

A Study of the Nitrogen NMR Spectra of Azoles and their Solvent Dependence

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Ab initio calculated values of the nuclear magnetic shielding constants and nuclear quadrupole coupling constants of nitrogen atoms in azoles are compared with experimental data. The calculations are performed within the multiconfigurational SCF response approach. The solvent dependence of the molecular properties is accounted for, and it is described using solvent response theory. The experimental data for ^{14}N resonance half-height width are reported for a number of different solvents. For both NMR parameters studied, we find a fair agreement of the measured and calculated values. The analysis of the solvent dependence of the shielding constants and quadrupole coupling constants for all the nitrogen atoms shows that the main experimental trends are well reproduced in the calculations.

I. Introduction

The accuracy of ab initio calculation of NMR parameters, such as shielding constants, spin–spin coupling constants, and nuclear quadrupole coupling constants (NQCC) has increased significantly over the past few years (see, e.g., ref 1). Following this progress of theoretical methods, the comparison of calculated NMR parameters and the corresponding experimental data reveals the significance of effects not included in ab initio calculations for isolated molecules. Primarily, for standard NMR data, solvent effects on the NMR parameters are of concern.

Recently, systematic experimental investigation of solvent effects on NMR spectra has become possible. These investigations involve the study of the same molecule in a variety of solvents under similar conditions and this allows the investigators to isolate various aspects of the solvent effects on the molecular property studied.^{2–5}

In the present work, in order to understand the effect of the solvent on NMR parameters, we analyze the shielding constants and NQCC's of the nitrogen atoms in a complete set of parent structures of N-methyl-substituted azoles (see Figure 1). Within this group of molecules we have at our disposal a total of 23 chemically nonequivalent nitrogen atoms and the analysis of their NMR properties, when solvated in a number of solvents, provides a fairly large set of data. Furthermore, Witanowski et al. have reported and discussed the experimental data for the

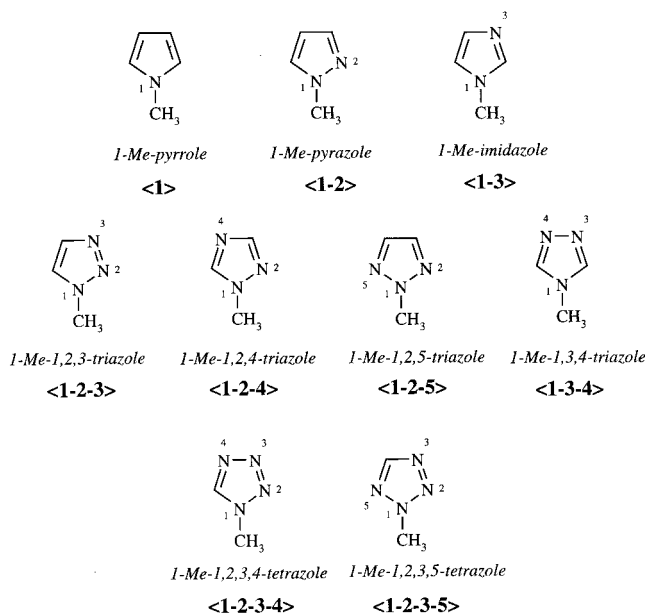


Figure 1. The structure of the studied 1-Me-azoles and the numbering of the nitrogen atoms. The in-plane CH bond of the methyl group is directed toward N2 in (1-2-5) and C2 in (1-3-4).

magnetic shielding in these azoles in refs. 2–5, as well as ab initio calculations at the Hartree–Fock level.⁵ They found that the solvent effects on the nitrogen shielding constants are substantial and distinct for the different nitrogen atoms. Presently, we report also a corresponding set of the experimental data for ^{14}N resonance linewidths for the molecular systems

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concerned in the same set of solvents. Therefore, this choice of compounds is advantageous for comparing experimental and theoretical data and it may improve our understanding of solvent effects on NMR parameters.

We present calculations of nitrogen NMR parameters for the following compounds: 1-methyl-pyrrole, 1-methyl-pyrazole, 1-methyl-imidazole, 1-methyl-1-2-3-triazole, 1-methyl-1-2-4-triazole, 1-methyl-1-2-5-triazole, 1-methyl-1-3-4-triazole, 1-methyl-1-2-3-4-tetrazole, and 1-methyl-1-2-3-5-tetrazole. The numbering of the nitrogen atoms is shown in Figure 1. We use the symbol $\langle k-l \dots \rangle$ for the 1-Me- k - l ...-azole, e.g., $\langle 1-3 \rangle$ stands for 1-methyl-imidazole or $\langle 1-3-4 \rangle$ for 1-methyl-1-3-4-triazole. Attention is drawn to the numbering system adopted (see ref 5), consistent with the numbering system for, e.g., oxazoles and different from the (confusing) system employed sometimes in the literature. Note that, for 1-methyl-1-2-5-triazole, the calculated values for N2 and N5 differ only due to the arrangement of the methyl group (and, similarly, for N3 and N4 in 1-methyl-1-3-4-triazole). Previously, in a similar study,⁶ following ref 7, these compounds were called 2-methyl-1-2-3-triazole, and 4-methyl-1-2-4-triazole, respectively, and a different numbering of atoms was used.

For the ab initio calculations of the electronic structure and molecular properties we use multiconfiguration SCF (MCSCF) wave functions. Since all the molecules studied are isoelectronic, we are able to treat the effects of correlation in all of them at the same level of theory, and obviously we use the same atomic basis set for all the molecules. From these two points, we can safely assume that the ab initio values of the molecular properties for the different molecules are of similar quality. In the present work the solvent effects are computed employing the (multiconfiguration) self-consistent reaction field approach.⁸⁻¹¹ The solvent is described as a dielectric medium, and, what is most important for ab initio studies, a formalism that yields gauge-origin independent shielding constants for solvated molecules has been developed.^{12,13} Recently, other models of the solvent have also been applied to study nitrogen shielding constants,^{14,15} in a different set of molecules.

