Nitrogen and Deuterium Hyperfine Structure in the Rotational Spectrum of Piperidine

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We reinvestigated by microwave Fourier transform spectroscopy the rotational spectra of the axial and equatorial isotopomers of piperidine and N-deutero piperidine. The rotational, centrifugal, and nitrogen quadrupole coupling constants were improved, the deuterium quadrupole coupling constants were determined. The principal coupling tensor elements for nitrogen were estimated.

Introduction

Since 1965 the microwave spectrum of piperidine, $C_5H_{10}N-H$, was investigated by several authors. Parkin, Buckley, and Costain are the authors of the last publication [1]. The molecule was observed in its chair form. The normal and the N-deuterated isotopomer were assigned in their axial and equatorial conformers.

As the resolution was increased by microwave Fourier transform (MWFT) spectroscopy [2] we reinvestigated the spectra with the main aim, to improve the accuracy of the ^{14}N nuclear coupling constants and to determine the deuterium nuclear quadrupole coupling. In the course of our work the centrifugal distortion constants could be improved.

Experimental

We used commercially available piperidine. The deuterated isotopomer was prepared as follows: In a separatory funnel 4 ml of a 40% sodium deuterooxide (NaOD) solution in D_2O (99 atom% D) were mixed with 1 ml of piperidine. After a few minutes of manual shaking the two phases were separated. The upper phase containing the deuterated substance was good enough to be used without further purification.

We used our MWFT spectrometers in G- (4–6 GHz) [3], J- (5.3–8 GHz) [4], and X-band (8–12.4 GHz) [5]. The spectra were recorded at temperatures around −50 °C and pressures between 0.5 and 5 mTorr (0.1 to 0.7 Pa). The results are given in Tables 1 to 4. To eliminate overlap effects the frequencies of the multiplet components were determined by a least square fit of the time domain signal [6]. Part of the measurements are given in Tables 1 and 4*.

Analysis

The hfs splittings of the normal isotopomers (complete list) were analyzed by diagonalizing the hamiltonian matrix neglecting matrix elements nondiagonal in the quantum number J (programme SUZIQS [7]). For the deuterated species first order theory with the coupling scheme $F_1 = J + I_1$ and $F = F_1 + I_2$ was used [8] (programme Q2FIT/Q2SIM [9]). The results are given in Table 5 together with the rotational and centrifugal distortion constants according to Watson's S reduction for the III^r representation in fourth order [10]. For the centrifugal distortion analysis (programme ZFAP4 [11]) the hypothetical center frequency ν_0 of each transition measured in this work was used, which was calculated in course of the hfs analysis by the programme SUZIQS [7] for both isotopomers. We supplemented our measurements for the centrifugal distortion analysis by those reported in Tables II to V of [1]. Their quadrupole correction ν_{quad} was applied. Because of the lower accuracy of the Stark measurements those transitions have not been used, that do not agree with the calculated frequencies within the tripled value of the standard deviation. We were able to fit the rotational and five centrifugal distortion constants with acceptable correlation. For

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* The complete list of measured transitions is available under number TNA 20 at the Universitätsbibliothek, Westring 400, D-2300 Kiel. – Tables 4–7 see p. 845–847.

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Table 1. Part of measured transitions of piperidine H axial. Experimental frequencies of a component ν_{obs}, hfs splitting $\Delta\nu_{hfs} = \nu_{obs} - \nu_0$, deviation of the hfs analysis $\delta\Delta\nu_{calc-obs}$, hypothetical unsplit line ν_0, deviation of the centrifugal distortion anaylsis $\delta\nu_{calc-obs}$.

