

NMR properties of N_3^- . A comparison of theory and experiment

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Received 22 May 1995

Abstract

Theoretical and experimental values of nuclear quadrupole coupling constants, nuclear shielding constants and indirect spin–spin coupling constants in the azide ion are compared and discussed. The calculated ab initio values of the parameters have been obtained using multiconfiguration self-consistent field (MC SCF) reference wavefunctions, and their dependence on the approximations in the computational scheme is analyzed in detail. Our own experimental results are given for nuclear quadrupolar relaxation rates and shielding constants, and the theoretical results are compared with the values extracted from these and previous experiments.

1. Introduction

During recent years, significant progress has been made in the ab initio calculation of molecular properties characterizing the NMR spectrum. Application of methods that yield gauge-origin independent results has made accurate calculations of the shielding constants possible. Various approximations that include correlation effects in the linear response theory have been developed and yield promising results for indirect spin–spin coupling constants. A comparison [1] of the vinyl lithium spectrum simulated using parameters determined ab initio with the experimental spectrum shows that accurate results may presently be obtained. We have successfully applied the same approach in the calculation of shielding constants and spin–spin coupling constants of many other molecules [2–7]. For a description of various other ab initio methods used for calculation of these prop-

erties and examples of practical applications we refer to the reviews [8–11] and other recent works [12–15].

The calculation of the nuclear quadrupole coupling constants (NQCC) is in principle simpler than the calculation of the other properties, as it only requires knowledge of the unperturbed wavefunction. For each nucleus the NQCC tensor is proportional to the electric field gradient (EFG) and the quadrupole moment of the nucleus. For small molecules, accurate results of high-level calculations of the electric field gradient combined with measurements of quadrupole coupling constants can be used to determine the value of the nuclear quadrupole moment [16]. In recent calculations such factors as the dependence on rovibrational levels [17] or a perturbing electric field (this may be used to simulate the environment in a crystal) [18] have also been analyzed.

Recently, Cremer and Kruger [19] compared cal-

culated EFG and measured NQCC for a series of small and larger molecules containing nitrogen nuclei. Using the more accurate results for small molecules they determined an ‘effective quadrupole moment’ for ^{14}N , which corrects for computational approximations in less accurate methods, and used it for larger systems. It appears that for post-HF methods the basis set deficiencies are the main problem, and since a much larger basis is used in this work, we shall not follow their approach.

Although the accurate calculation of EFGs requires that correlated wavefunctions and large basis sets are used, the main problem lies in their comparison with experimental data. The nuclear quadrupole resonance measurements for the solid state may yield direct information about the EFG tensor, but the difference between the EFG of an isolated molecule and the same molecule in a solid may be significant. In the standard NMR experiment for a solution or a liquid, the linewidth is dependent on the NQCC. However, it also depends on molecular tumbling and it is difficult to extract accurate information about EFGs from the measured linewidths. The accurate experimental results used for comparison with ab initio results have usually been taken from microwave spectra. For the N_3^- ion the high symmetry of the system simplifies significantly the interpretation of the experimental data. The EFG tensors for both nuclei are diagonal, and the ratio of the nuclear relaxation times for the central and terminal nitrogen atoms provides an unbiased estimate for the ratio of the corresponding quadrupole coupling constants.

2. Ab initio calculations

We have here used multiconfiguration SCF reference functions. The calculations have been performed using a suite of programs called Hermit [20], Sirius [21] and Abacus [22]. The theory and implementation of linear response methods for MCSCF functions have been described [23,24]; to obtain the EFG tensor only a calculation of average values of the corresponding operator is required.

We compare the ab initio results with experimental data for nuclear quadrupole coupling constants, shielding constants and spin–spin coupling constants in the azide ion. For each of the properties, we are

interested in a somewhat different aspect of the calculations. For the nuclear quadrupole coupling constants, the measured and computed ratio of quadrupolar relaxation rates are in reasonable agreement. Therefore we use the ab initio values for individual nuclear quadrupole coupling constants in a further analysis of experimental data.

Most of our previous calculations were carried out for the shielding constants. We use here a technique similar to the one we recently used in a series of calculations on molecules isoelectronic with N_3^- , that is for cyclopropene [2], HN_3 and various isomers of CH_2N_2 [4,6] and CH_3CN and CH_3NC [7]. The convergence of the N_3^- results with respect to the basis set and active space can thus be compared with these previous calculations. In this sense, the shielding constants permit an estimate of the adequacy of the various approximations to the wavefunction. Although the quality of the results for the shielding may not be directly related to the accuracy of the other properties, such a comparison is still helpful.