In section II we briefly outline the theory; sections III and IV give some details on both the experimental procedures and the calculations. The results are discussed in section V, and a final section is devoted to the conclusions.

II. The ab Initio Calculation of NMR Parameters

A. Shielding Constants. The NMR shielding constant is a second-order property, which can be determined by solving linear response equations. For nucleus K , it can be obtained as the second derivative of the energy $E(\mathbf{B}, \mathbf{m})$ with respect to the external field \mathbf{B} and the nuclear magnetic moment \mathbf{m}_K

$$\sigma(K) = 1 + \frac{\partial^2 E(\mathbf{B}, \mathbf{m})}{\partial \mathbf{B} \partial \mathbf{m}_K} \Big|_{\mathbf{B}=\mathbf{m}_K=0} \quad (1)$$

The linear response theory for MCSCF wave functions has been discussed in detail, see, e.g., ref 16. We use the implementation of MCSCF response theory in the DALTON program,¹⁷ and by applying Gauge Invariant Atomic Orbitals (GIAO's), we obtain gauge invariance of the calculated shielding constants¹⁸ (for a review and additional references to recent works, see ref 1).

B. Nuclear Quadrupole Coupling Constants. The dominant relaxation mechanism for quadrupolar nuclei (those with spin larger than $1/2$) is governed by the *nuclear quadrupole*

moment. Upon assumption that the molecular rotation is isotropic, and can be described by a single correlation time τ_c , the line width is proportional to the inverse relaxation time.¹⁹ The half-height width of the resonance signal $\Delta\nu_{1/2}$ can be expressed as

$$\Delta\nu_{1/2} \propto \frac{1}{T_q} = \frac{3}{40} \frac{2I_K + 3}{I_K^2(2I_K - 1)} \left(1 + \frac{\eta_K^2}{3} \right) \left(\frac{eq_K}{\hbar} V_{K,zz} \right)^2 \tau_c \quad (2)$$

where I_K is the nuclear spin, and we denote the electric quadrupole moment of the nucleus as eq_K and the nuclear quadrupole coupling constant is $eq_K V_K$. The components of the *electric field gradient* at the nucleus K , \mathbf{V}_K , are by definition arranged so that

$$|V_{K,zz}| \geq |V_{K,yy}| \geq |V_{K,xx}| \quad (3)$$

and the asymmetry parameter η_K in eq 2 is

$$\eta_K = \frac{V_{K,xx} - V_{K,yy}}{V_{K,zz}} \quad (4)$$

The electric field gradient at the nucleus K is the property obtained from the ab initio calculation using the operator

$$\hat{V}_K = - \sum_i \frac{3r_{iK}^2 \mathbf{1} - \mathbf{r}_{iK}^T \mathbf{r}_{iK}}{r_{iK}^5} + \sum_{L \neq K} Z_L \frac{3\mathbf{R}_{KL}^2 \mathbf{1} - \mathbf{R}_{KL}^T \mathbf{R}_{KL}}{R_{KL}^5} \quad (5)$$

and it is obtained more easily than the nuclear shielding constant since, for variational electronic wave functions, it is an expectation value.

In the present study we will not analyze the (unknown) correlation time for the molecular rotation τ_c and we neglect the anisotropy of the rotation. In our comparisons of ab initio results with the experimental line widths we assume the same value of τ_c for all the nitrogen nuclei within one molecule, and we compare the ratios of measured and computed line widths. In practice, in each of the molecules the smallest width is observed for the methyl-substituted N atom and we define the ratio of other line widths with respect to that one. The approximation of identical and isotropic correlation times for molecular rotation with respect to chemically nonequivalent nitrogen atoms within the same nuclei is probably the weakest point of our analysis. However, the calculated and observed ratios of the linewidths concerned are compatible to each other (see below); therefore, this approximation should be deemed reasonable.

C. Solvation Effects. The solvated molecule is placed in a spherical cavity immersed in a homogeneous, isotropic, linear dielectric medium. The charge distribution of the solute induces polarization charges in the medium. The interactions between the induced polarization charges and the charge distribution of the solute lead to an extra term in the energy functional for the solvated molecule,^{8-11,20}

$$E(\mathbf{B}, \mathbf{m}) = E_{\text{vac}}(\mathbf{B}, \mathbf{m}) + E_{\text{sol}}(\mathbf{B}) \quad (6)$$

The first term is

$$E_{\text{vac}}(\mathbf{B}, \mathbf{m}) = \frac{\langle O | H_{\text{vac}} | O \rangle}{\langle O | O \rangle} \quad (7)$$

where H_{vac} is the vacuum Hamiltonian and $|O\rangle$ is the electronic wave function of the solute. The second term is the equilibrium

solvent contribution to the energy of a solvated molecule

$$E_{\text{sol}}(\mathbf{B}) = \sum_{lm} g_l \langle T_{lm} \rangle^2 \quad (8)$$

where g_l is the cavity function and the charge moments are denoted as $\langle T_{lm} \rangle$. This expression is obtained by performing a multipole expansion of the charge distribution of the solvated molecule and then solving an integral equation which gives the polarization field of the induced polarization charges in the dielectric medium. The term $E_{\text{sol}}(\mathbf{B})$ depends implicitly on the magnetic fields, as the energy term is evaluated using magnetic field dependent orbitals. Since the externally applied magnetic field is time-independent, and since we are concerned with time-independent molecular magnetic properties, we utilize the equilibrium expression for the solvation energy.

