Ab initio Study of Nitrogen-14 Nuclear Quadrupole Coupling and NMR Signal Linewidths in Some Azoles*

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Ab initio values of Nitrogen ^{14}N Nuclear Quadrupole Coupling Constants (NQCC's) are calculated for a series of methyl-substituted azoles in the Multiconfigurational SCF (MCSCF) approximation. The four triazoles and two tetrazoles studied here are all isoelectronic. This enabled us to use the same level of approximation – basis set and active space – for all the molecules. The computed NQCC's are used to estimate the relative widths of the ^{14}N NMR signals, assuming an identical effect of molecular tumbling for all the nuclei in a molecule and neglecting solvent effects. The linewidths for the unsubstituted N atoms are, in agreement with experiment, much larger than for the methyl-substituted N atom. For the 1-methyl-tetrazole we present also the NMR shielding and spin-spin coupling constants and discuss in some more detail the dependence of all calculated NMR properties on the basis set and correlation effects.

Key words: ^{14}N NQCC, Azoles, MCSCF, *Ab initio*, Electron Correlation.

1. Introduction

In recent years, noticeable progress has been made in *ab initio* calculations of the molecular properties that characterise NMR spectra. With the application of magnetic gauge-origin independent methods, the determination of ever more accurate shielding constants has become possible. Using linear response approaches which include the effects of electron correlation, also the calculation of spin-spin coupling constants has become feasible.

The calculation of Nuclear Quadrupole Coupling Constants (NQCC's) is in principle simpler than the calculation of the shieldings or spin-spin coupling constants, since it requires only the knowledge of the unperturbed wave function. For each nucleus, the NQC tensor is proportional to the Electric Field Gradient (EFG) and to the quadrupole moment of the nucleus. For small molecules, the measurement of the NQCC's coupled to the extremely accurate calculation of the EFG has been used to determine the value of the Nuclear Quadrupole Moment [1 -3]. In some cases, also the dependence on rovibrational levels [4] or a perturbing electric field – simulating the environment in a crystal [5] – was studied.

A variety of *ab initio* methods which include correlation effects may nowadays be applied to compute NQCC's for polyatomic systems. The following relatively short list is intended to illustrate some recent applications. Palmer's studies have involved the SCF and Møller-Plesset Second Order Perturbation Theory (MP2) calculation of NQCC's in a number of molecular systems [6 - 10]. NQCC's of various nuclei have been studied using the Møller-Plesset Fourth Order Perturbation Theory including Singles, Doubles and Quadruples (MP4(SDQ)) by Huber and co-workers [11-14]. Recently, Density Functional Theory (DFT) techniques were used to compute the NQCC's (see e. g. [15, 16]). Different methods have been compared in calculations of formamide [17]. For the ^{14}N NQCC's, it was observed that MP2 overshoots the correlation effects when compared with presumably more accurate Coupled Cluster with Double substitutions (CCD, also known as QCID) [18], and Quadratic