For the spin–spin coupling constants, we have included all coupling mechanisms (Fermi contact, spin–dipole, paramagnetic spin–orbit and diamagnetic spin–orbit) in the calculation. Indeed, an analysis of their contributions shows that for both constants (1J and 2J) it is insufficient to include only the Fermi contact term. Only one of the constants (1J) is known from experiment, the other represents the coupling between two magnetically equivalent nuclei.

2.1. Active space

The azide ion is isoelectronic with HN_3 and CH_2N_2 . A calculation of MP2 natural orbitals confirmed that the RAS-I approximation used for these molecules [4,6] is also appropriate for N_3^- . In this approximation, as in all the other MCSCF functions used here, the core orbitals were treated as inactive. The RAS2 subspace included all the occupied valence orbitals and the other two valence π -type orbitals, which both have large occupation numbers in the MP2 calculation. The RAS3 subspace included the remaining valence orbitals (σ_g and σ_u) with a maximum of two electrons in these orbitals. Assuming the order $\sigma_g\pi_{ux}\pi_{uy}\delta_g\sigma_u\pi_{gx}\pi_{gy}\delta_u$ we can de-

scribe our RAS-I function as: inactive – (2, 0, 0, 0, 1, 0, 0, 0), RAS2 – (2, 2, 2, 0, 2, 1, 1, 0) and RAS3 – (1, 0, 0, 0, 1, 0, 0, 0). Due to the high symmetry of N_3^- , the corresponding CI expansion had only ≈ 12500 determinants and we were able to consider various extensions of the active space.

In addition to the results for RAS-I function, we also report the results for our final and most accurate wavefunction called RAS-E (E for extended active space). In this approximation, the RAS2 subspace is the same as in RAS-I. In the doubly occupied RAS3 subspace we included (3, 1, 1, 0, 2, 2, 2, 0) orbitals, where the extra orbitals have been added according to MP2 natural orbital occupation number sequence. For this MCSCF function the CI expansion has more than 360000 determinants.

In a series of test calculations, we also investigated three other active space selections. The first was intermediate between RAS-I and RAS-E, with (2, 0, 0, 0, 2, 1, 1, 0) orbitals in RAS3 subspace. In the next approximation, we moved one orbital from RAS3 to RAS2. In a final test we investigated the role of δ orbitals. In the doubly occupied RAS3 subspace we have included (2, 1, 1, 1, 2, 2, 2, 1) orbitals. In comparison to RAS-I, in all these intermediate calculations the shielding for the central atom is much closer to the experimental value, the end atom shielding does not change or is a few ppm further away from experiment. Also the calculated value of the EFG for the last of these functions is very close to RAS-E, so we will not discuss any of these intermediate approximations in detail.

We would like to emphasize the role of the correlation effects in these calculations. We have often observed that SCF results may be totally unreliable for similar electron-rich molecules [1–7], and therefore we do not discuss here the N_3^- SCF values. For example, the ratio of the nuclear relaxation times computed from the SCF data differs by an order of magnitude from the correlated and experimental values. Hence, we present only the results for correlated functions.

2.2. Basis set

In our previous studies [4,6], we compared the RAS-I results for basis sets H II and H III and found that the results do not differ significantly. Here, we

use systematically an even larger basis H IV. For the nitrogen atom it is a [11s7p3d1f/8s7p3d1f] basis, corresponding to a total of 153 CGTOs for the ion.

We have also used the RAS-I function to test a basis set larger than H IV. We uncontracted two of the tight s functions, to obtain a better description of the region close to the nuclei. Since all the computed quantities (NQCC and σ for both nuclei, 1J and 2J) differ from the H IV results by less than 1%, the H IV basis was finally used in all the calculations with larger active spaces.

In all calculations of the shielding constants we have used the so-called gauge including atomic orbitals (GIAOs), also known as London atomic orbitals [25]. It has been shown that they can be efficiently applied to eliminate gauge dependence of the results in magnetic property calculations. We have used a formulation valid for arbitrary approximations to the wavefunction [26].