For a spherical cavity, the cavity function is given by

$$g_l = -\frac{1}{2} R_{\text{cav}}^{-(2l+1)} \frac{(l+1)(\epsilon-1)}{l+(l+1)\epsilon} \quad (9)$$

where R_{cav} is the radius of the cavity, ϵ is the dielectric constant of the dielectric medium, and l is the order parameter of the multipole expansion.

The MCSCF wave function of the solvated molecule is determined by a direct, restricted-step, second-order MCSCF strategy^{11,21} utilizing the energy functional in eq 6. The derivatives of the solvent energy functional in terms of wave function parameters and magnetic parameters have been presented in ref 12.

III. Experimental Section

The compounds studied were prepared by published procedures.²⁻⁵ In the NMR measurements particular care was taken to use very pure and dry solvents as reported previously.²⁻⁵ The samples were prepared and handled under a dry argon atmosphere in glove bags. The ¹⁴N NMR half-height width measurements were performed on a Bruker AM500 spectrometer (11.7 Tesla) at 35 ± 0.2 °C, as maintained by a VT unit, at a frequency of 36.14 MHz. The Lorentzian line shape fitting was employed for the least-squares estimates of the resonance frequencies of interest, the phases of the signals, their line widths, and intensities, and the linear base line drift. In all cases the standard deviations of the linewidths concerned were below 2% of their magnitude. They are reported such that the last digit is uncertain. A more detailed description of the experimental procedures can be found in earlier works of one of us,²⁻⁵ from which we quote the experimental, bulk susceptibility corrected values of the nitrogen NMR shieldings of the azole systems under study, referenced externally to that in neat liquid nitromethane. The NMR shielding data quoted here relate to dilute solutions in cyclohexane (0.1 M or less).

IV. Calculations

Geometries for all the azoles studied here were optimized, at the MP2 level with a 6-311G** basis set, using the GAUSSIAN 94 program.²² The spatial constraint of C_s symmetry was imposed. In test calculations we have checked that the rotation of the methyl group does not affect the results significantly, as confirmed by the small differences between the values of the studied parameters in <1-2-5> and <1-3-4> triazoles. In all the following calculations, performed using the DALTON program,¹⁷ a basis set called H II, taken from Huzinaga's compilation²³ and successfully used in previous

TABLE 1: Absolute Shieldings and Chemical Shifts (ppm)

	<1>		<1-2>		<1-3>	
	N	N1	N2	N1	N3	
σ	123.80	72.09	-36.82	115.48	3.84	
$\Delta\sigma^b$	236.36	184.65	75.74	228.04	116.40	
exptl ^c	235.19	181.28	65.69	225.02	111.50	
	<1-2-3>			<1-2-4>		
	N1	N2	N3	N1	N2	N4
σ	41.25	-102.18	-82.09	67.64	-23.88	19.53
$\Delta\sigma$	153.81	10.38	30.47	180.20	88.68	132.09
exptl	149.50	7.51	20.58	176.07	78.95	122.91
	<1-2-5>			<1-3-4>		
	N1	N2	N5	N1	N3	N4
σ	22.54	-54.96	-58.36	116.20	-58.26	-52.98
$\Delta\sigma$	135.10	57.60	54.20	228.76	54.30	59.58
exptl	133.07	47.97	47.97	226.00	47.00	47.00
	<1-2-3-4>					
	N1	N2	N3	N4		
σ	50.44	-107.46	-141.23	-60.21		
$\Delta\sigma$	163.00	5.10	-28.67	52.35		
exptl	159.55	8.42	-23.31	43.23		
	<1-2-3-5>					
	N1	N2	N3	N5		
σ	-5.78	-118.70	-70.14	-37.49		
$\Delta\sigma$	106.78	-6.14	42.42	75.07		
exptl	106.99	-3.41	41.40	73.09		

^a Calculated absolute shielding for nitrogen in ppm. ^b Calculated shielding with respect to nitromethane (difference between σ and the assumed nitromethane value, -112.56 ppm, see ref 5). ^c Experimental shielding with respect to that in neat liquid nitromethane (bulk susceptibility corrected).

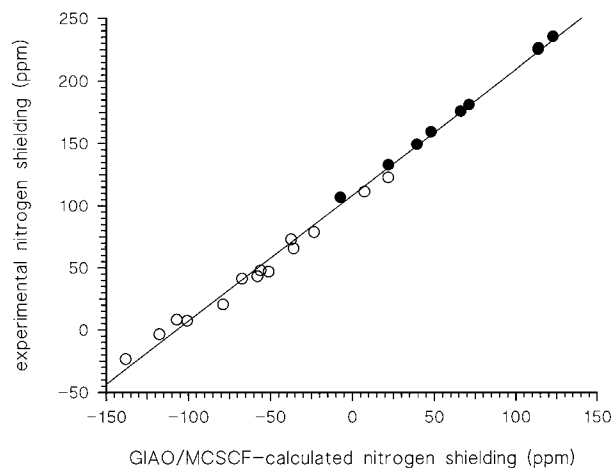


Figure 2. Comparison of calculated (cyclohexane) and experimental (solutions in cyclohexane) shielding constants. The solid black circles represent pyrrole-like nitrogen atoms (N1), while the open circles refer to pyridine-type nitrogen atoms, N2–N5.

similar studies,^{6,24} was employed. For the C and N atoms, it is a [9s5p1d/5s4p1d] set, whereas for the H atoms, the contraction is [5s1p/3s1p], which, for example, for the triazoles, yields in total 162 CGTO orbitals.