$J, K_-, K_+ - J', K'_-, K'_+$ $F - F'$	ν_{obs}/GHz	ν_0/GHz	$\Delta\nu_{hfs}$/MHz	$\delta\nu_{calc-obs}$/kHZ	$\delta\Delta\nu_{calc-obs}$/kHz
1, 1, 0 − 0, 0, 0		8.889573		1	
2 − 1	8.889530		−0.043		−1
1 − 1	8.889790		0.217		2
0 − 1	8.889130		−0.443		5
2, 2, 1 − 2, 0, 2		5.879924		−6	
3 − 3	5.879590		−0.334		−3
2 − 2	5.881098		1.174		6
1 − 1	5.878737		−1.187		8
3, 2, 1 − 3, 2, 2		5.432871		−3	
4 − 4	5.433082		0.211		0
3 − 3	5.432238		−0.633		1
2 − 2	5.433379		0.508		−2
3, 0, 3 − 2, 0, 2		17.124192		1	
4 − 3	17.124214		0.022		−1
3 − 2	17.124163		−0.029		2
2 − 1	17.124163		−0.029		−2
4, 3, 1 − 4, 3, 2		5.239771		−5	
5 − 5	5.240019		0.248		1
4 − 4	5.239086		−0.685		−2
3 − 3	5.240261		0.490		0
6, 5, 2 − 6, 3, 3		9.623073		−5	
7 − 7	9.622994		−0.079		−1
6 − 6	9.623276		0.203		−2
5 − 5	9.622941		−0.132		4
7, 5, 2 − 7, 5, 3		9.211319		−5	
8 − 8	9.211446		0.127		0
7 − 7	9.211011		−0.308		0
6 − 6	9.211509		0.190		0
10, 8, 2 − 10, 8, 3		8.411749		−4	
11 − 11	8.411980		0.231		0
10 − 10	8.411217		−0.532		0
9 − 9	8.412056		0.307		0
11, 11, 1 − 11, 9, 2		11.316662		29	
12 − 12	11.315886		−0.776		1
11 − 11	11.318423		1.761		0
10 − 11	11.315656		−1.006		−1
15, 13, 2 − 15, 13, 3		5.926614		5	
16 − 16	5.926888		0.274		2
15 − 15	5.926010		−0.604		−2
14 − 14	5.926949		0.335		0

example the correlation for piperidine axial is given in Table 6.

One may notice that the quadrupole coupling constants χ_{bb}(N) of the two axial isotopomers agree within the standard errors. This behavior is shown also by the equatorial species as these constants should not be influenced by the rotation in the inertial axes system induced by deuteration. The coupling constants χ_{bb}(N) of the axial and equatorial conformation differ slightly. In general we improved the accuracy of the quadrupole coupling constants χ_{gg}(N) at least by a factor of ten. The quadrupole coupling constants of the deuterated species are not reported in the literature.

The deuteration of the proton bond to the nitrogen induces a noticeable rotation in the inertia axes system of piperidine axial. Unfortunately the precise structure of piperidine is not known. The angle of

Table 2. Part of measured transitions of piperidine D axial. Experimental frequencies of a component ν_{obs}, hfs splitting with respect to the strongest hfs component $\Delta\nu_{hfs}=\nu_{obs}-\nu'_{obs}$, deviation of the hfs analysis $\delta\Delta\nu_{calc-obs}$, hypothetical unsplit line ν_0, deviation of the centrifugal distortion anaylsis $\delta\nu_{calc-obs}$.