2.3. Geometry

We have used the CEPA geometry of Botschwina [27], $R = 1.1911 \text{ \AA}$, and all numbers other than those listed in Table 1 refer to this geometry. We denote the central nitrogen atom as N1, the end atom as N2. To estimate the geometry dependence of the EFG and the shielding constants we have carried out a sequence of calculations at different geometries using the RAS-I function and the H IV basis set (an analysis of the spin–spin coupling as a function of geometry would require too much computer time at this level). We have considered only the symmetric stretch of the ion, and we find that for this wavefunc-

Table 1
Geometry dependence of NQCC and shielding constants^a

	$R - 0.1 \text{ au}$	R	$R + 0.1 \text{ au}$
NQCC			
$V_z(N1)$	-1.653	-1.274	-0.895
$V_z(N2)$	+1.309	+1.885	+2.506
ratio W_2 / W_1 ^b	0.63	2.2	7.8
shielding constants			
$\sigma(N1)$	26.44	6.06	-18.04
$\sigma(N2)$	208.41	178.00	138.67

^a RAS-I approximation, V_z in MHz, absolute shielding in ppm.

^b $W_2 / W_1 = [V_z(N2) / V_z(N1)]^2$.

tion the energy minimum is very close to our assumed reference geometry (within 0.007 au). As shown in Table 1, the NQCC and the shielding constants depend very strongly on geometry. Even more pronounced is the geometry dependence of the ratio W_2/W_1 , since the changes in $V_z(N1)$ and $V_z(N2)$ are in opposite directions.

3. Results

3.1. Shielding constants

The results for the shielding constants are shown in Table 2. For the central nitrogen atom, the RAS-I value is in good agreement with experiment, and there is significant improvement for RAS-E. Also in our other RAS calculations the results for the central atom were in better agreement with experiment than for RAS-I. For the end atom there is a difference of about 35 ppm between RAS-I and experiment. This is significantly larger than the differences we have observed for HN_3 and CH_2N_2 in the same approach.

The shielding of the end nitrogen is practically unaffected by changes in the active space, it is almost the same in the RAS-I and RAS-E calculations. For the other intermediate RAS calculations we have done $\sigma(\text{N}2)$ was either the same, or ≈ 185 ppm. A possible explanation is that none of our MCSCF functions describes sufficiently the dynamic

Table 2
Comparison of calculated and experimental chemical shifts

	σ this work ^a	chem. shift this work ^a	Exp.	
			this work ^b	reference
N1	-3.12	-131.88	-129.60	-130.9 ^c -132 ^d
	(6.06)	(-141.06)		
N2	179.60	-314.60	-277.96	-281.4 ^c -281 ^d
	(178.00)	(-313.00)		

^a RAS-E results are shown, with RAS-I results in parentheses, conversion to chemical shift using nitromethane standard: $\sigma(\text{CH}_3\text{NO}_2) = -135.00$ ppm.

^b At $T = 308$ K, -129.40 and -277.87 at $T = 318$ K.

^c The results of Ref. [28] converted to nitromethane standard in Ref. [29].

^d Ref. [30].

Table 3
Contributions to the indirect spin–spin coupling constants ^a

	¹ <i>J</i>	² <i>J</i>
Fermi contact	-9.54	-1.46
spin–dipole	0.68	3.50
paramagnetic spin–orbit	-1.94	2.15
diamagnetic spin–orbit	0.02	-0.06
total	-10.79	4.14

^a RAS-I approximation, ¹⁵N–¹⁵N coupling, in Hz.

correlation effects; another is that for an ion the shielding measured in experiment is strongly affected by the interaction with the environment. In view of the very strong dependence of $\sigma(\text{N}2)$ on geometry, we have not considered further calculations at the equilibrium geometry.

3.2. Indirect spin–spin coupling constants

We report in Table 3 and discuss below the computed and literature indirect spin–spin coupling constants for ¹⁵N–¹⁵N coupling; in our ¹⁴N experiment they are not observed because of the quadrupole moment of the nucleus. For a fixed molecular geometry the constants for various isotopes are proportional to the magnetogyric coefficients for the nuclei. In the RAS-I approximation and for the equilibrium geometry we obtain ¹*J* = -10.79 Hz, the corresponding experimental value is 11.32 ([28], sign unknown). Comparing these two values, we conclude that ¹*J* is negative. There is no experimental result for ²*J*, we find ²*J* = 4.14 Hz.