We use a RAS SCF wave function, similar for all the (isoelectronic) molecules studied. The active space of RAS SCF is also identical with that we have applied earlier, RAS-A of ref 6. We have 10 inactive orbitals of σ symmetry. The main correlation effects are described within RAS2, including six π

TABLE 2: Calculated Shielding Constant Increments with Respect to Vacuum, in ppm^a

ϵ	$\langle 1 \rangle$		$\langle 1-2 \rangle$		$\langle 1-3 \rangle$	
	N1	N1	N2	N1	N3	
cyclohexane	-1.80	-1.28	0.98	-2.44	3.49	
benzene	-1.99	-1.44	1.10	-2.80	4.03	
diethyl ether	-3.22	-2.35	1.83	-4.46	6.49	
hexanol	-4.30	-3.10	2.47	-6.05	8.73	
acetone	-4.57	-3.32	2.61	-6.35	9.19	
methanol	-4.67	-3.43	2.64	-6.60	9.49	
water	-4.83	-3.52	2.77	-6.83	9.81	

	$\langle 1-2-3 \rangle$			$\langle 1-2-4 \rangle$		
	N1	N2	N3	N1	N2	N4
cyclohexane	-2.17	1.58	3.38	-1.93	0.50	2.39
benzene	-2.46	1.77	3.80	-2.15	0.55	2.73
diethyl ether	-4.03	2.77	6.05	-3.53	0.74	4.46
hexanol	-5.61	3.67	8.09	-4.75	0.92	6.03
acetone	-5.81	3.81	8.53	-4.99	0.94	6.36
methanol	6.02	3.97	8.79	-5.19	1.09	6.48
water	-6.23	4.09	9.10	-5.32	1.04	6.77

	$\langle 1-2-5 \rangle$			$\langle 1-3-4 \rangle$		
	N1	N2	N5	N1	N3	N4
cyclohexane	-0.70	0.77	0.79	-3.11	4.68	4.55
benzene	-0.83	0.85	0.88	-3.50	5.25	5.12
diethyl ether	-1.52	1.36	1.39	-5.55	8.34	8.09
hexanol	-2.12	1.83	1.85	-7.47	11.18	10.80
acetone	-2.21	1.94	1.96	-7.91	11.76	11.35
methanol	-2.30	2.01	2.07	-8.31	11.99	11.60
water	-2.37	2.05	2.09	-8.44	12.49	12.09

	$\langle 1-2-3-4 \rangle$			
	N1	N2	N3	N4
cyclohexane	-2.76	0.57	3.18	2.44
benzene	-3.14	0.55	3.61	2.76
diethyl ether	-5.34	0.56	6.02	4.47
hexanol	-7.40	0.49	8.21	6.10
acetone	-7.78	0.47	8.66	6.43
methanol	-8.06	0.47	9.00	6.62
water	-8.32	0.45	9.33	6.88

	$\langle 1-2-3-5 \rangle$			
	N1	N2	N3	N5
cyclohexane	-1.62	1.20	2.98	0.15
benzene	-2.18	1.40	3.28	0.21
diethyl ether	-4.84	2.95	5.23	0.68
hexanol	-5.77	3.13	6.92	0.54
acetone	-5.94	3.27	7.30	0.52
methanol	-6.18	3.38	7.54	0.59
water	-6.25	3.46	7.85	0.54

^a $\sigma(\text{solvent}) - \sigma(\text{vacuum})$.

orbitals, with arbitrary electron occupation. At the same time, two electrons may be excited out of eight σ orbitals included in RAS1 or into six σ orbitals of RAS3. The CI expansion for such a wave function includes approximately 1.25 million determinants.

To compare the computed absolute shielding with experimental chemical shifts we use -112.56 ppm, taken from ref 5, as the neat nitromethane value. The relative differences between nitrogen nuclei and the solvent shifts are not affected by the choice of this value.

The values of the static dielectric constant used in all the calculations were²⁵ vacuum, 1.000; cyclohexane, 2.024; benzene, 2.238; diethyl ether, 4.335; hexanol, 13.30; acetone, 20.70; methanol, 32.63; and water, 78.54. They differ slightly from the values of ref 4, due to a difference in the temperature.

TABLE 3: Calculated $p(\text{solvent})$ Parameters Describing the Solvent Effect on the Shielding

solvent	$(\epsilon-1)/(\epsilon+2/3)$	$p(\text{solvent})^a$
cyclohexane	0.3806	0.3516
benzene	0.4262	0.3990
diethyl ether	0.6667	0.6526
hexanol	0.8806	0.8723
acetone	0.9220	0.9174
methanol	0.9499	0.9462
water	0.9790	0.9790

^a The parameters of the nonlinear fit, see text.

