Calculation of ^{14}N Quadrupole Coupling Constants on Optimized Molecular Structures of N-methylpyrrole

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^{14}N quadrupole coupling constants (nqcc) were calculated on optimized molecular structures of the C_s conformers I (Fig. 2) and II (Fig. 3) of N-methylpyrrole. The B3PW91/6-311+G(df,pd) model was used for calculation of the electric field gradients (efg), and eQ/h = 4.5617(43) MHz/a.u. for conversion of the efg's to nqcc's (Fig. 1). From among a number of optimization models, good agreement between calculated and experimental nqcc's for both conformers is obtained on B3LYP/6-31G(d,p) optimized structures.

These calculated nqcc's are not sufficiently different to allow us to favor one conformer over the other as that on which the nqcc's were measured. Both sets are in good agreement with the experimental nqcc's.

B3LYP/aug-cc-pVTZ energy calculations show that conformer II is about 0.07 kcal/mol lower in energy than conformer I, which is a local minimum.

NUCLEAR QUADRUPOLE COUPLING CONSTANT

The nuclear quadrupole coupling constant (nqcc) is the spectroscopic measurement of the energy of interaction of the nucleus of an atom with the gradient of the molecular field (efg) at the site of the nucleus.

The components χ_{ij} of the nqcc tensor are related to the components q_{ij} of the efg tensor by

$$\chi_{ij} = (eQ/h)\, q_{ij}$$

Q is the electric quadrupole moment of the nucleus.

ELECTRIC FIELD GRADIENT

The components q_{ij} of the electric field gradient tensor are given by

$$q_{ij} = \Sigma Z(3r_i r_j - \delta_{ij} r^2)/r^5 - \langle \Psi | \Sigma (3r_i r_j - \delta_{ij} r^2)/r^5 | \Psi \rangle$$

The first sum is over nuclei, the second over electrons.

METHOD OF CALCULATION

eQ/h is taken as best-fit parameter determined by linear regression analysis of calculated efg's versus experimental nqcc's.

This method assumes that errors inherent in model are systematic and corrected, at least in part, by best-fit value of eQ/h.