It should be pointed out that for both constants only the diamagnetic spin–orbit contribution is negligible. For ¹*J*, the Fermi contact term yields $\approx 85\%$ of the total constant. However, the paramagnetic spin–orbit contribution, which constitutes about 20% of ¹*J*, is larger than the difference between the theoretical and experimental values and clearly cannot be neglected in accurate calculations. For ²*J*, the (absolute value of the) Fermi contact term is smaller than the positive paramagnetic and the spin–dipole contributions. Finally, for both constants, we find a large anisotropic component, 23.61 Hz for ¹*J* and 12.71 Hz for ²*J*.

We have not studied the spin–spin coupling constants for any wavefunctions with extended active

spaces. The only value known from experiment, the trace of 1J , has been reproduced satisfactorily. Secondly, since the Fermi contact term is not dominant, every calculation requires consideration of all coupling mechanisms. That means solving 39 response equation which for wavefunctions with large CI expansions becomes too expensive.

3.3. Nuclear quadrupole coupling constants

For the NQCC we first briefly describe the relationship of the data derived from experimental NMR studies to the calculated properties. We shall discuss the ab initio results having defined the relevant quantities.

In fluids, the quadrupolar coupling constants (combined with the asymmetry parameters of the EFG tensors) can be determined from quadrupolar NMR relaxation times of the pertinent nuclei provided that the characteristics of random molecular tumbling are known. Quadrupolar relaxation times can be calculated from the resonance linewidths assuming that the field inhomogeneity broadening and other, non-quadrupolar, contributions to the linewidth can be estimated. In the extreme narrowing regime [31], which is perfectly adequate for small molecules dissolved in non-viscous fluids, the longitudinal and perpendicular quadrupolar relaxation times are identical. For the azide anion where the electric field gradients exhibit axial symmetry (the asymmetry is zero) the NMR experimental data and the molecular quantities of concern to us are related according to

$$\begin{aligned} (W_k - \Delta W_k) \pi &= 1/T_{2k} = 1/T_{1k} \\ &= \frac{3}{8} [2\pi V_z(k)]^2 \tau_c, \end{aligned} \quad (1)$$

where W_k is the resonance linewidth of the k th nucleus (in Hz), ΔW_k is the contribution to the linewidth of factors other than quadrupolar interactions, $V_z(k)$ is the quadrupolar coupling constant (in the units of Hz) and τ_c (in s) is the correlation time of random reorientations of the principal axis z .

Because the principal symmetry axis is the same for all the nuclei, the correlation time entering Eq. (1) is also the same for these nuclei. Thus, even when τ_c is not known, the ratio of quadrupolar relaxation times for N1 and N2 gives the squared

ratio of the corresponding quadrupolar coupling constants. In this case, we avoid the arbitrary assumptions regarding molecular reorientation that are usually made for molecules of lower symmetry.

The ab initio results for the electric field gradient give us directly the tensor components of NQCC. We quote the results obtained for ^{14}N and the V_z component, in MHz. For the central N atom we obtain in the RAS-I approximation -1.2736 , and in the RAS-E calculation -1.2857 . For the end nitrogen atom, we find $+1.8849$ and $+2.2127$, respectively. For the measured ratio $W_2/W_1 = [V_z(\text{N2})/V_z(\text{N1})]^2$ from these results we obtain $W_2/W_1 = 2.19$ for the RAS-I function, and for the more accurate RAS-E wavefunction $W_2/W_1 = 2.96$. A similar result, $W_2/W_1 = 3.06$, was obtained when we included in the active space δ -type orbitals. Our own experimental values are: $W_2/W_1 = 3.42$ at $T = 308$ K, and $W_2/W_1 = 3.29$ at $T = 318$ K. They compare favourably with a previous measurement, $W_2/W_1 = 3.13$ [30]. On the other hand, a semiempirical estimate of this ratio gave the wrong order of magnitude [30].

In view of the reasonable agreement between the theoretical and experimental ratios of the quadrupolar coupling constants (NQCCs) for the two N atoms, we can expect that the individual calculated NQCCs are also reasonable. This enables us to evaluate the correlation time for the relevant principal axis of the EFG tensor, which in this case also corresponds to the correlation time of molecular tumbling. The estimates for τ_c at two temperatures are given in Table 4. The small differences between τ_c computed from the N1 and N2 data reflect the nonequivalence of the measured and calculated W_2/W_1 ratio.

