A Reanalysis of ^{14}N Nuclear Quadrupole Coupling and Methyl Internal Rotation in the Rotational Spectra of Monomethyl Oxazoles and Isoxazoles

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Z. Naturforsch. **45a**, 911–922 (1990); received May 10, 1990

Dedicated to Professor John Sheridan

Previously published rotational frequencies of 2-, 4-, and 5-methyl oxazole and of 3- and 5-methyl isoxazole are reanalysed to obtain correct rotational constants (*A* constants in the first place) on the basis of hypothetically unsplit rotational centre frequencies. With these, r_0-structural parameters of the respective methyl group could be determined, thus allowing us to consider the influence of methyl substitution on the ^{14}N-quadrupole coupling tensor and the structural relevance of the internal rotor angle given by torsional analysis.

^{14}N nuclear quadrupole hfs and IAM methyl torsional analyses were redone with the correct rotational constants.

Introduction

The frequency components of ^{14}N-quadrupole hyperfine structure (hfs) and methyl-torsional fine structure (fs) in the rotational (microwave) spectra had already been measured in Bangor with conventional Stark spectroscopy and in Kiel with microwave Fourier transform (MWFT) technique. The results and experimental details concerning the synthesis or procurement of substances, the assignment of fs- and hfs-components, and experimental spectroscopic parameters were published in [1] (monomethyl oxazoles) and [2] (monomethyl isoxazoles).

So we have very precise frequency data for five monomethyl derivatives originating from systematically substituting on the basic structures (parent molecules) oxazole and isoxazole. Possible conclusions drawn from analysis thus gain in generality and weight. Two interesting questions arising in the context of hfs- and fs-analyses are whether the electronic environment of the ^{14}N-nucleus is noticeably modified on methyl substitution and whether the internal rotor angle coming out of torsional analysis can be relied on as structural information. These questions are dealt with in detail in the Discussion of this paper. Answers can be obtained through the mediation of r_0-structures by an ^{14}N-quadrupole tensor transformation into a reference system like the principal quadrupole tensor axes system or the principal inertial axes system of the respective species to make possible a general comparison.

Partial methyl r_0-structures, connected with the r_0-structures of oxazole and isoxazole, have to be fitted to the rotational constants of the methyl derivatives from centrifugal distortion (cd) analyses of hypothetically unsplit rotational centre frequencies. Fs- and hfs-analyses have to be performed with these rotational constants. Dipole-forbidden transitions of the torsional E-species must be centrifugally corrected separately before the respective torsional splitting can be used for torsional analysis. As these points were not adhered to in [1] and [2], I had to redo the quantum mechanical analyses (cd, fs and hfs) and r_0-structural fits, to resume the comprehensive discussion on this improved basis and to publish the results in this paper.

Quantum Mechanical Analyses

According to the three perturbations of free molecular rotation which appear in the microwave spectra as cd-displacements and fs- and hfs-splittings, I evaluated the measured frequency data with cd-, fs- and hfs-analyses. They could be performed one after the other independently from each other. Considering experimental accuracy, reciprocal interactions of the

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Table 1. Measured frequency components of the methyl torsional fine structure (fs) and the ^{14}N-quadrupole hyperfine structure (hfs) in the rotational spectra (power spectra with a microwave pulse spectrometer) of monomethyl oxazoles and isoxazoles.

In this work only the first three rotational lines are listed for each methyl compound. The complete list of measured transitions is deposited at the Universitätsbibliothek der Universität Kiel * under number TNA 21. The experimental data are compared with predictions according to hfs-, fs-, and centrifugal distortion (cd-) analyses. Frequencies, splittings, and deviations in MHz. The rotational level with the higher energy value is marked in the headline with single primes. The most intense component, which all hfs-splittings refer to, is listed first for each rotational transition.

Γ: torsional (fs) symmetry species, E # dipole-forbidden E-species line;
ν_{exp}: measured frequency component;
$\Delta\nu_{AE}$: measured torsional splitting referring to the A-species calculated by averaging the torsional splittings of all hfs-components for the respective rotational transition; single standard deviations in kHz in parentheses;
ν_0: hypothetically unsplit rotational centre frequency (hfs and fs eliminated);
δ_{hfs}, δ_{fs}, δ_{cd}: deviations of predictions from experimental frequencies or splittings;
*: not used for ^{14}N-quadrupole hfs-analysis;
**: not used for methyl torsional analysis;
***: not used for centrifugal distortion analysis because of a Student's t-test;
nm: frequency component not measured;
}: frequency components overlaid (not separately resolved).

Table 1.1. 2-Methyl Oxazole.

J'	K'_-	K'_+	–	J''	K''_-	K''_+	F'–F''	Γ	ν_{exp}	δ_{hfs}	$\Delta\nu_{AE}$	δ_{fs}	ν_0	δ_{cd}
1	1	0	–	1	0	1	2–2	A	6 444.144		15.248 (32)	−0.158	6 430.743	−0.062
				*				E	6 459.410					
							1–1	A	6 444.344	−0.030				
								E	nm					
							2–1	A	6 443.685	−0.005				
								E	6 458.974					
							1–2	A	6 444.774	0.004				
								E	6 459.980					
							0–1	A	6 442.729	0.000				
								E	6 457.959					
1	1	1	–	0	0	0	2–1	A	11 812.592		−55.659 (56)	0.028	11 798.880	0.059
								E	11 756.941					
							1–1	A	11 811.491	0.003				
								E	11 755.896					
							0–1	A	11 814.240	−0.001				
								E	11 758.509					
2	0	2	–	1	1	1	3–2	A	7 256.447		55.173 (49)	−0.090	7 269.896	−0.014
								E	7 311.617					
							2–1	A	7 257.872	0.005				
								E	7 312.985					
							1–0	A	7 254.618	−0.002				
								E	7 309.867					
							2–2	A	nm					
								E	7 311.921					
							1–1	A	7 257.363	−0.002				
								E	7 312.522					

Table 1.2. 4-Methyl Oxazole.

J'	K'_-	K'_+	–	J''	K''_-	K''_+	F'–F''	Γ	ν_{exp}	δ_{hfs}	$\Delta\nu_{AE}$	δ_{fs}	ν_0	δ_{cd}
1	1	1	–	0	0	0	2–1	A	11 837.160		−2.540 (4)	−0.005	11 835.607	−0.017
								E	11 834.625					
							1–1	A	11 836.266	−0.002				
								E	11 833.726					
							0–1	A	11 838.516	−0.011				
								E	11 835.971					
2	1	2	–	1	0	1	3–2	A	17 026.657		−2.251 (3)	−0.008	17 025.053	−0.009
								E	17 024.405					
							2–1	A	17 025.710	0.001				
								E	17 023.460					
							1–1	A	17 026.868	−0.007				
								E	17 024.621					
							1–0	A	17 027.378	0.000				
								E	17 025.122					
2	2	0	–	1	1	1		A	31 362.06		8.04	−0.66	31 357.871	−0.079
				*.**				E	31 370.10					

* Westring 400, D-2300 Kiel 1, FRG.