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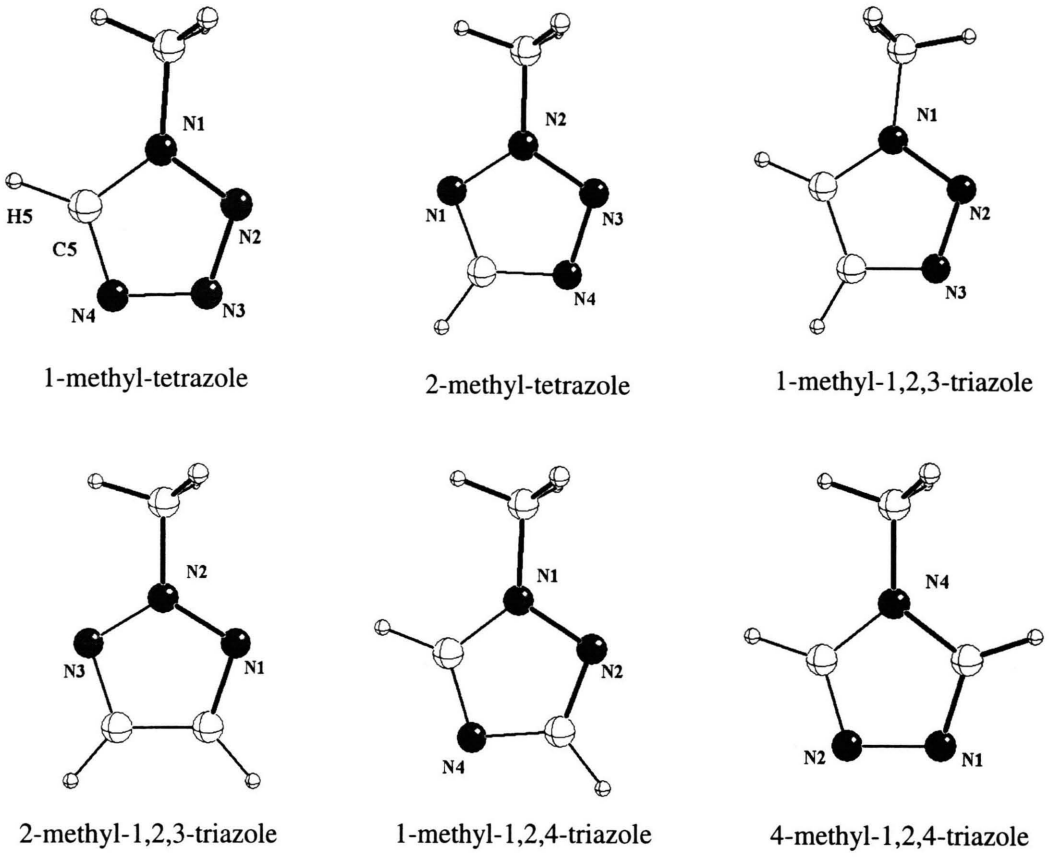

Fig. 1. The azoles studied in this work.

CI (QCISD) [19] values, while various Restricted Active Space SCF (RASSCF) [20] results yield a smaller correlation correction (see also [10] for results for formamide).

Ab initio calculations of NQCC's have also been performed recently on molecular clusters [21, 22] at the SCF level of theory, and on solids, by Schwartz and co-workers employing DFT [23], and by Palmer within the SCF approximation [24 - 26].

Cremer and Kruger [27] compared calculated EFG and measured NQCC's for a series of molecules – both small and large – containing ^{14}N. Using the more accurate results for small molecules, they determined an "effective quadrupole moment" for ^{14}N, which they applied to correct the results for larger systems. Similar scaling has been sometimes used for ^{14}N by other authors, see e. g. [6].

Different *ab initio* methods have their advantages and drawbacks in the calculation of NQCC's. In direct SCF calculations very large basis sets can be used; we exploit this feature here. The advantage of variational methods including correlation effects, like Multiconfigurational SCF (MCSCF), is that the EFG tensor is computed as the average value of an operator. In non variational methods, like CCD or Coupled Clusters including Singles and Doubles (CCSD) [28], more complicated equations must be solved, essentially amounting to derivative calculations. On the other hand, even for a molecule of the size of an azole, it is not simple to obtain a balanced description of all the correlation effects in the wavefunction within MCSCF, whereas perturbation theory methods do not favour any chosen orbitals. This may be relevant in a study of properties related to specific atoms. It appears that dynamic correlation effects, usually not easy to describe in MCSCF, are not too important for properties related to nuclear spin such as NMR properties dependent primarily on the electron density close to the nucleus.

Although accurate calculation of EFG's requires the use of correlated wave functions and large basis sets, the main problem often lies in the comparison with experiment. Nuclear Quadrupole Resonance measurements for solids may yield direct information on the EFG tensor, but the difference between a molecule in the solid and the same isolated molecule may be significant. In a standard NMR experiment in solution or in a liquid, the linewidth of the signal depends upon the NQCC's. However it also depends on the molecular tumbling, and extracting accurate information on the EFG tensors from the measured linewidths may be difficult. Accurate experimental results suitable for direct comparison with *ab initio* values are obtained mainly from microwave spectroscopy.