$J, K_-, K_+ - J', K'_-, K'_+$ $2F_1, 2F - 2F'_1, 2F'$	ν_{obs}/ GHz	ν_0/ GHz	$\Delta\nu_{hfs}$/ MHz	$\delta\nu_{calc-obs}$/ kHz	$\delta\Delta\nu_{calc-obs}$/ kHz
2, 1, 1 − 2, 1, 2		5.246594		2	
4, 2 − 4, 2	5.246065		−0.658		12
4, 6 − 4, 6					
4, 4 − 4, 4	5.246135		−0.588		9
6, 4 − 6, 4	5.246672		−0.051		12
6, 8 − 6, 8	5.246723				
6, 6 − 6, 6	5.246812		0.089		6
2, 4 − 2, 4	5.247105		0.382		− 7
3, 2, 1 − 3, 2, 2		4.976186		5	
6, 4 − 6, 4	4.975545		−0.832		0
6, 8 − 6, 8					
6, 6 − 6, 6	4.975589		−0.788		0
8, 6 − 8, 6	4.976377				
8, 10 − 8, 10					
8, 8 − 8, 8	4.976433		0.056		− 1
4, 2 − 4, 2	4.976681		0.304		− 9
4, 6 − 4, 6					
4, 4 − 4, 4	4.976723		0.346		− 2
4, 2, 2 − 4, 2, 3		9.049439		28	
8, 6 − 8, 6	9.049318		−0.155		− 7
8, 10 − 8, 10					
10, 8 − 10, 8	9.049473				
10, 12 − 10, 12					
6, 4 − 6, 4	9.049537		0.064		−11
6, 8 − 6, 8					
10, 11 − 10, 10					
6, 6 − 6, 6	9.049589		0.116		−12
4, 3, 2 − 4, 1, 3		9.260685		29	
6, 4 − 6, 4	9.260520		−0.081		5
6, 8 − 6, 8					
6, 6 − 6, 6	9.260601				
10, 8 − 10, 8					
10, 12 − 10, 12					
10, 10 − 10, 10	9.260672		0.071		− 1
8, 6 − 8, 6	9.260914		0.313		12
8, 10 − 8, 10					
8, 8 − 8, 8	9.260986		0.385		0
4, 3, 1 − 4, 3, 2		4.622753		− 7	
8, 6 − 8, 6	4.622080		−0.897		−14
8, 10 − 8, 10					
8, 8 − 8, 8	4.622097		−0.879		− 4
10, 8 − 10, 8	4.622977				
10, 12 − 10, 12					
10, 10 − 10, 10					
6, 4 − 6, 4	4.623209		0.232		−10
6, 8 − 6, 8					
6, 6 − 6, 6	4.623240		0.263		−11
6, 5, 2 − 6, 3, 3		9.507775		1	
10, 8 − 10, 8	9.507557		−0.083		6
10, 12 − 10, 12					
14, 12 − 14, 12	9.507639				
14, 16 − 14, 16					
14, 14 − 14, 14	9.507661		0.021		12
12, 10 − 12, 10	9.508088		0.449		0
12, 14 − 12, 14					
12, 12 − 12, 12	9.508110		0.471		11
10, 9, 2 − 10, 8, 2		4.496088		3	
18, 16 − 18, 16	4.495498		−0.148		2
18, 20 − 18, 20					
18, 18 − 18, 18					
22, 20 − 22, 20	4.495646				
22, 24 − 22, 24					
22, 22 − 22, 22					
20, 18 − 20, 18	4.497107		1.461		− 5
20, 22 − 20, 22					
20, 20 − 20, 20					
14, 11, 3 − 14, 11, 4		9.070307		− 3	
28, 26 − 28, 26	9.069770		−0.778		0
28, 30 − 28, 30					
28, 28 − 28, 28					
30, 28 − 30, 28	9.070549				
30, 32 − 30, 32					
30, 30 − 30, 30					
26, 28 − 26, 28	9.070605		0.056		− 1
26, 24 − 26, 24					
26, 26 − 26, 26					

Table 3. Part of measured transitions of piperidine H equatorial (see Table 1).

$J, K_-, K_+ - J', K'_-, K'_+$ $F - F'$	ν_{obs}/GHz	ν_0/GHz	$\Delta\nu_{hfs}$/MHz	$\delta\nu_{calc-obs}$/kHz	$\delta\Delta\nu_{calc-obs}$/kHz
1, 1, 0 – 0, 0, 0		8.964455		0	
1 – 0	8.966882		2.427		2
1 – 1	8.963242		−1.213		− 1
1 – 2	8.964698		0.243		0
2, 1, 1 – 1, 0, 1		17.838893		0	
0 – 1	17.840633		1.740		0
1 – 1	17.839051		0.158		5
1 – 2	17.837680		−1.213		− 1
2 – 2	17.838315		−0.578		− 5
2 – 3	17.839195		0.302		0
6, 5, 1 – 6, 5, 2		4.898974		0	
5 – 5	4.899186		0.212		1
6 – 6	4.898639		−0.335		− 1
7 – 7	4.899108		0.134		0
10, 7, 4 – 10, 5, 5		17.410629		10	
9 – 9,	17.410810		0.181		− 7
10 – 10	17.410325		−0.304		2
11 – 11	17.410757		0.128		3
10, 10, 1 – 10, 9, 1		4.836630		18	
9 – 9	4.836557		−0.073		−13
10 – 10	4.836777		0.147		1
11 – 11	4.836557		−0.073		8
11, 9, 2 – 11, 9, 3		8.397617		14	
10 – 10	8.397736		0.119		0
11 – 11	8.397408		−0.209		1
12 – 12	8.397709		0.092		0

rotation can only be estimated. We assumed that the structure of piperidine is similar to that of cyclohexane [12]. r(C–C) = 1.535 Å, r(C–H) = 1.102 Å, ∢CCC = 111.4°, ∢HCH = 110°, and the N–H bond coincides with a C–H bond.

