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# $^{14}\text{N}$ Nuclear Quadrupole Coupling and Methyl Internal Rotation in N-*tert*-butylacetamide as Observed by Microwave Spectroscopy

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## ABSTRACT

The rotational spectrum of N-*tert*-butylacetamide,  $\text{CH}_3(\text{C}=\text{O})(\text{NH})\text{C}(\text{CH}_3)_3$ , was measured in the frequency range from 2 to 26.5 GHz using a molecular beam Fourier transform microwave spectrometer. Only one conformer with *trans* configuration and  $\text{C}_s$  symmetry was observed. Torsional splittings up to 4.3 GHz occurred in the spectrum due to the internal rotation of the acetyl methyl group  $\text{CH}_3(\text{C}=\text{O})$  with a barrier height of approximately  $65\text{ cm}^{-1}$ . Hyperfine structures arise from the quadrupole coupling of the  $^{14}\text{N}$  nucleus appeared for all rotational-torsional transitions. The data set was reproduced with the programs *XIAM* and *BELGI-CI-*

*hyperfine*, an extended version of the *BELGI-C<sub>1</sub>* code which includes the effect of the <sup>14</sup>N quadrupole coupling, to root-mean-square deviations of 16.9 kHz and 3.0 kHz, respectively. Quantum chemical calculations were performed to complement the experimental results. The *BELGI-C<sub>1</sub>-hyperfine* code was also used to refit the recently published microwave data of N-ethylacetamide to measurement accuracy.

KEYWORDS: rotational spectroscopy, large amplitude motion, acetyl methyl group, *BELGI-C<sub>1</sub>*

## INTRODUCTION

The microwave spectrum of a molecule possessing internal rotation of a methyl group exhibits torsional splittings of all rotational lines into large amplitude motion (LAM) symmetry species components, and can no longer be treated using a rigid-rotor model. Several programs have been developed to treat this problem, i.a. *IAM*,<sup>1</sup> *XIAM*,<sup>2</sup> *BELGI-C<sub>s</sub>*<sup>3</sup> and *BELGI-C<sub>1</sub>*,<sup>4</sup> *Erham*,<sup>5</sup> and *RAM36*.<sup>6</sup> They use different coordinate systems, e.g. the *XIAM* code uses the combined axis method; Erham sets up and solves an **E**ffective **R**otational **H**AMitonian; and *BELGI-C<sub>s</sub>*, *BELGI-C<sub>1</sub>*, as well as *RAM36* use the rho axis method.

If the molecule has, in addition to the methyl top, a nucleus with a nuclear spin larger than ½ (for example a <sup>14</sup>N nucleus with  $I = 1$ ), a hyperfine structure (hfs) will occur in the spectrum. The combination of <sup>14</sup>N quadrupole coupling and methyl internal rotation can be handled with the program *RAM36*, but only for molecules with C<sub>s</sub> symmetry.<sup>7</sup> Using the program *XIAM*, the frame symmetry is not restricted to C<sub>s</sub>. *XIAM* treats nuclear quadrupole interactions with one coupling nucleus in a first order approximation, which is sufficient to fit the hyperfine structure of nuclei with relatively small quadrupole moments like <sup>14</sup>N. However, the program *XIAM* has its disadvantages at treating internal rotations with low barrier heights, since only a limited number

of parameters can be fitted and also since the torsional interactions between different  $v_t$  states are not taken into account explicitly. Higher order terms cannot be easily implemented in the program.

*N-tert*-butylacetamide (TBAA),  $\text{CH}_3(\text{C}=\text{O})(\text{NH})\text{C}(\text{CH}_3)_3$ , with the structure depicted in Figure 1 is the typical example of a molecule with one methyl internal rotation and  $^{14}\text{N}$  quadrupole coupling. TBAA has an amide bond, which connects the acetyl methyl group  $\text{CH}_3(\text{C}=\text{O})$  and the *tert*-butyl group. We expect the spectrum of TBAA to be that of a simple acetyl-methyl-top molecule since: (i) the *tert*-butyl rotor has a moment of inertia about 20 times larger than that of a methyl group, and (ii) splittings arising from internal rotations of the three methyl groups within the *tert*-butyl moiety should be quite small, since the barrier heights are expected to be approximately  $1000\text{ cm}^{-1}$ , close to that of the methyl group in ethyl fluoride.<sup>8</sup>