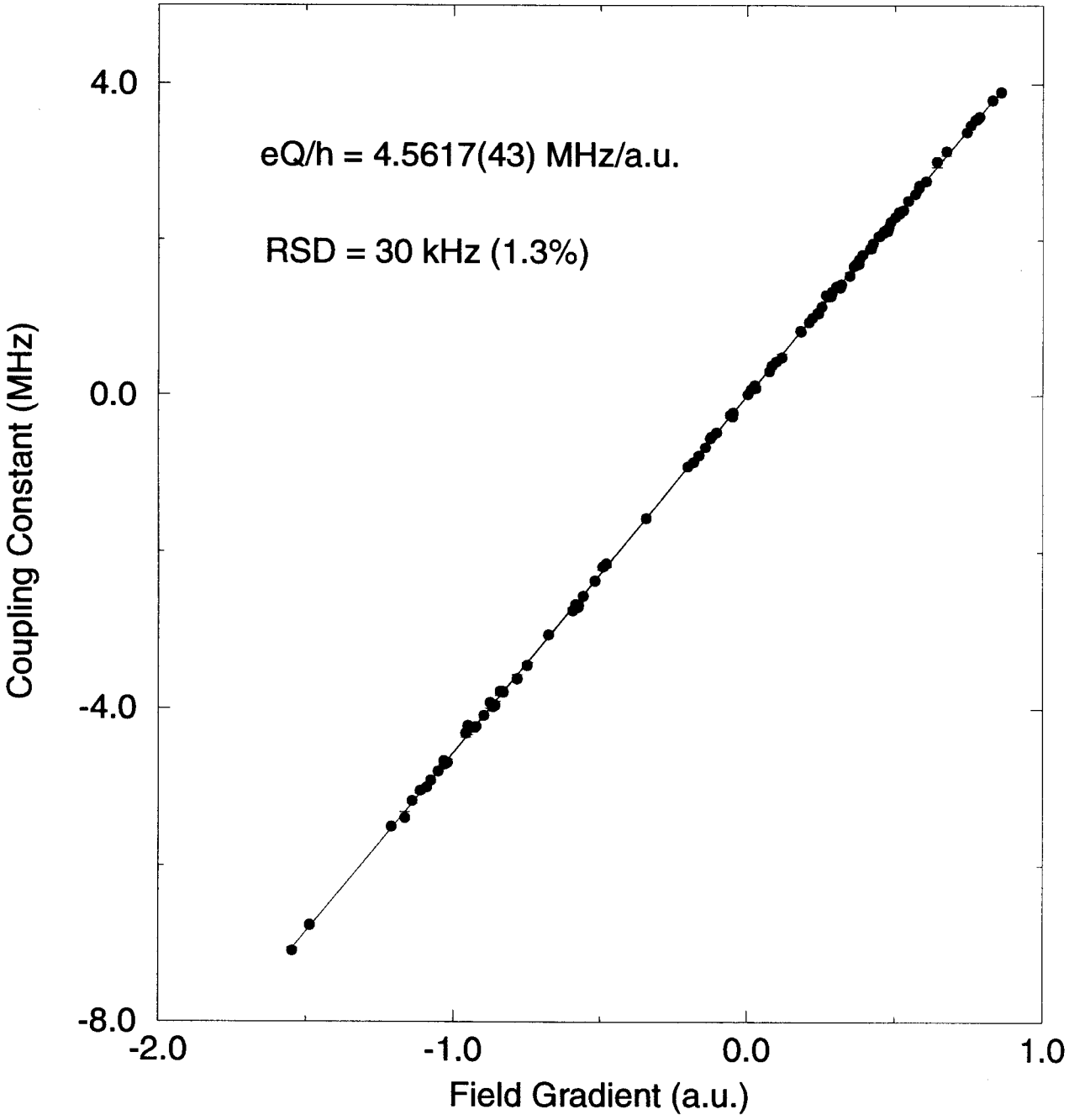

Figure 1. Calibration of B3PW91/6-311+G(df,pd) model. Ref.(1).

N-Methylpyrrole

Conformer I

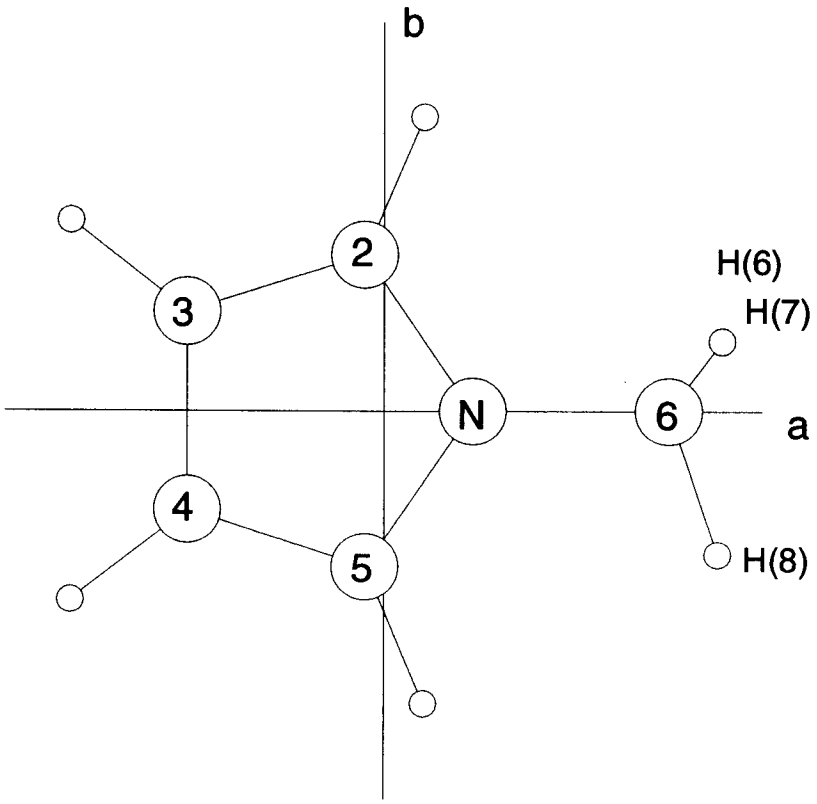

Figure 2. Atomic numbering.