Table 1.3. 5-Methyl Oxazole.

J'	K'_-	K'_+	–	J''	K''_-	K''_+	F'–F''	Γ	ν_{exp}	δ_{hfs}	$\Delta\nu_{AE}$	δ_{fs}	ν_0	δ_{cd}
2	0	2	–	1	0	1	3–2	A	12 303.308		−0.024	0.000	12 303.232	−0.083
			*,**					E	12 303.284					
2	1	1	–	1	1	0	3–2	A	13 365.081		−0.098 (7)	−0.002	13 364.974	−0.081
								E	13 364.980					
							2–1	A	13 364.428	−0.007				
								E	13 364.323					
							1–0	A	13 366.133	−0.001				
								E	13 366.045					
2	1	2	–	1	1	1	3–2	A	11 460.138		0.102 (1)	−0.008	11 459.980	−0.089
								E	11 460.239					
							2–1	A	11 459.424	−0.002				
								E	11 459.526					

Table 1.4. 3-Methyl Isoxazole.

J'	K'_-	K'_+	–	J''	K''_-	K''_+	F'–F''	Γ	ν_{exp}	δ_{hfs}	$\Delta\nu_{AE}$	δ_{fs}	ν_0	δ_{cd}
1	1	1	–	0	0	0	2–1	A	11 735.149		−10.835 (9)	−0.024	11 730.494	−0.005
								E	11 724.319					
							1–1	A	11 733.622	0.002				
								E	11 722.794					
							0–1	A	11 737.434	0.002				
								E	11 726.587					
2	1	2	–	1	0	1	3–2	A	16 895.288		− 8.006 (4)	−0.030	16 890.648	−0.010
								E	16 887.284					
							2–1	A	16 893.770	0.001				
								E	16 885.767					
							1–0	A	16 897.672	−0.002				
								E	16 889.666					
							2–2	A	16 895.410	−0.010				
								E	16 887.408					
							1–1	A	16 893.597	−0.001				
								E	16 885.583					
2	2	0	–	2	1	1	3–3	A	17 025.266		61.481 (26)	0.004	17 011.466	0.027
								E	17 086.764					
							2–2	A	17 022.015	0.002				
								E	17 083.471					
							1–1	A	17 027.074	−0.003				
								E	17 088.588					
							2–3	A	17 023.656	−0.005				
								E	17 085.112					

Table 1.5. 5-Methyl Isoxazole.

J'	K'_-	K'_+	–	J''	K''_-	K''_+	F'–F''	Γ	ν_{exp}	δ_{hfs}	$\Delta\nu_{AE}$	δ_{fs}	ν_0	δ_{cd}
1	1	1	–	0	0	0	2–1	A	11 851.768		−37.644 (7)	−0.073	11 841.322	−0.018
								E	11 814.118					
							1–1	A	11 850.701	0.001				
								E	11 813.064					
							0–1	A	11 853.387	−0.020				
								E	nm					
2	1	2	–	1	0	1	3–2	A	17 072.236		−22.941 (6)	−0.095	17 061.800	−0.029
								E	17 049.298					
							2–1	A	17 071.180	−0.006				
								E	17 048.246					
							1–0	A	17 073.880	−0.001				
								E	17 050.940					
							1–1	A	17 071.091	0.002				
								E	17 048.141					
2	2	0	–	2	1	1	3–3	A	17 155.377		188.538 (62)	−0.338	17 124.525	−0.083
								E	17 343.899					
							2–2	A	17 153.139	−0.004				
								E	17 341.634					
							1–1	A	17 156.612	0.010				
								E	17 345.256					
							3–2 }	A	17 154.271	0.006				
							2–3 }	E	17 342.762					

three perturbations can be neglected. A negligibly small interaction between e.g. methyl torsion and ^{14}N-quadrupole coupling can be inferred from the small standard deviations (8–17 kHz) of the hfs-analyses presented in Table 3 and from the just as small standard deviations of the torsional splittings $\Delta\nu_{AE}$ in Table 1. Hfs-multiplets need not to be frequency corrected, because, compared to a mean full line width of 50 kHz, the mean hfs-splitting of 600 kHz is so wide that neighbouring line profiles very seldom overlap and the quadrupole coupling constants are hardly influenced.

Table 1 contains the experimental frequency components ν_{exp}, the torsional splittings $\Delta\nu_{AE}$, the hypothetically unsplit centre frequencies ν_0 and deviations δ_{hfs}, δ_{fs} and δ_{cd} of the experimental data with respect to prospective calculations with the final results of hfs-, fs-, and cd-analyses. In Table 1 only the first three rotational lines are listed for each methyl compound. Frequencies measured in Bangor with conventional microwave spectroscopy (to be identified in Table 1 by their two digits' precision after the decimal point) have only been employed for cd-analysis. Spectroscopy in Bangor with unstabilized microwave radiation sources lead to full line widths at half height (FWHH) on the order of 1 MHz [3] compared with 50 kHz with MWFT-spectroscopy in Kiel. ^{14}N-hfs multiplets could thus not be resolved, and torsional splittings turned out to be systematically too narrow because of a partial overlap of neighbouring line profiles, as may be verified considering the signs of torsional splitting $\Delta\nu_{AE}$ and deviations δ_{fs} in Table 1 nearly always being the same. For the three methyl oxazoles gathered up, the sum of all 90 Bangor deviations δ_{fs} is $\sum\delta_{fs} = 73.28$ MHz, if we take all δ_{fs}-entries coinciding in their sign with the corresponding torsional splitting $\Delta\nu_{AE}$ as positive and the other ones as negative values.