Chemically, TBAA belongs to the class of acetamides; it is used as a biochemical for proteomics research. Many acetamides have been the object of our microwave studies, i.a. *N*-ethylacetamide (EAA),  $\text{CH}_3(\text{C}=\text{O})(\text{NH})\text{CH}_2\text{CH}_3$ ,<sup>9</sup> and *N,N*-diethylacetamide,  $\text{CH}_3(\text{C}=\text{O})\text{N}(\text{CH}_2\text{CH}_3)_2$ ,<sup>10</sup> aiming to determine conformational and dynamical properties of structural motif within larger biological systems like entacapone, LSD (D-lysergic acid diethylamide), and melatonins. In our recent investigation on EAA,<sup>9</sup> we observed only one conformer with  $C_1$  symmetry under molecular jet conditions. The microwave spectrum with 150 A and 121 E species torsional and hfs components was fitted using the program *XIAM* to a standard deviation of 9.8 kHz. Attempts to reduce the standard deviation to measurement accuracy of 2 kHz failed. We thus concluded that some higher order terms required to fit the spectrum of EAA were missing in the *XIAM* code, similar to the situation found in some other molecules where the barrier to internal rotation is comparably low ( $73.4782(1)\text{ cm}^{-1}$ ). Since the barrier height of the acetyl methyl group in TBAA

is expected to be close to that found in EAA, the same problem might occur by fitting the spectrum of TBAA using the program *XIAM*.

In many previous investigations, we succeeded to fit the microwave spectra of molecules with  $C_s$  symmetry and one methyl top with low barrier height to experimental accuracy using the program *BELGI-C<sub>s</sub>*, e.g. ethyl acetate,<sup>11</sup> vinyl acetate,<sup>12</sup> and methyl neopentyl ketone.<sup>13</sup> The program *BELGI* in the  $C_1$  version also shows its efficiency for molecules like allyl acetate,<sup>14</sup> linalool,<sup>15</sup> isoamylacetate,<sup>16</sup> allyl ketone,<sup>17</sup> butyl acetate,<sup>18</sup> pentyl acetate,<sup>19</sup> and hexyl acetate.<sup>20</sup> However, both *BELGI-C<sub>s</sub>* and *BELGI-C<sub>1</sub>* do not include the effect of quadrupole coupling.

We therefore decided to modify the *BELGI-C<sub>1</sub>* code to *BELGI-C<sub>1</sub>-hyperfine* by including weak nuclear quadrupole coupling using a first order perturbation approximation. We used this modified version to refit the data set of EAA given in Ref. 9. Since the program *BELGI-C<sub>1</sub>* is an extended version of the program *BELGI-C<sub>s</sub>*, it is possible to use the *BELGI-C<sub>1</sub>-hyperfine* code to fit the spectra of molecules with  $C_s$  symmetry by setting all the out-of-plane terms to zero. As we shall see below, this program was also successfully applied to TBAA, exhibiting  $C_s$  symmetry.

The remainder of this paper is divided into sections dealing with: the results of quantum chemical calculations and a short presentation of the theoretical model, experimental details, assignments and fits of the spectral data, and a brief discussion of our results.

## THEORETICAL

**Quantum chemical calculations.** All calculations were carried out at the MP2/6-311++G(d,p) level of theory using the program *GAUSSIAN 09*.<sup>21</sup>

**Conformational analysis.** In TBAA, the rotation about the  $C_3$ - $C_5$  bond (for atom numbering see Figure 1) by varying the dihedral angle  $\gamma = \angle(O_4-C_3-C_5-H)$  corresponds to the internal rotation of

the acetyl methyl group. The rotations about the C<sub>9</sub>-C<sub>10</sub>, C<sub>9</sub>-C<sub>14</sub>, and C<sub>9</sub>-C<sub>18</sub> bonds correspond to internal rotations of the three *tert*-butyl methyl groups. The rotation about the C<sub>3</sub>-N<sub>1</sub> bond by varying the dihedral angle  $\theta = \angle(\text{O}_4\text{-C}_3\text{-N}_1\text{-C}_9)$  creates *trans* and *cis* amides. A stable *cis* and a stable *trans* conformation were found, which will be called the *cis* conformer and the *trans* conformer throughout this paper. The *cis* conformer was predicted to have the rotational constants  $A = 3159.3$  MHz,  $B = 1362.5$  MHz, and  $C = 1216.1$  MHz, as well as the dipole moment components  $\mu_a = 4.19$  D,  $\mu_b = 2.18$  D, and  $\mu_c = 0.11$  D. The *trans* conformer, shown in Figure 1, has C<sub>s</sub> symmetry. Its predicted rotational constants are  $A = 3307.1$  MHz,  $B = 1365.5$  MHz, and  $C = 1237.8$  MHz, and the calculated dipole moment components are  $\mu_a = 1.04$  D,  $\mu_b = 3.81$  D, and  $\mu_c = 0.00$  D. The Cartesian coordinates of both conformers are given in Table S-1 in the supporting information (SI). It should be noted that the *trans* conformer is 21.15 kJ·mol<sup>-1</sup> lower in energy than the *cis* conformer. Therefore, we do not expect to observe the *cis* conformer in our spectrum under molecular jet conditions, and only focus on the *trans* conformer in this paper.