Here we obtain the NQCC's of the ^{14}N nuclei of six triazoles and tetrazoles by computing the EFG tensor with MCSCF wave functions. The molecules are:

1-methyl-tetrazole; 2-methyl-tetrazole;
1-methyl-1,2,3-triazole; 2-methyl-1,2,3-triazole;
1-methyl-1,2,4-triazole; 4-methyl-1,2,4-triazole.

Both the molecules and the numbering of the relevant atoms are shown in Figure 1.

For 1-methyl-tetrazole we have studied in some detail the role of various approximations in the MCSCF wavefunction, and in addition we have employed also MP2. A selected basis set and RASSCF active space were used for all the other molecules. Finally we compare the measured and computed ratio of the quadrupolar relaxation rates for all the Nitrogen atoms.

Relatively old experimental data [29, 30] for the signal linewidths and semiempirical estimates [30] are available for these systems. These estimates are based on the use of the INDO method to obtain bond-order and charge-density matrix elements and of the Townes and Dailey approach [31] to compute the EFG tensors. With the exception of the SCF calculations of Palmer *et al.* [6] for the two tetrazoles, there are to our knowledge no more recent *ab initio* NQCC data for these molecules.

For the 1-methyl-tetrazole system we also present results for the chemical shielding and spin-spin coupling constants (involving ^{15}N). Although different perturbing operators describe various NMR properties, they all probe the electron density close to the nuclei. Therefore it is of interest to see how accurately all these properties – NQCC's, shielding constants and spin-spin couplings – can be reproduced with the same reference MCSCF wavefunction.

In the calculation of the shielding constants we use the Gauge Including Atomic Orbitals (GIAO's), also known as London Atomic Orbitals (LAO's) [32]. The formulation we use is valid for arbitrary approximations to the wave function [33]. GIAO's ensure the gauge invariance of the results of magnetic properties, as well as improving basis set convergence [34].

For the indirect spin-spin coupling constants we have included all coupling mechanisms (Fermi contact – FC, spin-dipole – SD, paramagnetic spin-orbit – PSO – and diamagnetic spin-orbit – DSO) in the calculation [35, 36]. We have calculated all the coupling constants, but we discuss here only those for which experimental data are available for comparison.

2. Theory

2.1. ^{14}N NMR linewidths and NQCC tensors

In ^{14}N NMR spectroscopy the quadrupolar moment of ^{14}N and the resulting signal broadening has always been partly a problem, and partly a way to obtain information on the electronic structure of the molecule. The quadrupolar relaxation rates of ^{14}N nuclei, and the corresponding signal widths, depend on the EFG at the nuclei and on the molecular rotations. Assuming an approximate description of the molecular tumbling and calculating accurate values of the EFG at the nuclei, the signal width in a given molecule can be determined.

We follow the usual assumptions (see e. g. Abragam [37]), and, being interested in relative widths of ^{14}N NMR spectra, we assume isotropic rotation and that the system is described by a single value of the correlation time. Thus for a given nucleus [37]

$$\frac{1}{T_q} = \frac{3}{40}\frac{2I+3}{I^2(2I-1)}\left(1+\frac{\eta^2}{3}\right)\left(\frac{eQ}{\hbar}\frac{\partial^2 V}{\partial z^2}\right)^2 \tau_c, \quad (1)$$

where T_q is the quadrupolar relaxation time, I the nuclear spin, eQ the nuclear quadrupole moment and $\partial^2 V/\partial z^2 = V_{zz}$ the maximum absolute component of the EFG tensor (assumed to be the z component). Finally, η is the asymmetry parameter

$$\eta = \frac{V_{xx} - V_{yy}}{V_{zz}}, \quad 0 \le \eta \le 1, \quad (2)$$

where by definition

$$|V_{zz}| \geq |V_{yy}| \geq |V_{xx}|, \; V_{xx} + V_{yy} + V_{zz} = 0 \qquad (3)$$

and τ_c is the correlation time. Equation (1) is valid in the extremely narrowing regime, which is perfectly adequate for small molecules in non-viscous fluids [37]. Within this set of assumptions the linewidths are proportional to $1/T_q$.