3.4. Experimental

The existing literature data [30] refer to sodium azide in water solution, where the azide anion and

Table 4
Correlation times for reorientation of N_3^- anion in *o*-dichlorobenzene solution

Atom	NQCC (MHz)	$T = 308$ K		$T = 318$ K	
		W (Hz)	τ_c (s)	W (Hz)	τ_c (s)
N1	-1.2857	36.4	4.7×10^{-12}	30.7	3.9×10^{-12}
N2	2.2127	124.7	5.4×10^{-12}	101.0	4.4×10^{-12}

sodium cation are probably well-separated. However, the solvated anion forms hydrogen bonds with water molecules, which may distort the charge distribution within the anion. Moreover, in water solution azidium salts undergo partial hydrolysis so that the experimental spectrum may correspond to a dynamic equilibrium between N_3^- and N_3H [28]. We therefore decided to use an aprotic solvent, namely, *o*-dichlorobenzene. In order to achieve solubility and to separate the ions, we employed kryptofix 221, an agent that strongly complexes sodium cations and presumably prevents them from forming close ionic pairs with azide anions.

The ^{14}N NMR spectra were measured at 36.14 MHz on a Bruker AM500 spectrometer. The sample contained 36 mg (0.55 mmol) of sodium azide (analytical grade) dissolved in 2.5 ml of *o*-dichlorobenzene kept over molecular sieves. Solubility was achieved by adding ≈ 185 mg (≈ 0.55 mmol) of kryptofix 221 (Sigma). Nitromethane (0.3 M in acetone- d_6) was used as an external chemical shift reference standard. The temperature within the probe was controlled to within 0.2° using a BTV-1000 temperature control unit. Indications of the thermocouple from the temperature unit are taken as the sample temperatures. We assess the latter to be accurate to within $\pm 2^\circ$. The measurement conditions were as follows: pulse width 40 μ s, pulse delay 0 s, spectral width 15.5 kHz. 2000 scans were accumulated.

The linewidths of the resonance signals, W_1 and W_2 , were determined using the LORE program provided by Bruker Company. The corrections (ΔW_k) to the linewidths due to both field inhomogeneity effects and contributions of other, non-quadrupolar, relaxation mechanisms can be assessed to be of the order of 1–2 Hz. They were neglected as being comparable to the overall experimental error.

4. Conclusions

We have compared the ab initio values of NMR parameters with experimental data. MCSCF functions have been used, and with the increase of the active space the agreement of the results with experimental values is improved for most of the properties. There is no obvious further extension of basis set or

RAS that is required. It appears that an estimate of the geometry dependence of the computed quantities and of the solvent effect, which might be large for an ion, would be more important.

For the shielding constants and spin–spin coupling constants, the quality of the results is similar to that of our previous calculations for isoelectronic molecules. We assume electric field gradient calculations are of the same accuracy. Comparison of the calculated and measured ratios of nuclear quadrupolar relaxation times suggests that the computed electric field gradients for both nuclei are accurate.

The method of determining molecular reorientation times based on experimental quadrupolar relaxation rates and calculated EFG tensors does not seem more prone to error than other approaches that have long been used in NMR relaxation studies on molecular tumbling (for a review of recent progress in this field see Refs. [32,33]). Conversely, given the relative ease of measuring quadrupolar relaxation times directly from resonance linewidths, the approach demonstrated here may gain more significance, along with an increase in the reliability of ab initio EFG values.

Acknowledgement

This work has been supported by the Danish Natural Science Research Council (Grant No. 11-0924).

References

- [1] K. Ruud, T. Helgaker, P. Jørgensen and K.L. Bak, Chem. Phys. Letters 226 (1994) 1.
- [2] A. Barszczewicz, M. Jaszunski, K. Kamienska-Trela, T. Helgaker, P. Jørgensen, O. Vahtras, Theoret. Chim. Acta 87 (1993) 19.
- [3] K. Ruud, T. Helgaker, R. Kobayashi, P. Jørgensen, K.L. Bak and H.J.Aa. Jensen, J. Chem. Phys. 100 (1994) 8178.
- [4] M. Jaszunski, T. Helgaker, K. Ruud, K.L. Bak and P. Jørgensen, Chem. Phys. Letters 220 (1994) 154.
- [5] O. Vahtras, H. Ågren, P. Jørgensen, T. Helgaker and H.J. Aa. Jensen, Chem. Phys. Letters 209 (1993) 201.
- [6] A. Barszczewicz, T. Helgaker, M. Jaszunski, P. Jørgensen and K. Ruud, J. Chem. Phys. 101 (1994) 6822.
- [7] A. Barszczewicz, T. Helgaker, M. Jaszunski, P. Jørgensen and K. Ruud, J. Magn. Reson., in press.