**<sup>14</sup>N nuclear quadrupole coupling constants.** From the optimized structure of the *trans* conformer, a single point calculation of the electric field gradient was carried out at the B3PW91/6-311+(df,pd) level of theory using a calibration factor of eQ/h = 4.5586(40) MHz a.u.<sup>-1</sup>, which was calculated by Bailey.<sup>22</sup> This calculation yielded a nuclear coupling tensor with the diagonal elements  $\chi_{aa} = 1.9833$  MHz,  $\chi_{bb} = 2.0254$  MHz, and  $\chi_{cc} = -4.0087$  MHz, as well as the off diagonal elements  $\chi_{ab} = -0.1255$  MHz,  $\chi_{ac} = -0.0001$  MHz, and  $\chi_{bc} = 0.0016$  MHz. The <sup>14</sup>N nuclear quadrupole coupling constants (NQCCs) calculated with this method are in excellent agreement with the experimental values in many of our previous investigations on nitrogen containing molecules.<sup>9,10,23</sup>

**BELGI-C<sub>1</sub>-hyperfine.** As discussed in the introduction, we included the effect of weak nuclear quadrupole coupling in the C<sub>1</sub> version of the *BELGI* program,<sup>4</sup> and first tested this new version of our code on EAA, exhibiting C<sub>1</sub> symmetry.<sup>9</sup>

To deal with the hfs, we used a perturbation approach similar to that used for acetamide, a C<sub>s</sub> molecule with one methyl internal rotor (see Eq. 1 of Ref. 24), but we extended it by including terms allowed under C<sub>1</sub> symmetry. The procedure is the following: We first obtained the rotation-torsion eigenvalues and eigenvectors from the usual two-step diagonalization of the Hamiltonian H<sub>RT</sub> in the rho axis system. Our program was modified to output expectation values of  $\langle P_a^2 \rangle, \langle P_b^2 \rangle, \langle P_c^2 \rangle, \langle P_a P_b + P_b P_a \rangle, \langle P_a P_c + P_c P_a \rangle, \langle P_b P_c + P_c P_b \rangle$  in the rho axis system. We then put numerical values for these quantities into the standard hyperfine energy expression:

$$E_{hf}(I, J, F) = [\chi_{aa} \langle P_a^2 \rangle + \chi_{bb} \langle P_b^2 \rangle - (\chi_{aa} + \chi_{bb}) \langle P_c^2 \rangle + \chi_{ab} \langle P_a P_b + P_b P_a \rangle + \chi_{ac} \langle P_a P_c + P_c P_a \rangle + \chi_{bc} \langle P_b P_c + P_c P_b \rangle] 2 \frac{f(I, J, F)}{J(J+1)} \quad (1)$$

where  $f(I, J, F)$  is the Casimir function,<sup>25</sup> which allowed us to calculate the shifts for each rotation-torsion energy level, and therefore to calculate the shifts  $E_{hf}' - E_{hf}''$  of hfs components for each rotation-torsional transition. Using *BELGI-C<sub>1</sub>-hyperfine*, we can fit all hfs patterns, floating the nuclear quadrupole coupling constants together with the rotational and rotation-torsional parameters. The *BELGI-C<sub>1</sub>-hyperfine* code can also be used to treat molecules with C<sub>s</sub> symmetry like TBAA by fixing all out of plane C<sub>1</sub> terms to zero.

## EXPERIMENTAL

**Measurements.** TBAA, purchased from Alfa Aesar GmbH & Co Kg, Karlsruhe, Germany, has a stated purity of 98 % and was used without further purification. The substance was soaked on a pipe cleaner, used as carrier material, and placed upstream and very close the nozzle. Helium at a

pressure of 150 – 200 kPa was flown over the substance, and the helium-TBAA mixture was expanded into the vacuum chamber.