For the axial form we get an angle $\Delta\varphi = 1.3°$, for the equatorial form $\Delta\varphi = 0.2°$. By transformation [13] we determined the components of the coupling tensor in its principal axes system for the axial conformer: $\chi_{xx} = 1.74$, $\chi_{yy} = \chi_{bb} = 2.8013(18)$, $\chi_{zz} = -4.55$ MHz. The z axis has an angle $\varphi = 21.8°$ with the inertia a axis, the y axis is parallel to the inertia b axis. For χ_{ac} −2.17 MHz results. As the structural data are estimated, these values are also an estimate. We hesitate to give error limits.

General

In Table 7 we compare the ^{14}N-hfs data for the molecules piperidine, pyrrolidine [14], and morpholine [15] in axial and equatorial conformation for the normal and N-deuterated isotopomeres.

Independently from a precise knowledge of the structure it may be stated, that the χ_{bb} values agree within 2.775 ± 0.030 MHz. This is similar to the $\chi_{aa} = 3.04(20)$ MHz [16] of dimethylamine. The a axis in this molecule corresponds to the b axis in the above molecules.

It may be noticed from Table 7 that the χ_{xx} and χ_{zz} values of piperidine axial and pyrrolidine axial do not agree well. As the deuteration changes the position of the molecule in the inertia axes system only by a few degrees, and as the structure is only an estimate the errors of χ_{xx} and χ_{zz} may be estimated to ± 500 kHz. So we prefer the comparison of the χ_{bb} values and may state that the bonding situation in all three investigated secondary amines is similar.

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Table 4. Part of measured transitions of piperidine D equatorial (see Table 2).

$J, K_-, K_+ - J', K'_-, K'_+$ $F_1, F - F'_1, F'$	ν_{obs}/ GHz	ν_0/ GHz	$\Delta\nu_{hfs}$/ MHz	$\delta\nu_{calc-obs}$/ kHz	$\delta\Delta\nu_{calc-obs}$/ kHz
1, 1, 0 − 0, 0, 0		8.760588		11	
1, 0 − 1, 1	8.759367		−1.474		5
1, 2 − 1, 1					
1, 2 − 1, 2					
1, 1 − 1, 0					
1, 1 − 1, 2					
1, 1 − 1, 1					
2, 2 − 1, 1	8.760800		−0.042		13
2, 2 − 1, 2					
2, 3 − 1, 2	8.760842				
2, 1 − 1, 1					
2, 1 − 1, 0					
0, 1 − 1, 2	8.763020		2.178		1
0, 1 − 1, 1					
2, 2, 0 − 1, 1, 0		17.555167		32	
2, 3 − 2, 3	17.553736		−1.530		− 3
1, 1 − 0, 1	17.553924		−1.342		3
1, 2 − 0, 1					
2, 2 − 1, 1	17.555181		−0.085		5
2, 2 − 1, 2					
2, 3 − 1, 2					
2, 1 − 1, 0	17.555266				
3, 3 − 2, 2					
3, 2 − 2, 1					
3, 4 − 2, 3					
1, 2 − 1, 2	17.557585		2.319		1
3, 0, 3 − 2, 0, 2		16.766274		−13	
4, 3 − 4, 3	16.766116				
4, 5 − 4, 5					
4, 4 − 4, 4					
2, 1 − 2, 1	16.766283		0.168		−19
2, 3 − 2, 3					
2, 2 − 2, 2					
3, 2 − 3, 2	16.766585		0.470		12
3, 4 − 3, 4					
3, 3 − 3, 3					
4, 3, 1 − 4, 3, 2		4.314829		24	
4, 3 − 4, 3	4.314204		−0.836		7
4, 5 − 4, 5					
4, 4 − 4, 4	4.314242		−0.798		2
5, 4 − 5, 4	4.315040				
5, 6 − 5, 6					
5, 5 − 5, 5	4.315077		0.036		1
3, 2 − 3, 2	4.315257		0.217		− 3
3, 4 − 3, 4					
3, 3 − 3, 3	4.315293		0.252		− 3
10, 7, 3 − 10, 7, 4		10.797846		39	
10, 9 − 10, 9	10.797508		−0.469		− 1
10, 11, − 10, 11					
10, 10 − 10, 10	10.797528		−0.449		10
11, 10 − 11, 10	10.797976				
11, 12 − 11, 12					
11, 11 − 11, 11	10.798026		0.049		− 8
9, 8 − 9, 8					
9, 10 − 9, 10					
9, 9 − 9, 9	10.798046		0.070		10
12, 9, 3 − 12, 9, 4		8.447248		28	
12, 11 − 12, 11	8.446977		−0.374		2
12, 13 − 12, 13					
12, 12 − 12, 12	8.447011		−0.340		6
13, 12 − 13, 12	8.447351				
13, 14 − 13, 14					
11, 10 − 11, 10	8.447384		0.033		0
11, 12 − 11, 12					
13, 13 − 13, 13					
11, 11 − 11, 11	8.447420		0.070		0
15, 12 4 − 15, 11, 4		5.498578		40	
14, 14 − 14, 14	5.498476		−0.053		3
16, 16 − 16, 16					
14, 15 − 14, 15	5.498529				
14, 13 − 14, 13					
16, 17 − 16, 16					
16, 15 − 16, 15					
15, 15 − 15, 15	5.498680		0.152		− 3
15, 16 − 15, 16	5.498728		0.199		− 1
15, 14 − 15, 14					