The ratio of the quadrupolar relaxation rates given in Tables II and III has been obtained from (1). Since $1 \leq 1 + \eta^2/3 \leq 4/3$, these ratios are approximately proportional to the square of the ratio of the corresponding NQCC's.

3. Computational Details

All the MCSCF calculations were performed using the DALTON program [38], which was also employed to obtain the Linear Response [39, 40] results for the chemical shieldings and spin-spin coupling constants presented below. The MP2, CCD and QCISD calculations were performed with GAUSSIAN 94 [41].

Geometries were fully optimised at MP2 level using a 6-31G** basis set [42, 43]. For all the molecules we have assumed C_s symmetry. For 1-methyl-tetrazole we have calculated NQCC's for two optimised geometries, corresponding to different arrangement (a 180° rotation) of the methyl group, and found that there is almost no effect on any of the ^{14}N quadrupole coupling constants. In two of the molecules, pairs of N atoms differ only due to the chosen arrangement of the methyl group. Since the calculated NQCC differences are also very small, we have not analysed further the effect of the rotation of the methyl group.

Several sets were employed to study the basis set dependence at SCF level of the properties of the reference system, the 1-methyl-tetrazole. These included the so-called HII, HIII and HIV sets devised by Huzinaga [44]:

- HII: [9s5p1d | 5s4p1d] contracted set for N and C and [5s1p | 3s1p] for H;
- HIII: [11s7p2d | 7s6p2d] for N and C and [6s2p | 4s2p] for H;
- HIV: [11s7p3d1f | 8s7p3d1f] for N and C and [6s3p1d | 5s3p1d] for H.

Test calculations for the N_2 molecule show that even the first Huzinaga HII set furnishes very reasonable results for the Nuclear Quadrupole Coupling Constants of ^{14}N: a CASSCF calculation gives for the largest component $V_{zz} = -1.107328$ au, to be compared to e. g. a Fourth Order Many Body Perturbation Theory – MBPT(4) – value [1] of $V_{zz} = -1.115$ au. or $V_{zz} = -1.1657$ au. in the CCSD calculation of [28]. This and our SCF study of 1-methyl-tetrazole (Table II), together with size and computer cost considerations, appeared to be convincing arguments to employ Huzinaga's HII set for all our electron correlated calculations.

Another option in calculations of the NQCC tensor of a single atom is to use locally dense basis sets [12], but we are interested here in relative linewidths, and in such case it is preferable to run the calculation for all the atoms at the same time.

The occupied SCF orbitals are (in C_s symmetry) 18 A' and 4 A" for all molecules. Four Restricted Active Spaces were employed in the calculations for the 1-methyl-tetrazole. In the following, the notation $(N_i \,/\, N_a) \,/\, \left(n_i^{A'}, n_i^{A''} \,/\, n_{RAS1}^{A'}, n_{RAS1}^{A''} \,/\, n_{RAS2}^{A'}, n_{RAS2}^{A''} \,/\, n_{RAS3}^{A'}, n_{RAS3}^{A''}\right)$ will be employed to denote how the N_i inactive and N_a active electrons are divided within the inactive (i), RAS1, RAS2 and RAS3 spaces. n_k^Γ indicates the number of orbitals of symmetry Γ in the subspace k.

- RAS-A: (20 / 24) / (10, 0 / 8, 0 / 0, 6 / 6, 0). The corresponding CI expansion included ca. 1.25 million determinants.
- RAS-B: (28 / 16) / (14, 0 / 4, 0 / 0, 6 / 6, 0). 320000 determinants. RAS-B was employed only in some calculations of spin-spin coupling constants.
- RAS-C: (22 / 22) / (10, 1 / 8, 0 / 0, 5 / 8, 0). 960000 determinants.
- RAS-D: (22 / 22) / (10, 0 / 8, 0 / 0, 5 / 8, 1). We observe that the extra orbital of A" symmetry in RAS3 was mainly localised on N1. The number of determinants is about 1 million.