Fs- and cd-analyses were alternately iterated to arrive at final rotational constants for a subsequent hfs-analysis. The results of the third cycle of iteration between fs- and cd-analysis are comprised in Table 2. Methyl internal rotation fs-analyses were calculated according to the internal axis method (IAM) with the computer program KC3IAM [4], a modified and extended version of Woods' program ([5–7]). KC3IAM needs absolute torsional A- and E-species line frequencies as input. Hypothetically unsplit A-species centre frequencies were obtained by applying prospected hfs-displacements to measured A-species hfs-components. The torsional splitting $\Delta\nu_{AE}$ of a rotational line is the arithmetic mean of the fs-splittings of all hfs-components for this transition, thus giving the previously mentioned standard deviation in parentheses. Absolute E-species centre frequencies can easily be derived from A centre frequencies and corresponding $\Delta\nu_{AE}$ splittings. Fourth order cd-analyses were performed according to Watson's A-reduction ([8, 9]) with the program ZFAP4 (release 4.5 by Dr. V. Typke) for all available rotational centre frequencies ν_0 hypothetically unsplit by methyl torsion or ^{14}N-quadrupole coupling. Δ-constants are necessary for a centrifugal correction of dipole-forbidden E-species lines with KC3IAM, and with $\varkappa \approx -0.7$ the oxazole and isoxazole methyl derivatives are no near prolate top molecules which would have suggested Watson's S-reduction. In comparison with results from a cd-analysis of A-species lines as shown in [1] and [2], the rotational constants B and C did not change much for hypothetical centre frequencies, in contrast to the rotational constant A which differs as much as 14 MHz (in the case of 2-methyl oxazole). Oxazole and isoxazole heterocyclic rings are composed of elements from the first row of the periodic classification which have a similar atomic mass. Because of this rather homogeneous distribution of masses the principal inertia axis a is almost collinear with the methyl bond axis in the case of the methyl derivatives, i.e., the angle $\measuredangle(a, i)$ listed in Table 2 comes out rather small by the fs-analysis. That is also the reason why for all five monomethyl-substituted molecules we get very similar rotational constants and centrifugal parameters as far as the latter ones could be determined with adequate accuracy. The moments of inertia I_α of the methyl group coincide quite well in a range from 3.19 to 3.20 amuÅ^2. In the framework of a simple rigid model of the methyl group, this value corresponds to a quite plausible C-H-distance of from 1.089 to 1.091 Å (108.9–109.1 pm). The model consists of three H-atoms with masses m_H, each bonded to a C-atom at a C–H-bond distance r with the tetrahedral angle τ between two C–H-bonds, respectively.

$$r = \sqrt{\frac{2I_\alpha}{3m_H(1-\cos\tau)}} \cdot \sin\frac{\pi}{3} = r(I_\alpha). \qquad (1)$$

As can be clearly seen from Table 2, the standard deviations σ_{fs} of the torsional analyses strongly depend on the barrier heights V_3 hindering internal rotation of the methyl group. The better experimental frequency accuracy of the MWFT-technique of about 10 kHz

has further limited the range of applicability of Woods' program. Contrary to [10], for reduced hindering potentials lower than about $s = 30$ ($V_3 = 1100$ cal/mol or 4600 J/mol) one should abandon Woods' program with its simplifications and approximations and calculate more accurately.

^{14}N-quadrupole hfs-analyses were carried out with the rotational constants from Table 2 for A-species hfs-multiplets only, because E-species lines almost perfectly coincide with A-lines when superimposed and therefore do not contribute any further information (no interaction between methyl torsion and ^{14}N-quadrupole coupling). According to a first order perturbation treatment, linearly combined coupling constants $\chi_+ = \chi_{bb} + \chi_{cc}$ and $\chi_- = \chi_{bb} - \chi_{cc}$ were fitted to experimental hfs-splittings with respect to the most intense hfs-component of the respective rotational transition. We used the computer programs HT1NQ, QUAD, and DH14KS. The results of these analyses are contained in Table 3 together with some comparative data for the parent molecules oxazole [11] and isoxazole ([12, 13]) as far as they were accessible from literature. The precision and convergence of the fitting calculations prove a first order perturbation treatment to be fully sufficient in our cases. An off-diagonal coupling element χ_{ab} can thus experimentally not be determined, it can only be obtained by quadrupole tensor transformation (see the Discussion).

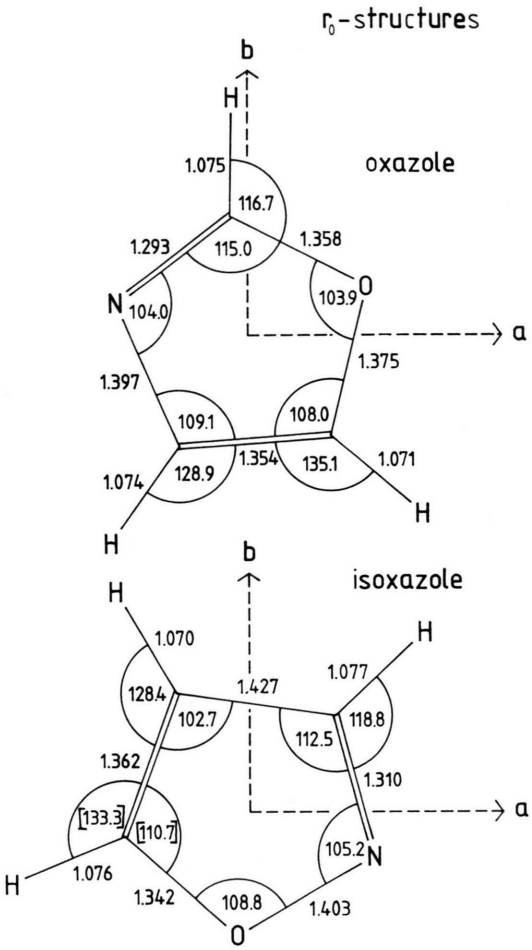


Fig. 1. r_0-structures of the parent molecules oxazole and isoxazole.
Bond angles (in degrees °) and lengths (in Å) have been obtained by fitting 13 structural parameters, i.e. six angle and seven length parameters, to nine sets of rotational constants of the most abundant normal isotopic species and eight isotopically single-substituted derivatives (oxazole: [11], isoxazole: [14]). Fixed bond angles in square brackets. We used a conversion factor of 505.3790 GHz · amuÅ^2 to convert a moment of inertia into a rotational constant and vice versa.

Discussion

For oxazole [11] and isoxazole [13] complete ^{14}N-quadrupole coupling tensors or, equivalently, the principal tensor elements χ_{zz}, χ_{xx}, χ_{yy} and thus the angle $\measuredangle(z, a)$ between the principal quadrupole tensor axis z and the principal inertial axis a, were determined. As the off-diagonal coupling elements χ_{ab} of the monomethyl derivatives could not be fixed spectroscopically, I could not diagonalize the ^{14}N-quadrupole tensors in the respective molecular principal inertia axes system to make possible a direct comparison of principal tensor elements, but had to resort to tensor transformation methods.

The adequate transformation angle depends on the principal quadrupole tensor's rotational position relative to the molecular framework and on molecular structures. So in the beginning, I presupposed the relative tensor positions of the parent molecules also for the methylated species. I then tried to improve the r_0-structures of the methyl derivatives by an r_0-structural optimization of the methyl partial structures. I assumed a plausible methyl configuration consisting of three H-atoms tetrahedrally bonded to a C-atom with bond distances of 1.088 Å (108.8 pm) and connected it to oxazole and isoxazole r_0-structures. With the computer program MWSTR the distances between both were then fitted to the rotational constants in Table 2.

Table 2. Results from alternately iterated IAM methyl internal rotation (fs) and centrifugal distortion (cd) analyses of the microwave spectra of oxazole and isoxazole monomethyl derivatives.
Single standard deviations in units of the last digit in parentheses, fixed values in brackets.