N-Methylpyrrole

Conformer II

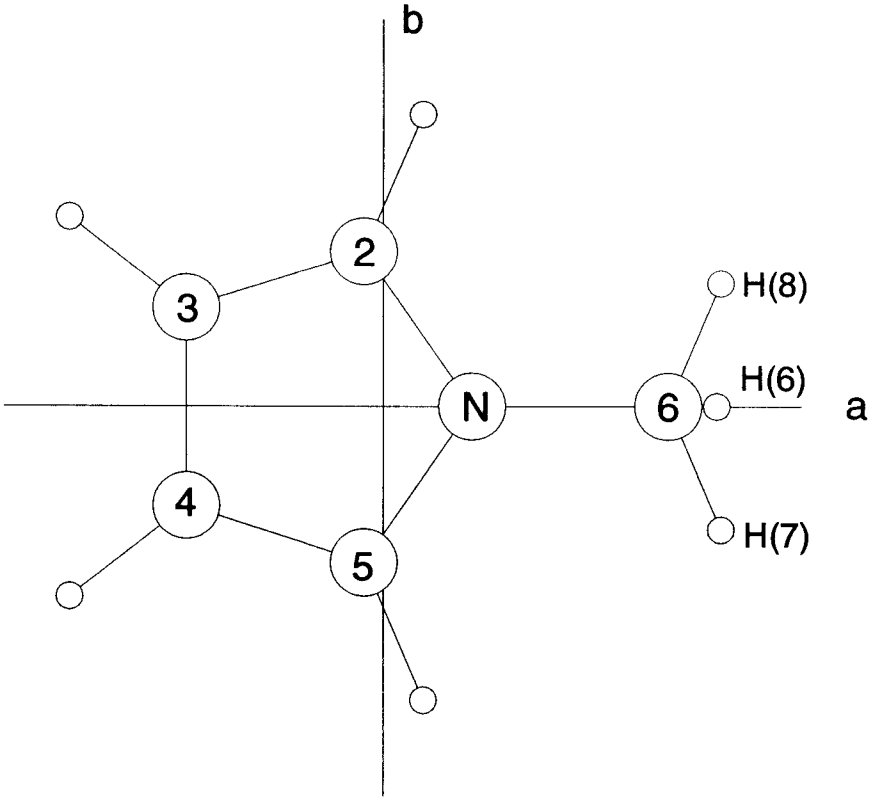

Figure 3. Atomic numbering.

Table 1

N-methylpyrrole I and II. Root mean square (rms) difference (kHz) between calculated and experimental nqcc's as functions of optimization model. For conformer II, optimized and experimental NC(6) (methyl carbon) and N(1)C(2) bond lengths, and C(5)NC(2) angle. Angstroms and degrees.

	rms		Conformer II		
Optimization Model	I	II	NC(6)	NC(2)	C(5)NC(2)
HF/6-31G(d,p)	34	33	1.4428	1.3630	108.57
HF/6-31G(2d,2p)	41	41	1.4402	1.3609	108.58
HF/6-31G(3d,3p)	36	35	1.4422	1.3622	108.58
B3LYP/6-31G(d,p)	**12**	**8**	**1.4503**	**1.3767**	**108.85**
B3LYP/6-31G(2d,2p)	23	25	1.4474	1.3741	108.94
B3LYP/6-31G(3d,3p)	22	22	1.4494	1.3745	108.94
B3PW91/6-31G(d,p)	37	40	1.4450	1.3721	108.96
B3PW91/6-31G(2d,2p)	53	56	1.4424	1.3699	109.03
B3PW91/6-31G(3d,3p)	49	52	1.4442	1.3704	109.04
MP2/6-31G(d,p)	61	68	1.4495	1.3736	109.31
MP2/6-31G(2d,2p)	81	87	1.4486	1.3724	109.43
B3LYP/6-31G(d,p)[a]	-	12	1.4505	1.3765	108.86
MP2/6-31G(d,p)[a]	-	63	1.4501	1.3733	109.31
Experimental r_z[b]	-	79	1.451(3)	1.370(3)	109.2(4)

[a]Partial optimization with planar constraint (except for methyl hydrogens). [b](GED + MW) Ref. [2]. On this structure, rms = 6 kHz with eQ/h = 4.7425 MHz/a.u., which differs by 4% from calibration value.