A maximum of two holes were allowed in subspace RAS1, while a maximum of two electrons was allowed in subspace RAS3. Of the four wavefunctions described above, only RAS-A was employed in the electron correlated calculations of the NQCC's of the remaining five azoles. RAS-A was also used to compute the chemical shieldings and the dominant contributions to the spin-spin couplings of 1-methyl-tetrazole.

4. Results and Discussion

A comparison of various results for 1-methyl-tetrazole is shown in Table I. For each N atom, the last

Table I. ^{14}N NQCC tensors in 1-methyl-tetrazole (MHz)[a].

		[6]	This Work				
			HII	HIII	HIV	HII	HII
		SCF	SCF	SCF	SCF	MP2	RAS-A
N1	V_{11}	0.591	0.749	0.692	0.608	0.710	0.725
	V_{22}	2.255	2.165	2.193	2.115	1.792	1.895
	V_{33}	−2.846	−2.914	−2.885	−2.723	−2.502	−2.620
N2	V_{11}	−5.221	−5.263	−5.232	−5.250	−4.134	−4.630
	V_{22}	3.993	3.748	3.697	3.596	3.847	3.837
	V_{33}	1.229	1.516	1.535	1.653	0.288	0.793
N3	V_{11}	−4.965	−5.993	−6.035	−6.041	−4.520	−5.090
	V_{22}	3.397	3.186	3.071	3.071	3.499	3.324
	V_{33}	1.569	2.807	2.964	2.970	1.021	1.765
N4	V_{11}	−5.403	−5.293	−5.280	−5.292	−4.553	−4.755
	V_{22}	3.474[b]	3.172	3.161	3.070	2.795	2.980
	V_{33}	1.929	2.121	2.120	2.222	1.758	1.774

[a] The authors of [6] employed eQ = 0.0167 barn. The values in the table have been rescaled using eQ = 0.0202 barn.
[b] Considering the results of [6] for 1H-1,2,3,4 tetrazole, 2-Methyl-tetrazole and our SCF results, we have assumed a misprint in Table 3 of [6] and rearranged the last two tabulated components for the reference data, N4 atom.

component given is the π component of the tensor, one of the principal axes being perpendicular to the plane of the ring. We first compare the SCF results. Even our smallest HII basis set (156 CGTO's) is larger than used in 1980 by Palmer et al. [6]; the largest HIV basis includes 382 CGTO's. Nevertheless, as shown, all the values for N1, N2 and N4 are in good agreement, only for N3 the differences are larger. The differences are not only due to the choice of basis set, since our and the [6] calculations are performed for different geometries.

For all the V_{ii} components of all atoms, the correlation corrections obtained in MP2 and RAS-A approximations have the same sign. They are also always somewhat larger in MP2 than in RAS-A. Considering other numerical results (see e.g. ^{14}N in formamide [17], discussed above), we expect that MP2 overestimates and RAS-A underestimates slightly the influence of electron correlation. Correlation effects reduce the largest V_{zz} components for all the atoms. The effect is relatively small, approximately 10% for each atom. We may thus assume that further improvements in the description of electron correlations would not change very significantly the calculated NQCC's. We have compared the orientation of principal axes in different calculations. The variations were also not very significant and somewhat larger for N3 than for other atoms, when correlation effects were included.

Table II. Relative linewidths for the ^{14}N NMR signal in 1-methyl-tetrazole.