A, B, C: rotational constants in MHz from a cd-analysis of the centre frequencies v_0 in Table 1 according to Watson's A-reduction;
Δ_J, Δ_{JK}, Δ_K, δ_J, δ_K: fourth order centrifugal parameters in kHz according to Watson's A-reduction in the representation I^r;
n_{cd}: number of rotational lines used for cd-analysis;
σ_{cd}: standard deviation of the cd-analysis in kHz;
$w_1(s)$: first Fourier coefficient (dimensionless) when expanding the eigenvalues of Mathieu's differential equation;
$\measuredangle(a, i)$, $\measuredangle(b, i)$: angles between principal inertia axis a or b and internal rotation axis i in degrees (°);
As i lies in the a,b-plane, $\measuredangle(a, i)$ and $\measuredangle(b, i)$ are correlated: $\measuredangle(b, i) = 90° - \measuredangle(a, i)$ and $\measuredangle(c, i) = 90°$.
I_α: moment of inertia of the methyl group in amuÅ^2;
n_{fs}: number of rotational lines used for fs-analysis;
n_{AE}: number of torsional splittings used for fs-analysis;
σ_{fs}: standard deviation of the fs-analysis in kHz;
$\overline{\Delta\nu_{AE}}$: mean experimental torsional splitting in MHz.

Derived parameters below the broken line:

$\varkappa$: Ray's asymmetry parameter (dimensionless) $\varkappa = (2B - A - C)/(A - C)$;
s: reduced hindering potential (dimensionless);
V_3: barrier hindering internal rotation of the methyl group in cal/mol and J/mol;
F: reduced rotational constant of the internal rotation in GHz;
V_3 [cal/mol] $= F$ [GHz] $\cdot\ s/4.66018$;
λ_a, λ_b: direction cosines of the internal rotation axis i (cosines of $\measuredangle(a, i)$ and $\measuredangle(b, i)$; dimensionless).

	Methyl oxazoles						Methyl isoxazoles			
	2-		4-		5-		3-		5-	
A	9114.816	(14)	9240.8615	(82)	9303.9928	(97)	9150.4146	(64)	9231.071	(16)
B	3716.9858	(61)	3529.6351	(29)	3579.3522	(16)	3515.6048	(25)	3559.3984	(52)
C	2684.1301	(53)	2594.7342	(26)	2626.8481	(16)	2580.0775	(22)	2610.2362	(58)
Δ_J	0.204	(36)	0.2549	(81)	[0.0]		0.215	(24)	0.122	(34)
Δ_{JK}	2.04	(19)	2.044	(94)	2.191	(62)	1.36	(22)	1.42	(28)
Δ_K	0.36	(26)	1.194	(96)	[0.0]		0.65	(24)	[0.0]	
δ_J	0.114	(17)	0.0828	(52)	0.1107	(23)	0.0558	(95)	0.113	(15)
δ_K	−0.61	(34)	−0.17	(16)	[0.0]		0.82	(15)	[0.0]	
n_{cd}	65		87		52		24		27	
σ_{cd}	158		104		62		22		80	
$w_1(s)$	−0.4962	$(14)\cdot10^{-2}$	−0.50260	$(23)\cdot10^{-3}$	−0.29171	$(84)\cdot10^{-3}$	−0.16034	$(19)\cdot10^{-2}$	−0.37186	$(91)\cdot10^{-2}$
$\measuredangle(a, i)$	5.8	(14)	4.08	(31)	5.33	(16)	4.94	(64)	7.61	(87)
I_α	3.201	(12)	3.1905	(21)	3.1840	(68)	3.1983	(47)	3.1999	(90)
n_{fs}	24		38		17		22		22	
n_{AE}	24		40		17		22		22	
σ_{fs}	499		30		5		81		363	
$\overline{\Delta\nu_{AE}}$	139.743		57.562		2.038		82.463		84.847	
$\varkappa$	−0.6787728	(25)	−0.7186630	(12)	−0.71469718	(76)	−0.71522700	(99)	−0.7132802	(23)
s	20.022	(15)	34.0216	(30)	37.778	(20)	26.5595	(71)	21.622	(14)
V_3 [cal/mol]	719.4	(34)	1227.29	(97)	1365.8	(38)	955.2	(18)	777.4	(29)
V_3 [J/mol]	3011	(14)	5137.2	(40)	5717	(16)	3998.4	(74)	3254	(12)
F	167.51	(66)	168.18	(12)	168.55	(37)	167.68	(27)	167.63	(51)
$\measuredangle(b, i)$	84.2	(14)	85.92	(31)	84.67	(16)	85.06	(64)	82.39	(87)
λ_a	0.9949	(28)	0.99747	(40)	0.99568	(26)	0.9963	(10)	0.9912	(21)
λ_b	0.101	(24)	0.0711	(54)	0.0929	(28)	0.086	(11)	0.132	(15)

Table 2.1. Correlation matrices of parameters determined with cd-analysis.

a) methyl oxazoles

	2-methyl oxazole								4-methyl oxazole							
A	1.00								1.00							
B	0.74	1.00							0.87	1.00						
C	0.68	0.67	1.00						0.82	0.78	1.00					
Δ_J	0.38	0.37	0.62	1.00					0.62	0.61	0.53	1.00				
Δ_{JK}	0.41	0.42	0.13	−0.31	1.00				0.63	0.51	0.54	0.19	1.00			
Δ_K	0.41	0.02	0.26	0.72	−0.37	1.00			0.35	0.24	0.14	0.80	−0.09	1.00		
δ_J	0.28	0.47	−0.09	−0.33	0.87	−0.36	1.00		0.57	0.54	0.37	0.28	0.90	0.13	1.00	
δ_K	−0.26	−0.31	−0.06	0.33	−0.95	0.37	−0.86	1.00	−0.49	−0.38	−0.44	−0.08	−0.94	0.05	−0.92	1.00

	5-methyl oxazole				
A	1.00				
B	0.29	1.00			
C	0.14	0.40	1.00		
Δ_{JK}	0.83	0.18	0.08	1.00	
δ_J	0.15	0.54	−0.46	0.19	1.00

b) methyl isoxazoles

	3-methyl isoxazole								5-methyl isoxazole							
A	1.00								1.00							
B	0.89	1.00							0.77	1.00						
C	0.64	0.66	1.00						0.70	0.64	1.00					
Δ_J	0.72	0.82	0.59	1.00					0.68	0.74	0.63	1.00				
Δ_{JK}	0.65	0.54	0.07	0.54	1.00				0.70	0.59	0.31	0.86	1.00			
Δ_K	0.06	0.32	0.53	0.42	−0.44	1.00			–	–	–	–	–			
δ_J	0.40	0.52	−0.05	0.39	0.72	−0.04	1.00		0.10	0.33	−0.44	0.29	0.54	1.00		
δ_K	0.05	0.02	0.01	0.27	−0.23	0.12	−0.58	1.00	–	–	–	–	–	–		

Table 2.2. Correlation matrices of parameters determined with torsional analysis.