Table 2

Calculated and experimental ^{14}N nqcc's (MHz) in principal axes of inertia and nqcc tensors. α is the angle between the **x**-axis of the nqcc tensor and the a-axis of the inertia tensor. Calculated on the B3LYP/6-31G(d,p) structures of conformers I and II, and IIP (planar constraint); and on the experimental r_z structure.

	I	II	IIP	r_z[a]	Expt. χ[b]
χ_{aa}	1.841	1.827	1.839	1.763	1.8261(18)
χ_{bb}	1.047	1.052	1.048	1.015	1.0628(23)
χ_{cc}	-2.888	-2.879	-2.886	-2.778	-2.8889(16)
χ_{ab}	-0.019	0[c]	0[c]	0[c]	
χ_{ac}	0[c]	0.192	-0.036	0.005	
rms[d]	0.012	0.008	0.012	0.079	
χ_{xx}	1.841	1.835	1.839	1.763	
χ_{yy}	1.046	1.052	1.048	1.015	
χ_{zz}	-2.888	-2.887	-2.887	-2.778	
α	1.4°	2.7°			

[a]Ref. [2]. [b]Ref. [3]. [c]By symmetry. [d]Root mean square difference (MHz) between calculated and experimental nqcc's.

N-Methylpyrrole Conformer II

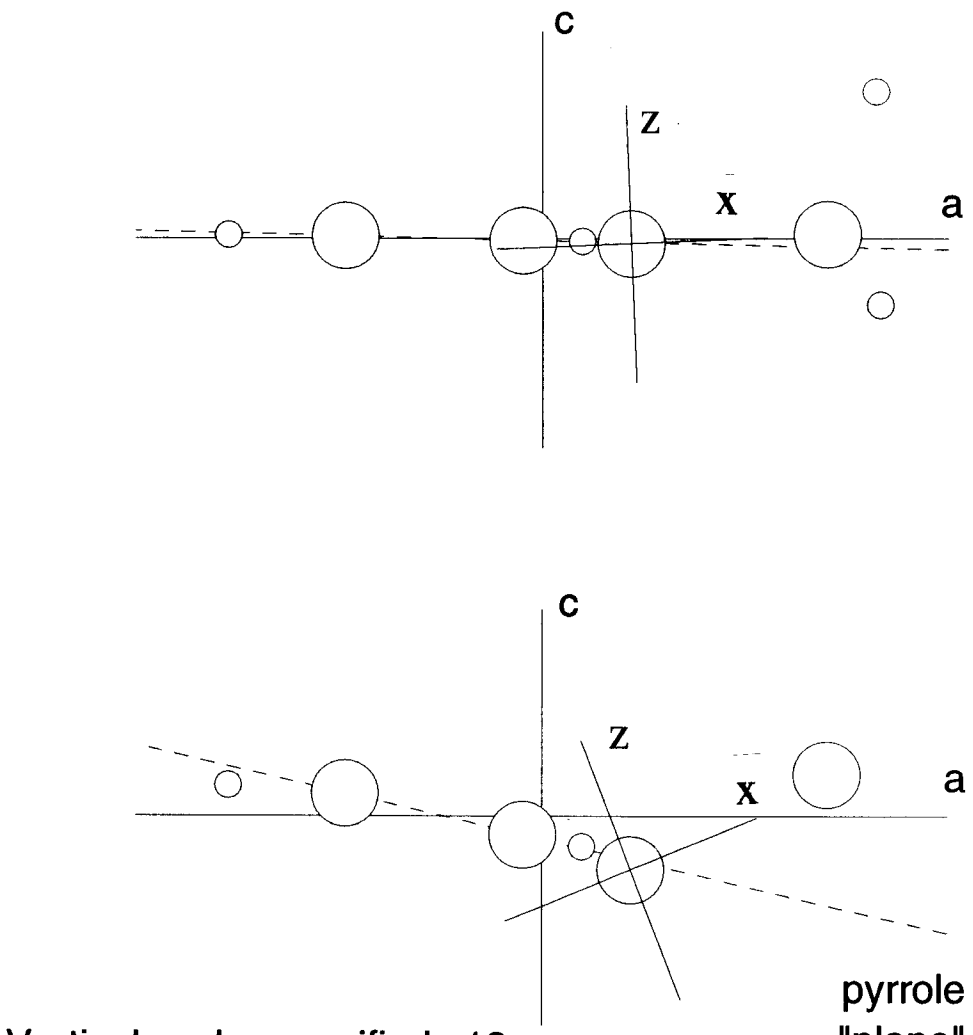

Figure 4. a,b,c are principal axes of inertia tensor.
x,y,z are principal axes of nqcc tensor.

Table 3

N-Methylpyrrole. B3LYP/6-31G(d,p) structure parameters of conformers I and II, and IIP (planar constraint). Experimental r_z parameters of IIP. Angstroms and degrees.

Parameter	I	II	IIP	r_z[a]
NC(2)	1.376	1.377	1.376	1.370(3)
C(2)C(3)	1.379	1.378	1.379	1.385(4)
C(3)C(4)	1.423	1.423	1.423	1.429
C(4)C(5)	1.378			
C(5)N	1.377			
C(2)H(2)	1.080	1.080	1.080	1.078(5)
C(3)H(3)	1.081	1.081	1.081	1.080(5)
C(4)H(4)	1.081			
C(5)H(5)	1.080			
C(5)NC(2)	108.8	108.8	108.9	109.2(4)
NC(2)C(3)	108.3	108.4	108.3	108.5(5)
C(2)C(3)C(4)	107.3	107.2	107.2	106.9