TABLE 4: $s(\text{nucleus})$ Parameters Describing the Solvent Effect on the Shielding

azole	nucleus	exptl ^a	calculated ^b $s(\text{nucleus})$
$\langle 1 \rangle$	N1	-6.76 ± 0.37	-4.95
$\langle 1-2 \rangle$	N1	-3.85 ± 0.70	-3.60
$\langle 1-2 \rangle$	N2	2.59 ± 0.77	2.82
$\langle 1-3 \rangle$	N1	-5.57 ± 0.83	-6.94
$\langle 1-3 \rangle$	N3	3.56 ± 0.84	10.01
$\langle 1-2-3 \rangle$	N1	-5.38 ± 0.41	-6.34
$\langle 1-2-3 \rangle$	N2	8.25 ± 1.60	4.21
$\langle 1-2-3 \rangle$	N3	4.21 ± 1.24	9.31
$\langle 1-2-4 \rangle$	N1	-3.46 ± 0.41	-5.45
$\langle 1-2-4 \rangle$	N2	4.29 ± 0.99	1.10
$\langle 1-2-4 \rangle$	N4	2.47 ± 0.65	6.89
$\langle 1-2-5 \rangle$	N1	-1.88 ± 0.86	-2.39
$\langle 1-2-5 \rangle$	N2	3.33 ± 0.87	2.11
$\langle 1-2-5 \rangle$	N5	3.33 ± 0.87	2.15
$\langle 1-3-4 \rangle$	N1	-6.96 ± 0.56	-8.65
$\langle 1-3-4 \rangle$	N3	8.74 ± 1.03	12.80
$\langle 1-3-4 \rangle$	N4	8.74 ± 1.03	12.38
$\langle 1-2-3-4 \rangle$	N1	-6.4 ± 0.4	-8.42
$\langle 1-2-3-4 \rangle$	N2	2.4 ± 0.8	0.61
$\langle 1-2-3-4 \rangle$	N3	8.4 ± 1.1	9.42
$\langle 1-2-3-4 \rangle$	N4	5.2 ± 0.7	6.99
$\langle 1-2-3-5 \rangle$	N1	-4.1 ± 0.4	-6.50
$\langle 1-2-3-5 \rangle$	N2	5.1 ± 1.1	3.66
$\langle 1-2-3-5 \rangle$	N3	5.5 ± 1.2	8.00
$\langle 1-2-3-5 \rangle$	N5	1.6 ± 0.8	0.63

^a Values determined in refs 2–5 from a multiparameter fit to the experimental data. ^b The parameters of the nonlinear fit, see text.

The radius of the cavity is determined by the largest distance from the center of mass to the outermost atom plus a van der Waals radius of that atom. For the compounds $\langle 1 \rangle$, $\langle 1-2 \rangle$, and $\langle 1-3 \rangle$ the cavity radius is 7.22 au, for the compounds $\langle 1-2-3 \rangle$, $\langle 1-2-4 \rangle$, $\langle 1-2-5 \rangle$, and $\langle 1-3-4 \rangle$ the cavity radius is 7.14 au and for the compounds $\langle 1-2-3-4 \rangle$ and $\langle 1-2-3-5 \rangle$ the cavity radius is 7.00 au. The molecular structures have a nonspherical shape but the charge distributions of the molecules are much closer to a spherical shape. For the dielectric medium models it is the charge distributions that determines the shape of the cavity.

Since we consider the solvent induced effects in the molecular properties, we do not perform geometry optimizations including the dielectric medium. Additionally, the computational efforts for geometry optimizations of solutes of this size with a RAS SCF wave function are substantial.

V. Results and Discussion

A. Shielding Constants in Vacuum and Cyclohexane. The calculated shielding constants in vacuum are shown in Table 1. In addition, we present in Figure 2 the fit of experimental and calculated shielding constants, the former taken from refs 2–5. We have used the results obtained in cyclohexane, and we have taken the averages of the calculated values for the two pairs of N atoms differing only due to the arrangement of the

TABLE 5: Experimental ^{14}N Resonance Half-Height Widths (in Hz) Obtained from Lorentzian Line Shape Fitting of ^{14}N NMR Spectra of 1-Me-azoles Taken at +35 °C

1-Me-azoles and nitrogen atoms	^{14}N resonance half-height widths (in Hz) for solutions in solvents specified, and relative widths (in parentheses) with respect to N1					
	cyclohexane	benzene	diethyl ether	acetone	methanol	water
<1>						
N1	89 (1.00)	77 (1.00)	58 (1.00)	71 (1.00)	70 (1.00)	138 (1.00)
<1-2>						
N1	82 (1.00)	76 (1.00)	62 (1.00)	73 (1.00)	120 (1.00)	133 (1.00)
N2	136 (1.66)	168 (2.21)	132 (2.13)	110 (1.51)	307 (2.56)	330 (2.48)
<1-3>						
N1	69 (1.00)	62 (1.00)	48 (1.00)	54 (1.00)	89 (1.00)	81 (1.00)
N3	120 (1.74)	149 (2.40)	112 (2.33)	138 (2.56)	368 (4.13)	220 (2.71)
<1-2-3>						
N1	51 (1.00)	51 (1.00)	47 (1.00)	44 (1.00)	97 (1.00)	75 (1.00)
N2	126 (2.47)	179 (3.51)	167 (3.55)	170 (3.86)	369 (3.81)	353 (4.98)
N3	119 (2.33)	179 (3.51)	162 (3.45)	169 (3.84)	413 (4.25)	332 (4.42)
<1-2-4>						
N1	70 (1.00)	68 (1.00)	58 (1.00)	65 (1.00)	98 (1.00)	109 (1.00)
N2	143 (2.04)	203 (2.99)	172 (2.97)	211 (3.25)	510 (5.21)	430 (3.94)
N4	113 (1.61)	143 (2.10)	107 (1.84)	123 (1.89)	354 (3.61)	272 (2.50)
<1-2-5>						
N1	65 (1.00)	67 (1.00)	52 (1.00)	53 (1.00)	88 (1.00)	126 (1.00)
N2	113 (1.74)	148 (2.21)	118 (2.27)	140 (2.64)	216 (2.45)	358 (2.84)
N5	113 (1.74)	148 (2.21)	118 (2.27)	140 (2.64)	216 (2.45)	358 (2.84)
<1-3-4>						
N1	41 (1.00)	59 (1.00)	45 (1.00)	47 (1.00)	113 (1.00)	69 (1.00)
N3	112 (2.73)	235 (3.98)	124 (2.76)	216 (4.60)	624 (5.68)	412 (5.97)
N4	112 (2.73)	235 (3.98)	124 (2.76)	216 (4.60)	624 (5.68)	412 (5.97)
<1-2-3-4>						
N1	38 (1.00)	82 (1.00)	48 (1.00)	71 (1.00)	75 (1.00)	70 (1.00)
N2	98 (2.58)	214 (2.61)	143 (2.98)	184 (2.59)	326 (4.35)	314 (4.49)
N3	105 (2.76)	257 (3.13)	178 (3.71)	220 (3.10)	365 (4.87)	344 (4.91)
N4	111 (2.92)	233 (2.84)	146 (3.04)	187 (2.63)	321 (4.28)	318 (4.54)
<1-2-3-5>						
N1	44 (1.00)	53 (1.00)	38 (1.00)	38 (1.00)	54 (1.00)	67 (1.00)
N2	103 (2.34)	163 (3.08)	135 (3.55)	155 (4.08)	193 (3.57)	300 (4.48)
N3	108 (2.45)	164 (3.09)	130 (3.42)	149 (3.92)	247 (4.57)	276 (4.12)
N5	109 (2.48)	167 (3.15)	125 (3.29)	164 (4.32)	267 (4.94)	290 (4.33)