	a) methyl oxazoles									b) methyl isoxazoles					
	2-methyl oxazole			4-methyl oxazole			5-methyl oxazole			3-methyl isoxazole			5-methyl isoxazole		
$w_1(s)$	1.00			1.00			1.00			1.00			1.00		
$\measuredangle(a, i)$	−0.99	1.00		−0.99	1.00		−0.69	1.00		−0.997	1.00		−0.99	1.00	
I_α	−0.95	0.95	1.00	−0.91	0.91	1.00	0.92	−0.37	1.00	−0.95	0.94	1.00	−0.73	0.79	1.00

Parent molecule r_0-structures were obtained by fitting (program MWSTR) 13 structural parameters, i.e. seven distances and six angles, to nine sets of rotational constants of the oxazole [11] and isoxazole [14] normal isotopic species and eight monosubstituted isotopomers, respectively, whose microwave spectra had originally been assigned for the purpose of r_s-structure determination. It is therefore easily understood that the available data did not suffice for a complete isoxazole r_0-structure fit, so that I had to fix the H-atom bond angle in 5-position at its r_s-structure value because otherwise it would have resulted with great uncertainty (110(12)°). In Fig. 1 I show these final oxazole and isoxazole r_0-structures in their principal molecular inertia a, b-axes systems; the angles 133.3° and 110.7° in the isoxazole 5-position are taken over from the r_s-structure [14] and were not r_0-fitted.

While optimizing the methyl partial structures, I only fitted the bond distance between the heterocyclic ring and the methyl group. The bond angle $\measuredangle(CH_3, \text{ring})$ was always held fixed. Two blocks can be discerned in Table 4 corresponding to two alternate treatments: One time I took over $\measuredangle(CH_3, \text{ring})$ as $\measuredangle(H, \text{ring})$ at the respective heterocyclic ring position, the other time I took the angle $\measuredangle(a, i)$ from torsional analysis seriously as structural information and adapted

Table 3. Results from ^{14}N-quadrupole hyperfine structure (hfs) analyses of the rotational spectra of monomethyl oxazoles and isoxazoles.
The hfs-analyses were performed according to first order perturbation theory using the rotational constants from Table 2. Nuclear quadrupole coupling constants in MHz, single standard deviations in units of the last digit in parentheses.

χ_+, χ_-: linear combinations of nuclear quadrupole coupling constants $\chi_+ = \chi_{bb} + \chi_{cc}$, $\chi_- = \chi_{bb} - \chi_{cc}$;
(χ_+, χ_-): correlation coefficient between χ_+ and χ_-;
n_{hfs}: number of rotational lines used for hfs-analysis;
n_{spl}: number of splittings used for hfs-analysis;
$\overline{\Delta\nu}_{\text{hfs}}$: mean experimental hfs-splitting in kHz;
σ_{hfs}: standard deviation of the hfs-fit in kHz.

Derived parameters below the broken line:

$\chi_{aa}^{\text{exp}} = \chi_+$
$\measuredangle(z, a)$: angle between principal ^{14}N-quadrupole coupling tensor axis z and principal inertia axis a in degrees (°); $\measuredangle(z, a)$ was calculated on the assumption that under methyl substitution the principal quadrupole tensor axes system remains unchanged in its relation to the respective heterocyclic ring and that the methyl-ring bond angle is the same as that of the H-atom in the unsubstituted species;
$|\chi_{ab}|, \chi_{zz}, \chi_{xx}$: unsigned value of the off-diagonal coupling element and the two transformation dependent principal coupling tensor elements calculated from the experimentally determined coupling constants χ_{aa}^{exp} and χ_{bb}^{exp} with the projection angle $\measuredangle(z, a)$.

a) Methyl oxazoles					b) Methyl isoxazoles		
	Methyl oxazoles			Oxazole [11]	Methyl isoxazoles		Isoxazole ([12], [13])
	2-	4-	5-		3-	5-	
χ_+	−1.547 (21)	−0.689 (10)	−2.215 (13)	3.92 (2)	−5.4324 (73)	−3.7140 (89)	−0.526 (50)
χ_-	−5.773 (26)	−5.287 (12)	−2.617 (10)	−0.84 (2)	−4.734 (11)	−3.393 (12)	−0.689 (50)
(χ_+, χ_-)	−0.38	−0.26	0.07		−0.26	−0.19	
n_{hfs}	16	15	19	10	22	19	2
n_{spl}	31	31	37	22	47	40	4
$\overline{\Delta\nu}_{\text{hfs}}$	695	597	328	1290	797	604	243
σ_{hfs}	17	9	8	66	8	9	
χ_{aa}^{exp}	1.547 (21)	0.689 (10)	−2.215 (13)	−3.92 (2)	5.4324 (73)	3.7140 (89)	0.526 (50)
χ_{bb}^{exp}	−3.660 (24)	−2.988 (11)	−0.201 (12)	1.54 (2)	−5.0832 (92)	−3.554 (10)	−0.609 (50)
$\chi_{cc} = \chi_{yy}$	2.113 (24)	2.299 (11)	2.416 (12)	2.38	−0.3492 (92)	−0.161 (10)	0.083 (50)
$\measuredangle(z, a)$	−78.3	64.8	−35.3	8.3	−86.0	66.5	48.0 (20)
$\lvert\chi_{ab}\rvert$	1.127	2.222	2.860	0.81	0.739	3.897	5.40
χ_{zz}	−3.894	−4.034	−4.240	−4.04	−5.135	−5.248	−5.42 (7)
χ_{xx}	1.781	1.735	1.824	1.66	5.484	5.408	5.34 (7)

$\measuredangle(CH_3, \text{ring})$ correspondingly, as pointed out below. With the projection angles $\measuredangle(z, a)$ resulting from the optimized structures of the methyl derivatives, I transformed the principal oxazole [11] and isoxazole [13] ^{14}N-quadrupole tensor elements χ_{zz} and χ_{xx} into the principal inertia axes system of the respective methyl compound according to