C(3)C(4)C(5)	107.2			
C(4)C(5)N	108.4			
NC(2)H(2)	120.6	120.6	120.6	120.7
C(2)C(3)H(3)	125.8	125.8	125.8	126.1
NC(5)H(5)	120.5			
C(5)C(4)H(4)	125.8			
Methyl Group				
NC(6)	1.450	1.450	1.450	1.451(3)
C(6)H(6)	1.095	1.096	1.096	1.100(5)
C(6)H(7)	1.095	1.093	1.092	1.100(5)
C(6)H(8)	1.091	1.093	1.092	1.100(5)
NC(6)H(6)	111.1	111.9	112.0	108.0(19)
NC(6)H(7)	111.1	109.6	109.6	108.0(19)
NC(6)H(8)	109.1	109.6	109.6	108.0(19)

[a]Ref. [2].

Table 4

N-Methylpyrrole. Absolute energies E_I and E_{II} of conformers I and II, respectively. Relative energy ΔE (kcal/mol).

Model	E_I (a.u.)	E_{II} (a.u.)	ΔE
HF/6-311++G(3df,3pd)	-247.921827	-247.922000	0.108
MP2/6-311+G(2d,2p)	-248.849901	-248.850072	0.108
B3LYP/6-311++G(3df,3pd)	-249.568630	-249.568762	0.083
B3LYP/6-311++G(3df,3pd)[a]	-249.568640	-249.568775	0.085
B3LYP/aug-cc-pVTZ	-249.574101	-249.574209	0.068

[a]Tight convergence.

RESULTS

- Root mean square difference between calculated and experimental nqcc's on B3LYP/6-31G(d,p) optimized molecular structures:

  Conformer I: 12 kHz (0.6%)
  Conformer II: 8 kHz (0.4%)

- Conformer II. Pyrrole skeleton is essentially planar, methyl carbon lies 0.093 Å above this plane (Fig. 4).

- Conformer II is lower in energy by about 0.07 kcal/mol than conformer I, which is a local minimum.

References

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2. N. Kurai, H. Takeuchi, and S. Konaka, *J. Mol. Struct.* **318**, 143 (1994).

3. S. R. Huber and A. Bauder, *Z. Naturforsch.* **49a**, 1063 (1994).

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