methyl group in triazoles. The relevant linear correlation for the 23 data points is (in ppm):

$$\sigma^{\text{exp}} = 1.0138\sigma^{\text{calc}} + 108.38 \quad (10)$$

with a standard deviation ± 5.54 ppm. In comparison to an analogous correlation with SCF calculated shieldings (ref 5), there is a significant improvement in the scaling factor which is now very close to the ideal value of unity (it was 0.8804 for RHF/6-31++G**). The standard deviation shows a very slight improvement with respect to a value of ± 5.76 ppm in SCF, and the free terms are reasonably close to each other.

The very good agreement between theoretical and experimental numbers indicates that our level of theory is appropriate for describing the molecular properties investigated here. The difference between our value of the free term, 108.38 ppm, and other values used for nitrogen shielding in nitromethane corresponds to a constant shift, and it is not relevant for further analysis of solvent effects on the shielding.

B. Solvent Effects on the Shielding Constants. For most of the nuclei the shielding changes smoothly with the dielectric constant of the solvent, as illustrated in Table 2. The only exceptions are N2 in 1-methyl-1-2-3-4-tetrazole, N5 in 1-methyl-1-2-3-5-tetrazole and N2 in 1-methyl-1-2-4-triazoles, and for these nuclei the calculated solvent effects are relatively small.

Generally, we observe that the shielding constant for the methyl-substituted nitrogen atom decreases with increasing static dielectric constant. We find an increase in the shielding constants of the other nitrogen atoms as the static dielectric constant increases. This reflects how the electronic density is polarized

due to the solvent and how the electronic density is either decreased or increased around the nitrogen atoms.²⁶

To describe the calculated solvent dependence of the shielding constants, we may use an equation of the form

$$\sigma(\text{nucleus, solvent}) = \sigma(\text{nucleus, vacuum}) + s(\text{nucleus})p(\text{solvent}) \quad (11)$$

where the parameter $s(\text{nucleus})$ describes the response of the nitrogen shielding to the interaction with the solvent and the parameter $p(\text{solvent})$ is related to the dielectric constant. Using eq 11 we reduce the number of parameters to be compared with other data from nucleus \times solvent to nucleus + solvent. We apply a simplified version of the formulae used to analyze the experimental data,⁵ since our model does not take into account specific solute-solvent interactions, such as hydrogen bonding. Furthermore, we note that our parameter $p(\text{solvent})$ does not correspond to the π^* parameter applied in the experimental studies.²⁻⁵ Fitting the calculated data according to eq 11 leaves the vectors s and p undetermined, since we can multiply one set of parameters by a constant if we simultaneously divide the other set by the same value. That value is fixed by the formula below relating $p(\text{solvent})$ to the dielectric constant.

Following eq 9 and neglecting all the other factors, we find that the dependence on ϵ can be rewritten as

$$p(\epsilon) = (\epsilon - 1)/(\epsilon + C) \quad (12)$$

where for purely dipolar interactions ($l=1$, see eqs 8-9), one should use $C = 0.5$, for purely quadrupolar interactions ($l=2$),

TABLE 6: Calculated EFG at the Nuclei of Nitrogen (V_{zz}), Asymmetry Parameter (η), and $\Delta\nu_{1/2}/\Delta\nu_{1/2}^{N1}$: Line Width Relative to Nitrogen N1 in the Same Molecule and Solvent^a