	Basis	N1	N2	N3	N4
SCF [6]		1	3.303	2.856	3.324
SCF	HII	1	3.205	3.925	3.098
SCF	HIII	1	3.189	4.015	3.112
SCF	HIV	1	3.526	4.465	3.455
RAS-A	HII	1	3.350	3.650	3.155
RAS-C	HII	1	3.338	3.613	3.240
RAS-D	HII	1	2.471	2.729	2.426
MP2	HII	1	3.21	3.38	3.18

The relative linewidths of ^{14}N signals computed for 1-methyl-tetrazole are shown in Table II. The linewidths of N1 is chosen to be 1. Again, the SCF results are similar in all the calculations for N1, N2, and N4. The difference for N3 is larger than seen for the NQCC, due to the approximate V_{zz}^2 dependence. The RAS-A, RAS-C, and MP2 results are very similar. In the RAS-D wavefunction we add to the active space a predominantly N1-based orbital, and thus mainly the linewidth for N1 is modified. We note that, in general, the increase of the basis set leads to an increase of the calculated relative linewidths of N2, N3, and N4. The effect of correlation is opposite, which usually means that there is, to some degree, a useful cancellation of errors. Finally, the RAS-A wavefunction, which was chosen for the study of the other azoles, yields results very similar to MP2. Both a CCD and a QCISD calculation – in the 6-31G** basis set – furnished results close to those obtained with the RAS-A or MP2 approximations, indicating stability of the results. The computational complexity of CCD and QCISD and the limitations of our current hardware didn't allow the use of larger basis sets, and even with the 6-31G** set a selection of the orbitals had to be done in order to make the QCISD calculation feasible. We have also performed test calculations using four different MCSCF wavefunctions for 1-methyl-1,2,3-triazole, and the variations of the results are similar to those displayed in Table II.

For the other azoles we discuss only the NMR signal linewidths, since there are no experimental data for their NQCC's. The calculated linewidths for all the ^{14}N signals in the azoles studied here are shown in Table III. The available experimental data we quote are from the end of the seventies [29, 30]. We do not include in the tables their fairly large error bars (see [29, 30]). More recent and precise data [45] indicate

Table III. Relative linewidths for the ^{14}N NMR signal in the triazoles and tetrazoles studied here[a].

		N1	N2	N3	N4
1-methyl-tetrazole	RAS-A	1	3.350	3.650	3.155
	Exp.	1	2.500	2.969	4.219
2-methyl-tetrazole	RAS-A	2.874	1	2.948	3.083
	Exp.	3.763	1	3.118	3.226
1-methyl-1,2,3-triazole	RAS-A	1	3.592	3.692	
	Exp.	1	3.923	3.231	
2-methyl-1,2,3-triazole	RAS-A	2.140	1	2.185	
	Exp.	2.304	1	2.304	
1-methyl-1,2,4-triazole	RAS-A	1	2.612		1.839
	Exp.	1	3.154		1.923
4-methyl-1,2,4-triazole	RAS-A	3.271	3.216		1
	Exp.	3.226	3.226		1

[a] Experimental data from [30] and [29]. Basis set is Huzinaga's HII.

Table IV. Shielding constants in 1-methyl-tetrazole (ppm).

	This work, RAS-A	Exp. abs.[a]	Exp.[b]
N1	50.3	15.55	–151.35
N2	–107.4	–127.51	–8.29
N3	–141.2	–150.09	14.29
N4	–60.2	–87.16	–48.64
C5	63.0	49.5	143.20
C_{Me}	162.5	158.9	33.80
H5	24.7	22.33	8.7
H_{Me}	28.9, 28.6, 28.6	27.13	3.9

[a] Conversion to absolute shielding: $\sigma(N) = -135.8$ (Nitromethane), $\sigma(C) = -192.7$ (TMS), $\sigma(H) = -31.03$ (TMS).
[b] [46].

Table V. Spin-spin coupling constants in 1-methyl-tetrazole[a],[b].