Table 5a. Piperidine chair axial. Rotational constants A, B, C, quartic centrifugal distortion constants of Watson's S reduction D_J, D_{JK}, D_K, d_1, d_2, Ray's asymmetry parameter $\varkappa$, number of fitted lines N_L, standard deviation of the fit of the centrifugal distortion analysis σ_{cd}, quadrupole coupling constants χ, number of fitted hfs components N_c, mean splitting $\Delta\nu_{hfs}$, standard deviation of the fit of the quadrupole coupling analysis σ_{hfs}, correlation of the quadrupole coupling constants $|(\chi^+, \chi^-)|$. Standard errors in parenthesis (in units of the least significant digit).

ax-$C_5H_{10}N$–H		ax-$C_5H_{10}N$–D	
A/GHz	4.4943030(67)	A/GHz	4.4404997(97)
B/GHz	4.3952753(67)	B/GHz	4.2541259(97)
C/GHz	2.5356089(70)	C/GHz	2.5052554(95)
D_J/kHz	1.05(11)	D_J/kHz	0.90(13)
D_{JK}/kHz	−1.4224(55)	D_{JK}/kHz	−1.337(11)
D_K/kHz	0.654(22)	D_K/kHz	0.624(17)
d_1/Hz	11.4(16)	d_1/Hz	8.0(42)
d_2/Hz	−13.24(93)	d_2/Hz	−18.5(27)
$\varkappa$	0.898884	$\varkappa$	0.807390
N_L	35	N_L	29
N_L [1]	117	N_L [1]	42
σ_{cd}/kHz	101	σ_{cd}/kHz	70
χ^+(N)/MHz	3.6763(11)	χ^+(N)/MHz	3.578(7)
χ^-(N)/MHz	1.9263(24)	χ^-(N)/MHz	2.034(11)
χ_{aa}(N)/MHz	−3.6763(11)	χ_{aa}(N)/MHz	−3.578(7)
χ_{bb}(N)/MHz	2.8013(12)	χ_{bb}(N)/MHz	2.806(5)
χ_{cc}(N)/MHz	0.8750(16)	χ_{cc}(N)/MHz	0.772(8)
N_c	102	χ^+(D)/MHz	0.147(12)
$\Delta\nu_{hfs}$/kHz	414	χ^-(D)/MHz	0.349(15)
σ_{hfs}/kHz	1.58	χ_{aa}(D)/MHz	−0.147(12)
$\|(\chi^+, \chi^-)\|$	−0.386	χ_{bb}(D)/MHz	−0.101(10)
		χ_{cc}(D)/MHz	0.248(9)
		N_c	103
		σ_{hfs}/kHz	7.3

Table 5b. Piperidine chair equatorial. Rotational constants A, B, C, quartic centrifugal distortion constants of Watson's S reduction D_J, D_{JK}, D_K, d_1, d_2, Ray's asymmetry parameter $\varkappa$, number of fitted lines N_L, standard deviation of the fit of the centrifugal distortion analysis σ_{cd}, quadrupole coupling constants χ, number of fitted hfs components N_c, mean splitting $\Delta\nu_{hfs}$, standard deviation of the fit of the quadrupole coupling analysis σ_{hfs}, correlation of the quadrupole coupling constants $|(\chi^+, \chi^-)|$. Standard errors in parenthesis (in units of the least significant digit).

