
Radical ^{14}N[b]	3.340	0.260
Radical ^{17}O[b]	14.517	0.622
Bridge ^{14}N[c]	1.903	0.343
Bridge ^{14}N[d]	5.575	0.378
^{35}Cl[e]	59.916	0.790

[a] Mu (singlet) trapped near O;
[b] μ trapped near O;
[c] μ trapped near bridge N;
[d] Mu (triplet) near bridge N;
[e] μ trapped near Cl.

Table 3. Nuclear quadrupole coupling constants and asymmetry parameters for the ^{14}N, ^{17}O, and ^{35}Cl nuclei in *p*-Cl-Ph-CH=N-TEMPO in ferromagnetic state in presence of trapped Mu near oxygen and μ near chlorine.

Nucleus		Trapping site	
		μ near ^{35}Cl	Mu near ^{17}O
^{35}Cl	e^2qQ[a]	59.687	70.091
	η	*0.790*	*0.034*
Bridge ^{14}N	e^2qQ[a]	5.492	5.002
	η	*0.654*	*0.421*
Radical ^{14}N	e^2qQ[a]	5.004	7.970
	η	*0.375*	*0.658*
Radical ^{17}O	e^2qQ[a]	15.518	13.583
	η	*0.457*	*0.964*

[a] In MHz.

and triplet Mu to the bridge N. We have also shown in Table 2 the ^{14}N NQI parameters for the radical N in the NO groups for Mu and μ bounded to radical O, because they involve comparable changes in going from the molecule to the cases when μ and Mu are trapped by radical O. We have also presented in Table 3, the e^2qQ and η for the ^{35}Cl, ^{14}N (for bridge and radical sites) and ^{17}O for the two cases where μ is trapped near Cl and Mu is trapped near O. From Tables 2 and 3, it can be seen that in the two typical cases of Mu trapped by the radical oxygen and μ trapped by the chlorine atom, other than the radical ^{14}N in the former case, the changes in the NQI parameters as compared to the bare systems are pronounced only at the nuclei of the atoms which trap the μ or Mu. Thus, the influence of the trapped μ or Mu appears to be quite short ranged. The comparable influence for the radical ^{14}N and ^{17}O nuclei for μ and Mu trapped by the radical oxygen is to be expected because of the strong bonding between the two neighboring atoms (Figure 1). In fact, one would expect similar comparable influences of μ and Mu bonding to the bridge nitrogen and its nearest neighbor atom and for μ bonding to the chlorine atom. However, the neighboring atoms in both these cases are carbons with ^{12}C or ^{13}C nuclei, which have zero spin and spin 1/2 respectively with zero quadrupole moments and even through the EFGs at these nuclei are expected to be comparable to their neighbors, it would bot be possible to observe them experimentally.

Finally, from Table 3, it is clear that the NQI parameters for ^{35}Cl, ^{14}N, and ^{17}O nuclei are very different for μ trapped at a site near the chlorine atom and Mu trapped in a singlet state at a site near the radical oxygen. As mentioned earlier, from our previous work [5, 7] these two sites appear to be the ones that can explain the observed μSR frequency [6] in *p*-Cl-Ph-CH=N-TEMPO. If the NQI parameters associated with these two trapping sites for μ and Mu could be observed by any special technique or analysis associated with the μSR signal, then it would be possible to decide which is the more likely site to explain the observed μSR frequency. Further, of additional μSR signals are observed in the future, it well help in the assignment of the μ or Mu trapping site responsible for these signals, if the associated NQI in Table 2 or similar NQI of the other nuclei than the immediate neighboring nuclei (already available in Table 2) for the other three trapping sites [5, 7] could be observed and compared with theoretical predictions.

4. Conclusions

Our analysis of the bare molecule and molecules with trapped Mu and μ shows that NQI's in these systems are rather sensitive to the electron distributions and provide a good description of the latter. The contributions to the NQI parameters are found to be almost entirely intramolecular in nature for both the bare system and systems with trapped μ and Mu.

For the bare system, the e^2qQ for ^{35}Cl seems to be the highest, followed by ^{17}O and the ^{14}N, the radical and bridge ^{14}N having very similar values. For η, on the other hand, the values are relatively large and comparable for ^{14}N and ^{17}O nuclei, while for ^{35}Cl, η is rather small. Possible reasons for these trends from physical considerations are pointed out. It would be helpful to have experimental results to verify these trends and compare them with the theoretical predictions.

The influence of μ and Mu on e^2qQ and η are found to be short ranged, mainly extending to the nucleus next to μ and Mu and also the next nearest neighbor. There is no particular trend as to whether the influence of μ or Mu is larger on the neighboring nuclei, showing that the electron distribution is significantly and comparably, affected by both μ and Mu.

For μ trapped near Cl, and Mu trapped near oxygen, due to the short range influence of the μ and Mu, the e^2qQ and η at the nuclei in the molecules are very different. So, if these parameters could be measured by some sophisticated technique related to μSR, one could reach conclusions about which of these centers is responsible from the analysis of muon magnetic hyperfine interaction [5, 7].

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