		vacuum	cyclohexane	benzene	diethyl ether	acetone	methanol	water
				(1)				
N1	V_{zz}	-0.605	-0.593	-0.591	-0.582	-0.573	-0.572	-0.571
	η	0.27	0.25	0.24	0.23	0.21	0.21	0.20
				(1-2)				
N1	V_{zz}	-0.651	-0.642	-0.641	-0.634	-0.627	-0.627	-0.626
	η	0.38	0.40	0.40	0.42	0.44	0.44	0.44
N2	V_{zz}	-0.966	-0.961	-0.960	-0.956	-0.952	-0.951	-0.951
	η	0.67	0.67	0.67	0.67	0.68	0.68	0.68
	$\Delta\nu_{1/2}/\Delta\nu_{1/2}^{N1}$	2.416	2.446	2.449	2.469	2.491	2.494	2.497
				(1-3)				
N1	V_{zz}	-0.568	-0.550	-0.548	-0.535	-0.521	-0.520	-0.518
	η	0.31	0.27	0.27	0.24	0.21	0.21	0.21
N3	V_{zz}	-0.903	-0.889	-0.887	-0.877	-0.866	-0.864	-0.863
	η	0.07	0.06	0.06	0.05	0.04	0.04	0.04
	$\Delta\nu_{1/2}/\Delta\nu_{1/2}^{N1}$	2.455	2.550	2.565	2.635	2.717	2.727	2.737
				(1-2-3)				
N1	V_{zz}	-0.538	-0.521	-0.519	-0.507	-0.494	-0.493	-0.491
	η	0.39	0.44	0.45	0.49	0.53	0.54	0.54
N2	V_{zz}	-0.959	-0.951	-0.950	-0.944	-0.938	-0.937	-0.936
	η	0.76	0.77	0.77	0.77	0.78	0.78	0.78
	$\Delta\nu_{1/2}/\Delta\nu_{1/2}^{N1}$	3.592	3.733	3.751	3.851	3.960	3.973	3.987
N3	V_{zz}	-1.059	-1.046	-1.044	-1.036	-1.026	-1.025	-1.023
	η	0.12	0.13	0.13	0.13	0.14	0.14	0.14
	$\Delta\nu_{1/2}/\Delta\nu_{1/2}^{N1}$	3.692	3.801	3.813	3.887	3.964	3.973	3.983
				(1-2-4)				
N1	V_{zz}	-0.620	-0.605	-0.604	-0.594	-0.582	-0.581	-0.580
	η	0.44	0.48	0.48	0.51	0.54	0.54	0.54
N2	V_{zz}	-0.960	-0.956	-0.956	-0.953	-0.950	-0.949	-0.949
	η	0.69	0.69	0.69	0.69	0.68	0.68	0.68
	$\Delta\nu_{1/2}/\Delta\nu_{1/2}^{N1}$	2.612	2.687	2.695	2.746	2.803	2.809	2.817
N4	V_{zz}	-0.868	-0.856	-0.854	-0.846	-0.836	-0.835	-0.834
	η	0.03	0.01	0.01	0.01	0.00	0.00	0.00
	$\Delta\nu_{1/2}/\Delta\nu_{1/2}^{N1}$	1.839	1.857	1.858	1.869	1.880	1.881	1.883
				(1-2-5)				
N1	V_{zz}	-0.672	-0.664	-0.663	-0.657	-0.651	-0.650	-0.650
	η	0.55	0.57	0.58	0.60	0.62	0.62	0.62
N2	V_{zz}	-0.998	-0.995	-0.994	-0.992	-0.990	-0.989	-0.989
	η	0.44	0.44	0.44	0.44	0.45	0.45	0.45
	$\Delta\nu_{1/2}/\Delta\nu_{1/2}^{N1}$	2.140	2.158	2.160	2.173	2.185	2.187	2.189
N5	V_{zz}	-1.010	-1.007	-1.007	-1.005	-1.002	-1.002	-1.002
	η	0.43	0.43	0.43	0.43	0.43	0.43	0.43
	$\Delta\nu_{1/2}/\Delta\nu_{1/2}^{N1}$	2.185	2.205	2.207	2.221	2.234	2.236	2.238
				(1-3-4)				
N1	V_{zz}	-0.565	-0.542	-0.540	-0.524	-0.507	-0.505	-0.503
	η	0.30	0.25	0.24	0.20	0.16	0.16	0.15
	V_{zz}	-1.024	-1.009	-1.007	-0.996	-0.984	-0.983	-0.981
	η	0.28	0.30	0.31	0.32	0.34	0.35	0.35
	$\Delta\nu_{1/2}/\Delta\nu_{1/2}^{N1}$	3.271	3.493	3.520	3.687	3.885	3.908	3.933
N4	V_{zz}	-1.014	-0.998	-0.996	-0.086	-0.974	-0.973	-0.971
	η	0.30	0.33	0.33	0.35	0.37	0.37	0.37
	$\Delta\nu_{1/2}/\Delta\nu_{1/2}^{N1}$	3.216	3.436	3.464	3.629	3.825	3.849	3.873
				(1-2-3-4)				
N1	V_{zz}	-0.552	-0.531	-0.528	-0.513	-0.496	-0.494	-0.491
	η	0.45	0.52	0.53	0.59	0.65	0.66	0.67
N2	V_{zz}	-0.976	-0.966	-0.966	-0.962	-0.958	-0.957	-0.957
	η	0.66	0.65	0.65	0.64	0.63	0.63	0.63
	$\Delta\nu_{1/2}/\Delta\nu_{1/2}^{N1}$	3.351	3.464	3.482	3.586	3.704	3.718	3.733
N3	V_{zz}	-1.072	-1.061	-1.059	-1.050	-1.040	-1.039	-1.038
	η	0.31	0.33	0.33	0.34	0.35	0.35	0.36
	$\Delta\nu_{1/2}/\Delta\nu_{1/2}^{N1}$	3.650	3.791	3.809	3.909	4.016	4.027	4.041
N4	V_{zz}	-1.002	-0.990	-0.988	-0.980	-0.971	-0.970	-0.969
	η	0.25	0.27	0.27	0.28	0.30	0.30	0.30
	$\Delta\nu_{1/2}/\Delta\nu_{1/2}^{N1}$	3.156	3.263	3.279	3.363	3.456	3.466	3.478
				(1-2-3-5)				
N1	V_{zz}	-0.564	-0.545	-0.543	-0.530	-0.516	-0.514	-0.513
	η	0.63	0.70	0.71	0.76	0.82	0.82	0.83
N2	V_{zz}	-0.977	0.971	-0.970	-0.966	-0.961	-0.960	-0.960