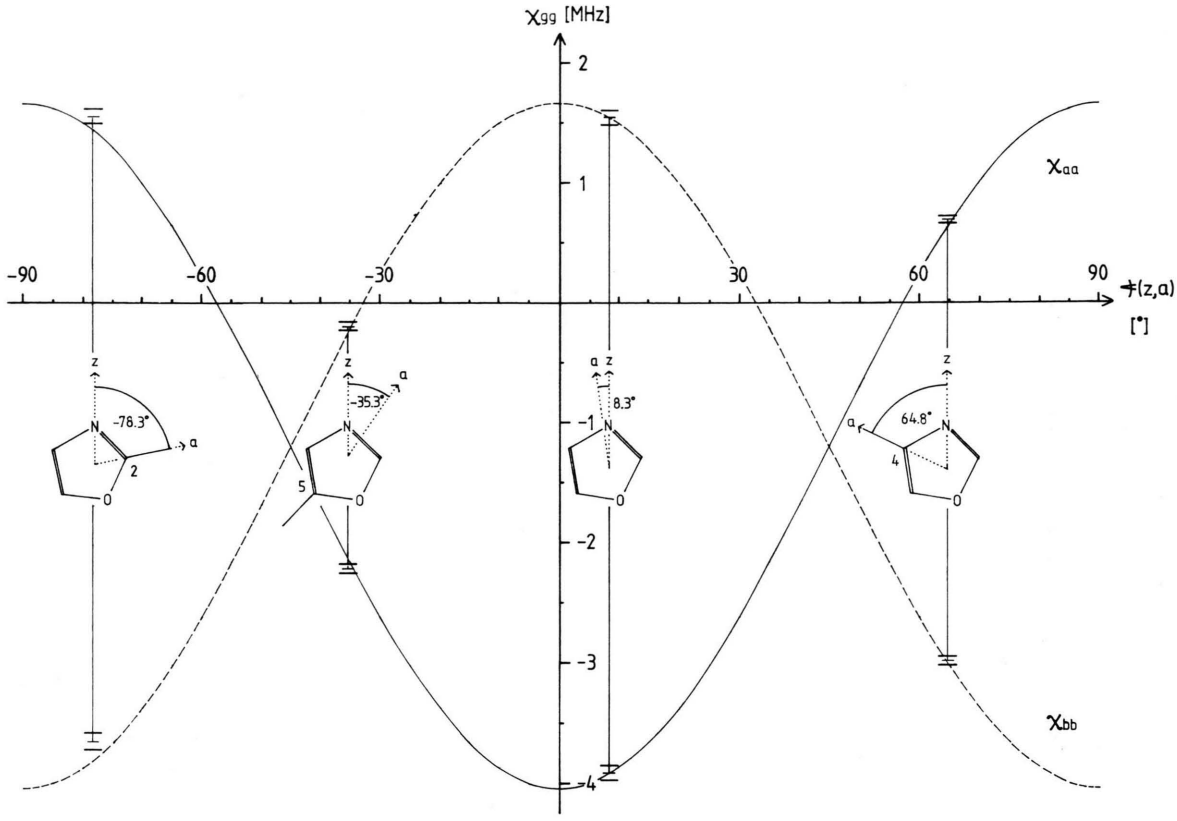
$$\chi_{aa} = \chi_{zz} \cos^2\{\measuredangle(z, a)\} + \chi_{xx} \sin^2\{\measuredangle(z, a)\} \quad (2\text{a})$$

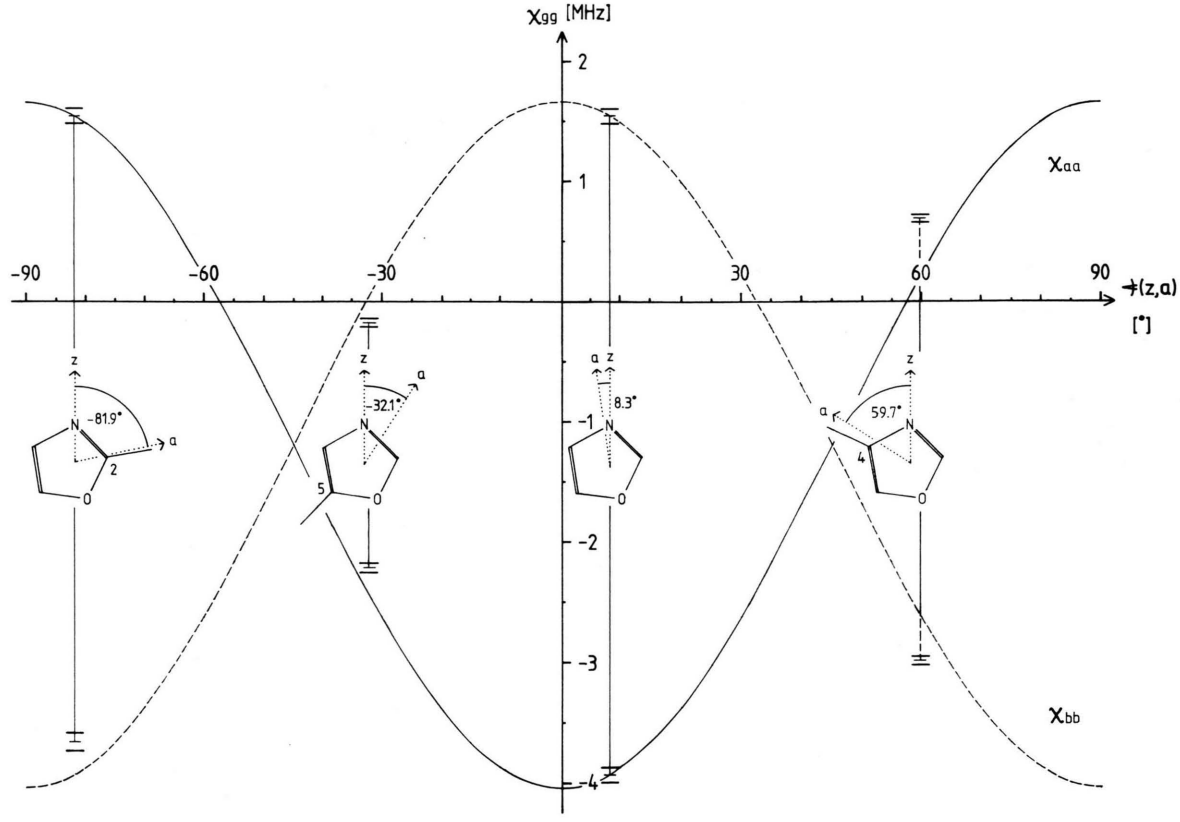
and

$$\chi_{bb} = \chi_{zz} \sin^2\{\measuredangle(z, a)\} + \chi_{xx} \cos^2\{\measuredangle(z, a)\}. \quad (2\text{b})$$