	This work, RAS	Ref. [46]
^1J(C5-H5)	238.4	217.3
^3J(C5-H_{Me})	1.9	2.2
^1J(C_{Me}-H_{Me})	166.4	143.6
^1J(C_{Me}-N1)	–22.1	–10.2
^2J(C_{Me}-C5)	2.8	3.3
^2J(N1-H5)	–7.5	–9.3
^2J(N1-H_{Me})	4.7	2.0
^3J(N3-H5)	–3.0	–3.0
^2J(N4-H5)	–9.5	–12.1

[a] The experimental data do not include the sign, which is attributed here according to the results of our calculations.
[b] For the H atoms of the methyl group we always use averages of three RAS-A values for the FC and DSO contributions, whereas RAS-B values obtained for the in-plane H atom of the methyl group were used for the SD and PSO contributions.

that even more important for comparison with *ab initio* calculations is the very strong solvent dependence of the observed linewidths. It appears that the changes of the experimental results with the solvent may be on the order of 20 - 30%, and therefore we are not going to analyse in detail the differences between our and experimental values for the unsubstituted N atoms. We note good agreement of most of the calculated and experimental values. Considering this and the stability of the results for 1-methyl-tetrazole shown in Table II, we may assume that the largest discrepancies (N4 in 1-methyl-tetrazole and N2, N3 in 1-methyl-1,2,3-triazole) probably reflect inaccuracies of the experiment or solvent effects rather than inadequacy of our calculation of NQCC's.

Our results for the chemical shieldings and for the spin-spin coupling constants in 1-methyl-tetrazole are shown in Tables IV and V. It can be seen from Table IV that for all the groups of atoms – N, C and H –, the calculated shielding differences (relative shifts) are in much better agreement with experiment [46] than the individual values. This indicates that the discrepancies are partly due to the conversion from the chemical shift to absolute shielding scale. Moreover, studies of the solvent dependence of the Nitrogen shielding [45] (including 1-methyl-tetrazole) indicate that variations of more than 10 ppm can be observed in going from one solvent to another. It appears that for N2, N3, and N4 the results are within this range of accuracy, and only the deviation for the methyl-substituted N1 atom is somewhat larger.

The spin-spin coupling constants have been obtained from two calculations. The most important FC contribution (and the simple DSO contribution) have been obtained using both the RAS-A and RAS-B wavefunctions, and we use the values of the RAS-A approximation. The PSO and SD terms, which are much smaller and at the same time much more difficult to compute, were calculated only with the simpler RAS-B wavefunction. The results shown in Table V are in satisfying agreement with experiment. In addition, we can compare the FC contributions from the two calculations, and we find that the differences between RAS-A and RAS-B are important mainly for $^1J(C_{Me}\text{-}N1)$, $^2J(N1\text{-}H_{Me})$ and $^2J(C_{Me}\text{-}C5)$. For each of these constants the step from RAS-B to RAS-A is an improvement, and extrapolation would bring the results into better agreement with experiment [46].

The overall accuracy of the shielding and spin-spin coupling constants seems to be satisfying. For

a molecule of the size of 1-methyl-tetrazole, one can hardly expect much better results. Moreover, the experimental data refer to a very different situation than the *ab initio* values, and temperature and solvent dependence should also be considered. There is no reason to assume that the NQCC results are less accurate since, as mentioned above, the calculation of NQCC's is in principle less demanding than the calculation of other properties.

5. Conclusions

With increasing accuracy of the *ab initio* calculations, theoretical results for NQC tensors and relaxation times are becoming more reliable. Our calculations of ^{14}N NQCC's and signal linewidths in 1-methyl-tetrazole give a good estimate of the dependence of these properties on the description of electron correlation and size of the basis set. The MCSCF wavefunction gives satisfying results for other NMR properties, and we expect similar if not higher accuracies for the NQCC's. More accurate calculations are presently possible – one can, e. g., use basis sets including over a thousand CGTO's and MCSCF expansions including up to 10^7 determinants. However, it appears that what is mainly needed for comparison with experiment is a description of the effects of the environment (see e. g. [17]).

In this work, we have restricted ourselves to calculations for single molecular geometries. Further extensions of theory, which yield an estimate of Nuclear Quadrupole couplings in a liquid, are possible. A good illustration is the study of liquid water and liquid neon by Huber [12], who used molecular dynamics simulations.

Such results can be combined with accurate experimental data from microwave and NMR spectra to analyse the NQC tensors and, once the values for the isolated molecule are known, to estimate and interpret the effects of intermolecular forces in the solution.

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