TABLE 6: (Continued)

	vacuum	cyclohexane	benzene	diethyl ether	acetone	methanol	water
			(1-2-3-5) (Continued)				
N3	η	0.58	0.58	0.58	0.59	0.59	0.59
	$\Delta\nu_{1/2}/\Delta\nu_{1/2}^{N1}$	2.948	3.036	3.045	3.104	3.168	3.182
	V_{zz}	-1.048	-1.036	-1.034	-1.026	-1.017	-1.015
	η	0.18	0.19	0.19	0.20	0.21	0.21
	$\Delta\nu_{1/2}/\Delta\nu_{1/2}^{N1}$	3.082	3.143	3.149	3.186	3.225	3.234
N5	V_{zz}	-0.978	-0.976	-0.976	-0.975	-0.973	-0.973
	η	0.50	0.49	0.49	0.49	0.49	0.49
	$\Delta\nu_{1/2}/\Delta\nu_{1/2}^{N1}$	2.874	2.980	2.992	3.063	3.141	3.159

^a V_{zz} and η in atomic units.

$C = 2/3$; the value of C can also be adjusted to fit the data.¹⁴ We find that for $C = 0.5$ the values of $p(\epsilon)$ obtained from eq 12 are in the range 0.452–0.981 for the solvents studied, for $C = 2/3$ the range is 0.426–0.979. Since the dependence of $p(\epsilon)$ on C is weakest for large dielectric constants, we use the value for the dielectric constant of water to adjust the scale for our fitted parameters, that is, we fix $p(\text{solvent}) = p(\epsilon)$ for water. As shown in Table 3, we then find that all the $p(\text{solvent})$ parameters derived from the fitting performed according to eq 11 are in good agreement with the $p(\epsilon)$ values estimated from eq 12 for the corresponding static dielectric constant. For the planar ring molecules studied here, it appears that the value $C = 2/3$ is more appropriate, the dipole interactions being less significant.

In Table 4 we compare the results for $s(\text{nucleus})$ with the parameters derived from the experimental data. First, we note that all our s -values for the methyl-substituted (pyrrole-like) N atoms are negative, and the values are in most cases of similar magnitude. For all the other atoms, $s > 0$. This is in agreement with the trends mentioned previously and with the experimental data. The magnitude of the computed and experimentally derived values is generally in agreement, although there are some exceptions. Presumably, the specific solute–solvent interactions like hydrogen bonding affects the shielding of pyridine-like N atoms more strongly than for the pyrrole-like atoms.

C. Nuclear Quadrupole Coupling Constants in Vacuum.

For the triazoles and tetrazoles, the vacuum NQCC values discussed below are the same as in Table 3 of ref 6.

The calculated line widths agree with experimental data much better than might have been expected. We have used a very simple model, eq 2 with the assumption of the same correlation time for all the nuclei in the molecule. Nevertheless, the calculated ratios of the line widths are all very reasonable.

As before, these vacuum calculations indicate that the theoretical level of the calculations gives a sufficiently accurate description of the physical properties investigated and we can safely analyze the solvent effects.

D. Solvent Effects on the Nuclear Quadrupole Coupling Constants.

The experimental data for all the half-height widths are shown in Table 5. In addition, the relative widths with respect to N1, the pyrrole-like atom, are tabulated for each molecule and for each solvent. These ratios can be compared directly with the corresponding ab initio results, the $\Delta\nu_{1/2}/\Delta\nu_{1/2}^{N1}$ values (see eq 2) in Table 6, where, again, the same correlation time τ_c , for the two nitrogen atoms is assumed. We note that the solvent dependence of the linewidths is rather complicated, the dielectric constant is not the only parameter affecting the linewidths. Thus, in the following comparison with the computed values we consider only the main trends rather than individual results for a single solvent.

The calculated solvent dependence is smooth for all the nuclei. To reduce the number of tabulated data we omit therefore

the hexanol results, for which there are no experimental values. For all the nitrogen atoms the electric field gradient (V_{zz}) becomes more positive (smaller in absolute value) with increasing static dielectric constant and reaches a limit for the static dielectric constant of water. This reflects the ability of the solvent to draw some of the electronic density away from the nuclei. For large dielectric constants the calculated ratios of the line widths to N1 are larger than observed in vacuum, in agreement with experiment. However, the calculated solvent dependence is clearly weaker than that observed experimentally, both for N1 line width in each azole and for the line widths ratios. These differences may be largely due to the changes of the correlation time τ_c with the solvent.

VI. Conclusions

From the vacuum calculations we have shown that, with respect to basis set and electron configuration, our MCSCF wave functions provide a good description of the investigated molecular properties: the nuclear magnetic shieldings and the line widths of the nitrogen atoms. Furthermore, the solvent calculations have given a surprisingly good description of how the molecular properties are modified by solvent changes, described here by changes in the static dielectric constant of the surrounding medium and how the induced polarization in the solvent changes the electronic wave function and thereby the molecular properties of the solute. It is important to note that our solvent model has not taken specific solute–solvent interactions like hydrogen bonding into account. These interactions have been shown to be of immense importance when investigating, e.g., linear and nonlinear electric polarizabilities and absorption spectra.^{27–31} In our work, the main solvent effects have been properly described within the applied solvent response theory. Even though specific solute–solvent interactions were not considered and a very simplified model of molecular rotation was assumed, the computed solvent-induced changes of both NMR properties—the shielding constants and resonance signal line widths—are in fair agreement with the experimental data.

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