eq-$C_5H_{10}N$–H		eq-$C_5H_{10}N$–D	
A/GHz	4.5272300(28)	A/GHz	4.5276291(91)
B/GHz	4.4372288(28)	B/GHz	4.2329732(90)
C/GHz	2.5429810(32)	C/GHz	2.4749189(98)
D_J/kHz	0.892(49)	D_J/kHz	0.92(14)
D_{JK}/kHz	−1.4702(34)	D_{JK}/kHz	−1.399(30)
D_K/kHz	0.634(38)	D_K/kHz	0.587(47)
d_1/Hz	−4.6(20)	d_1/Hz	−36.7(98)
d_2/Hz	−7.57(88)	d_2/Hz	−18.0(57)
$\varkappa$	0.909284	$\varkappa$	0.712910
N_L	29	N_L	35
N_L [1]	55	N_L [1]	20
σ_{cd}/kHz	46	σ_{cd}/kHz	123
χ^+(N)/MHz	−2.1007(42)	χ^+(N)/MHz	−2.122(6)
χ^-(N)/MHz	7.6121(57)	χ^-(N)/MHz	7.608(11)
χ_{aa}(N)/MHz	2.1007(42)	χ_{aa}(N)/MHz	2.122(6)
χ_{bb}(N)/MHz	2.7557(33)	χ_{bb}(N)/MHz	2.743(5)
χ_{cc}(N)/MHz	−4.8564(39)	χ_{cc}(N)/MHz	−4.865(7)
N_c	79	χ^+(D)/MHz	−0.232(9)
$\Delta\nu_{hfs}$/kHz	370	χ^-(D)/MHz	−0.002(22)
σ_{hfs}/kHz	2.8	χ_{aa}(D)/MHz	0.232(9)
$\|(\chi^+, \chi^-)\|$	−0.189	χ_{bb}(D)/MHz	−0.117(9)
		χ_{cc}(D)/MHz	−0.115(15)
		N_c	135
		σ_{hfs}/kHz	8.8

Table 6. Correlation matrices for values of Table 5. a) For the rotational and centrifugal distortion constants of ax-$C_5H_{10}N$–H. b) For the nuclear quadrupole coupling constants of ax-$C_5H_{10}N$–D.

A	1.000							
B	0.988	1.000						
C	0.945	0.945	1.000					
D_J	0.920	0.922	0.915	1.000				
D_{JK}	0.001	0.077	0.031	0.059	1.000			
D_K	−0.038	−0.081	0.178	0.012	−0.623	1.000		
d_1	−0.017	0.076	0.008	0.037	0.912	−0.534	1.000	
d_2	0.008	0.023	0.017	0.023	0.539	−0.268	0.675	1.000
χ_{aa}(N)	1.000							
χ_{bb}(N)	−0.205	1.000						
χ_{aa}(D)	−0.132	−0.087	1.000					
χ_{bb}(D)	0.061	0.037	−0.697	1.000				

Table 7. Piperidine, pyrrolidine, and morpholine: Elements χ_{aa}, χ_{bb}, χ_{cc}, χ_{ac} of the ^{14}N quadrupole coupling tensor in the intertia axes system. Components χ_{xx}, χ_{yy}, χ_{zz} of the ^{14}N coupling tensor in its principal axes system. Angle φ inclining the z axis from the a axis.

	Equatorial piperidine		Equatorial morpholine	
	$^{14}N-H$	$^{14}N-D$	$^{14}N-H$	$^{15}N-D$
χ_{aa}/MHz	2.1007(42)	2.122(6)	2.1491(24)	2.166(6)
χ_{bb}/MHz	2.7557(33)	2.743(5)	2.7966(25)	2.787(4)
χ_{cc}/MHz	−4.8564(39)	−4.865(7)	−4.9457(24)	−4.953(6)
	Axial piperidine		Axial pyrrolidine	
	$^{14}N-H$	$^{14}N-D$	$^{14}N-H$	$^{14}N-D$
χ_{aa}/MHz	−3.6763(11)	−3.578(7)	−3.3904(14)	−3.253(9)
χ_{bb}/MHz	2.8013(12)	2.806(5)	2.7642(14)	2.760(9)
χ_{cc}/MHz	0.8750(16)	0.772(8)	0.6262(20)	0.493(17)
χ_{ac}/MHz	−2.17		−1.88	
χ_{xx}/MHz	1.74		1.37	
χ_{yy}/MHz	χ_{bb}		χ_{bb}	
χ_{zz}/MHz	−4.55		−4.13	
φ	21.8°		21.5°	

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