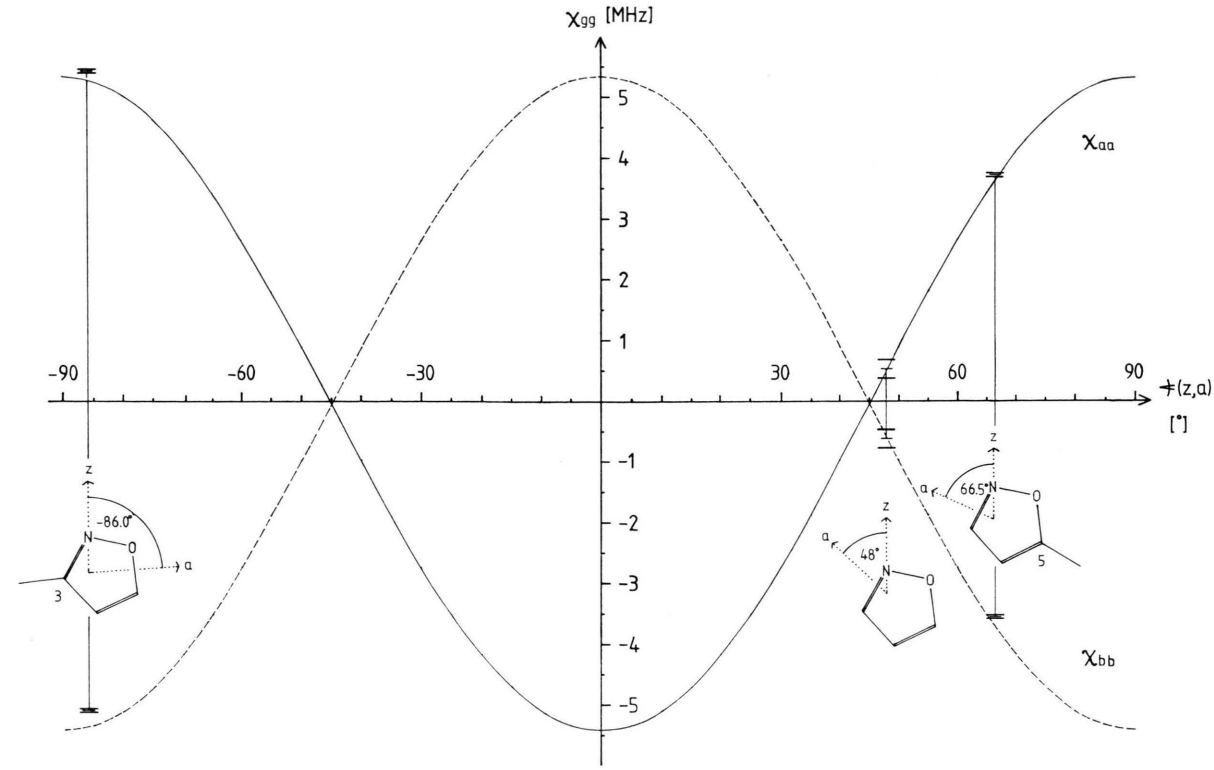
The experimental diagonal coupling elements χ_{aa}^{exp} and χ_{bb}^{exp} are also given in Table 4 with their triple standard deviations for a numerical comparison with the projected values. The angle $\measuredangle(CH_3, \text{ring})$ in block "$\measuredangle(a, i)$" of Table 4 was arrived at by parametrically varying a $\measuredangle(CH_3, \text{ring})$ taken over as $\measuredangle(H, \text{ring})$ from the respective parent molecule as starting-point, until the angle between methyl-bond axis and inertial axis a coincided with the absolute value of $\measuredangle(a, i)$. Torsional analysis only gives the direction cosine of the internal rotor axis and not the angle $\measuredangle(a, i)$ with sign. While varying $\measuredangle(CH_3, \text{ring})$, I selected the shortest of the two possible ways.

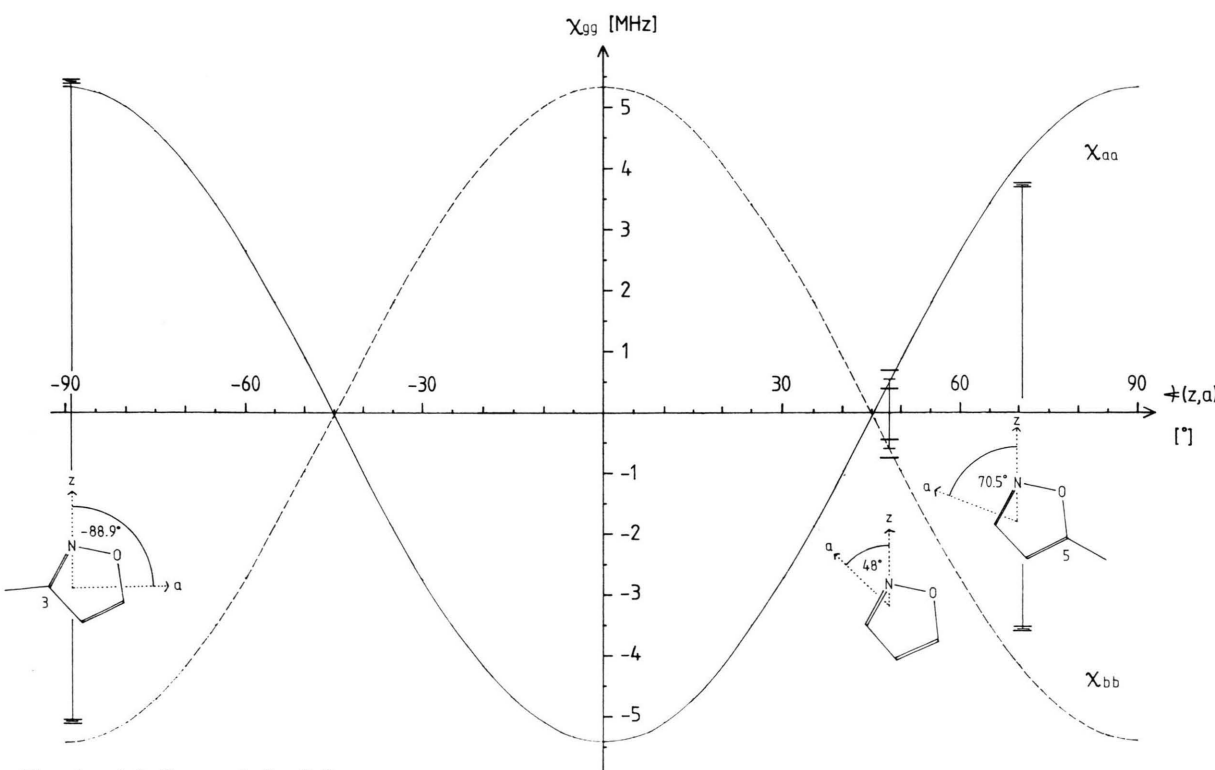
The agreement of experimental and projected diagonal coupling elements χ_{aa} and χ_{bb} can best be checked visually in Figures 2–5. Projected χ_{aa} and χ_{bb} are plotted as "sine curves" dependent on the projection angle $\measuredangle(z, a)$ according to (2a) and (2b), and experimental χ_{aa}^{exp}- and χ_{bb}^{exp}-values are drawn in as vertical bars with their triple standard deviations at the $\measuredangle(z, a)$-position entered in the appropriate quarter of Table 4.





Figs. 2 and 3: "oxazole-family".





Figs. 4 and 5: "isoxazole-family".