- [8] J.A. Tossell, ed., NATO ASI Series C, Vol. 386. Nuclear magnetic shieldings and molecular structure, Proceedings of the NATO Advanced Research Workshop, College Park, MA, USA (1992) (Kluwer, Dordrecht, 1993) p. 95.
- [9] W. Kutzelnigg, U. Fleischer and M. Schindler, *NMR Basic Principles Progr.* 23 (1990) 165.
- [10] R.H. Contreras and J.C. Facelli, *Annu. Rep. Nucl. Magn. Reson. Spectry.* 27 (1993) 255.
- [11] G.A. Webb, ed., Specialist periodical reports, nuclear magnetic resonance, Vols. 12–23 (The Royal Society of Chemistry, London, 1983–1994), chapters on theoretical aspects of nuclear shielding and spin–spin couplings.
- [12] S.P.A. Sauer, I. Paidarová and J. Oddershede, *Theoret. Chim. Acta* 88 (1994) 351.
- [13] J. Geertsen, J. Oddershede, W.T. Raynes and T.L. Marvin, *Mol. Phys.* 82 (1994) 29.
- [14] J. Gauss, *Chem. Phys. Letters* 229 (1994) 198.
- [15] H. Sekino and R.J. Bartlett, *Chem. Phys. Letters* 225 (1994) 486.
- [16] P. Pykko and A.J. Sadlej, *Chem. Phys. Letters* 227 (1994) 221.
- [17] J. Vojtik, L. Cespiva, I. Paidarova and J. Savrda, *Chem. Phys.* 150 (1991) 65.
- [18] D.M. Bishop and S.M. Cybulski, *J. Chem. Phys.* 100 (1994) 628.
- [19] D. Cremer and M. Kruger, *J. Phys. Chem.* 96 (1992) 3239.
- [20] T. Helgaker, P. Taylor, K. Ruud, O. Vahtras and H. Koch, Hermit, a molecular integral program.
- [21] H.J. Aa. Jensen, H. Ågren and J. Olsen, Sirius, a program for calculation of MCSCF wave functions.
- [22] T. Helgaker, K.L. Bak, P. Dahle, H.J. Aa. Jensen, P. Jørgensen, R. Kobayashi, H. Koch, K. Mikkelsen, J. Olsen, K. Ruud, P.R. Taylor and O. Vahtras, Abacus, a second-order MCSCF molecular property program.
- [23] J. Olsen and P. Jørgensen, *J. Chem. Phys.* 82 (1985) 3235.
- [24] P. Jørgensen, H.J. Aa. Jensen and J. Olsen, *J. Chem. Phys.* 89 (1988) 3654.
- [25] F. London, *J. Phys. Radium* 8 (1937) 397.
- [26] T. Helgaker and P. Jørgensen, *J. Chem. Phys.* 95 (1991) 2595.
- [27] P. Botschwina, *J. Chem. Phys.* 85 (1986) 4591.
- [28] J. Muller and H.Fr. Schroder, *Z. Anorg. Allg. Chem.* 450 (1979) 149.
- [29] D. Magan Kanjia, J. Mason, I.A. Stenhouse, R.E. Banks and N.D. Venayak, *J. Chem. Soc. Perkin II* (1981) 957.
- [30] M. Witanowski, L. Stefaniak and G.A. Webb, *J. Magn. Reson.* 36 (1979) 277.
- [31] A. Abragam, *The principles of nuclear magnetism* (Oxford Univ. Press, Oxford, 196) ch. 8.
- [32] J. Kowalewski, *Ann. Rep. NMR Spectry.* 22 (1989) 307.
- [33] J. Kowalewski, *Ann. Rep. NMR Spectry.* 23 (1991) 289.