Table 4. Bond lengths between heterocyclic ring and methyl group from r_0-structure fits to the experimental rotational constants (Table 2) of monomethyl oxazoles and isoxazoles; diagonal coupling elements χ_{aa} and χ_{bb} from a transformation of the oxazole and isoxazole principal ^{14}N-quadrupole coupling tensors into the principal inertia axes systems of the monomethyl derivatives

Angles in degrees (°), bond lengths in Å, nuclear quadrupole coupling constants in MHz.

a) block "$\measuredangle$ (H, ring)": The bond angle $\measuredangle$ (CH_3, ring) between heterocyclic ring (oxazole or isoxazole) and methyl group is assumed to be the same as that between heterocyclic ring and H-atom in the parent molecules. $\measuredangle$ (CH_3, ring) $\stackrel{!}{=}$ $\measuredangle$ (H, ring) is given according to Fig. 1 with single standard deviations in units of the last digit in parentheses.

b) block "$\measuredangle$ (a, i)" below the interrupted line: The internal rotor angle $\measuredangle$ (a, i) from Table 2 is taken as structural information thus fixing the methyl-heterocyclic ring bond angle $\measuredangle$ (CH_3, ring).

Bond angles $\measuredangle$ (CH_3, ring) kept fixed during r_0-structure $\overline{CH_3}$-ring-bond length fits in square brackets.

$\measuredangle$ (z, a): projection angle for the ^{14}N-quadrupole coupling tensor transformation (z: principal quadrupole tensor axis, a: principal inertia axis);
$\measuredangle$ (z, a) follows from either of the above assumptions under the presupposition that the quadrupole principal axes' relative rotational position remains uninfluenced by methyl substitution.

Experimental χ_{aa}^{exp}- and χ_{bb}^{exp}-values from Table 3 are given just for comparison with the projected ones triple standard deviations corresponding to Figs. 2–5 in units of the last digit in parentheses.

	Methyl oxazoles			Methyl isoxazoles	
	2-	4-	5-	3-	5-
$\measuredangle$ (H, ring)					
$\measuredangle$ (CH_3, ring) $\stackrel{!}{=}$ $\measuredangle$ (H, ring)	[116.7 (31)]	[128.94 (85)]	[116.9 (10)]	[118.8 (75)]	[116.0]
$\overline{CH_3}$-ring	1.5018	1.5066	1.5007	1.5135	1.5052
$\measuredangle$ (z, a)	−78.3	64.8	−35.3	−86.0	66.5
χ_{aa}	1.425	0.624	−2.135	5.288	3.633
χ_{bb}	−3.805	−3.004	−0.245	−5.368	−3.713
$\measuredangle$ (a, i)					
$\measuredangle$ (CH_3, ring)	[111.0]	[137.94]	[112.65]	[110.43]	[109.74]
$\overline{CH_3}$-ring	1.5146	1.5172	1.5101	1.5272	1.5244
$\measuredangle$ (z, a)	−81.9	59.7	−32.1	−88.9	70.5
χ_{aa}	1.548	0.206	−2.428	5.336	4.145
χ_{bb}	−3.928	−2.586	0.048	−5.416	−4.225
χ_{aa}^{exp}	1.547 (63)	0.689 (30)	−2.215 (39)	5.432 (22)	3.714 (27)
χ_{bb}^{exp}	−3.660 (72)	−2.988 (33)	−0.201 (36)	−5.083 (28)	−3.554 (30)

Figs. 2–5. Visual comparison of experimentally determined and from oxazole and isoxazole principal quadrupole tensor elements transformed coupling constants χ_{aa} and χ_{bb}.
"*Sine-curve*" *traces*: diagonal inertia axes coupling constants χ_{aa} and χ_{bb} dependent on the transformation angle $\measuredangle$ (z, a) according to

$$\chi_{aa} = \chi_{zz} \cos^2 \{\measuredangle (z, a)\} + \chi_{xx} \sin^2 \{\measuredangle (z, a)\} \quad \text{and} \quad \chi_{bb} = \chi_{zz} \sin^2 \{\measuredangle (z, a)\} + \chi_{xx} \cos^2 \{\measuredangle (z, a)\}.$$

χ_{zz}, χ_{xx}: principal ^{14}N-quadrupole tensor elements of oxazole and isoxazole.

Vertical bars: experimental values for the respective molecular species with triple standard deviations (horizontal error bars). For a numerical comparison, transformation angles $\measuredangle$ (z, a) and transformed coupling constants χ_{aa} and χ_{bb} at the points where "sine curve" traces and vertical bars intersect are listed in Table 4.

Figs. 2 and 4: transformation angle $\measuredangle$ (z, a) in accordance with block "$\measuredangle$ (H, ring)" in Table 4.

Figs. 3 and 5: transformation angle $\measuredangle$ (z, a) in accordance with block "$\measuredangle$ (a, i)" in Table 4.

A comparison of Fig. 2 with Fig. 3 and of Fig. 4 with Fig. 5 clearly shows that by assuming $\measuredangle(CH_3, \text{ring})$ to be the same as $\measuredangle(H, \text{ring})$ in the parent molecules, an optimal fit of the experimental vertical bars between the "sine curves" is attained. The horizontal displacements of the vertical bars in Figs. 3 and 5 are too large to be explained with a possible tilt angle of the methyl group of about 1–2°. On the basis of these considerations we may now answer the two questions raised in the introduction. In our cases, the angle $\measuredangle(a, i)$ of Woods' program seems to be merely a parameter for interpolating measured torsional splittings without much structural relevance. Methyl substitution only slightly changes electrical field gradients at the ^{14}N probe nucleus. Certain influences, however, are to be supposed comparing $\chi_{cc} \equiv \chi_{yy}$-values in Table 3 which should be transformation independent.

Finally, using the best transformation angles $\measuredangle(z, a)$ from the block "$\measuredangle$(H, ring)" of Table 4, I supplemented Table 3 with off-diagonal $|\chi_{ab}|$- and ^{14}N-quadrupole tensor principal χ_{zz}- and χ_{xx}-values as derived parameters according to

$$|\chi_{ab}| = \left| \frac{\chi_{aa}^{\text{exp}} - \chi_{bb}^{\text{exp}}}{2} \cdot \tan\{2[\measuredangle(z, a)]\} \right|, \tag{3}$$

$$\chi_{zz} = \frac{\chi_{aa}^{\text{exp}}}{1-\tan^2[\measuredangle(z, a)]} + \frac{\chi_{bb}^{\text{exp}}}{1-\cot^2[\measuredangle(z, a)]}, \tag{4a}$$

$$\chi_{xx} = \frac{\chi_{aa}^{\text{exp}}}{1-\cot^2[\measuredangle(z, a)]} + \frac{\chi_{bb}^{\text{exp}}}{1-\tan^2[\measuredangle(z, a)]}. \tag{4b}$$

The sign of χ_{ab} depends on how one chooses the directions of a, b-axes in a right-handed principal inertia coordinate system.

Acknowledgements

I thank Dr. W. Jäger for helpful discussions concerning the r_0-structure fits of the monomethyl derivatives and Dr. W. Kasten for providing his program KC3IAM which I used to refine the IAM torsional analyses. I further thank Prof. J. Sheridan for initiating our work with methyl-substituted oxazoles and isoxazoles at Kiel and Prof. H. Dreizler and Prof. H. Mäder for critically reading the manuscript.

Financial support from the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie is gratefully acknowledged. All numerical calculations were carried out at the Rechenzentrum der Universität Kiel.

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