The spectra were recorded using a supersonic jet Fourier transform microwave spectrometer operating in the frequency range from 2 to 26.5 GHz.<sup>26</sup> At first, a broadband scan from 9.0 to 12.8 GHz was carried out, where overlapping spectral segments were recorded in a step size of 0.25 MHz. All lines from the scans were remeasured in higher resolution with a measurement accuracy of about 2 kHz. They indicated a characteristic hfs due to the nuclear quadrupole coupling of the <sup>14</sup>N nucleus. A portion of the broadband scan is shown in Figure 2, a typical measurement at high resolution in Figure 3.

**Spectrum assignment.** We often begin the spectrum assignment with a rigid rotor model, in which the effects of internal rotation and nuclear quadrupole coupling are neglected. However, from some previous investigations, especially those on N-vinylformamide<sup>27</sup> and N-ethylacetamide,<sup>9</sup> we know that the NQCCs can be calculated in almost exact agreement with the experimental values using the method given in section *<sup>14</sup>N nuclear quadrupole coupling constants*. Therefore, in the case of TBAA, we took into account the effect of <sup>14</sup>N quadrupole coupling directly at the beginning, and assigned the observed hfs by comparing it with the calculated hyperfine frequencies. Some A species *Q*-branch transitions with their characteristic hyperfine patterns could be readily identified and fitted. Afterwards, the number of assigned A species transitions was gradually increased to 26 (with 110 hyperfine components). As a next step, we removed all assigned A species from the broadband scan and used the same procedure as reported in Ref. 9 to assign the E species lines. Since we expected the barrier height in TBAA to be close to that found in EAA (73.4782(1) cm<sup>-1</sup>), several *XIAM* predictions were performed, where we varied the barrier to internal rotation from 50 to 100 cm<sup>-1</sup> with a step width of 5 cm<sup>-1</sup>.



Good agreement between the calculated E species frequencies and the frequencies of the remaining lines in the scan was observed at  $65\text{ cm}^{-1}$ .

A global fit of TBAA including 26 A and 35 E species transitions with a total of 250 hyperfine components was carried out with the program *XIAM*. The root-mean-square (rms) deviation is 16.9 kHz. The same data set was refitted using the *BELGI-C<sub>1</sub>-hyperfine* code to a rms deviation close to the measurement accuracy of 2 kHz. The fit results are given in Table 1, the frequency list is available in Table S-2 in the SI.

## FITS AND DISCUSSIONS

**Results of the fits.** The microwave spectrum of the *C<sub>s</sub> trans* conformer of TBAA was assigned and fitted with the programs *XIAM* and *BELGI-C<sub>1</sub>-hyperfine*. Using the program *XIAM*, we fitted the transitions frequencies to determine 14 parameters, which are three linear combinations of the rotational constants  $B_J$ ,  $B_K$ ,  $B_{-}$ , three quartic centrifugal distortion constants  $D_J$ ,  $D_{JK}$ , and  $d_J$ , the NQCCs  $\chi_{aa}$ ,  $\chi_{bb}-\chi_{cc}$ , and  $\chi_{ab}$ , as well as five internal rotation parameters (the barrier to internal rotation  $V_3$ , three higher order terms  $D_{pi2J}$ ,  $D_{pi2K}$ ,  $D_{pi2-}$ , and the angle  $\delta$  between the internal rotor axis and the principal  $a$  axis). The results are given as Fit *XIAM* in Table 1.

Using the *BELGI-C<sub>1</sub>-hyperfine* code, 17 parameters were floated (with the rotational constant  $F$  of the internal rotor fixed at the value from the *XIAM* fit), i.e. the NQCCs  $\chi_{aa}$ ,  $\chi_{bb}$ , and  $\chi_{ab}$  in Eq. (1), together with the three rotational constants  $A$ ,  $B$ ,  $C$ , four centrifugal distortion constants  $\Delta_I$ ,  $\Delta_K$ ,  $\delta_I$ , and  $\delta_K$ , the  $D_{ab}$  parameter (multiplying the off-diagonal  $(P_a P_b + P_b P_a)$  terms), the potential barrier height  $V_3$ , the rotation-torsion coupling term  $\rho$ , and four higher order terms which represent the rotation-torsion interaction. All out-of-plane terms were set to zero due to the *C<sub>s</sub>* symmetry of TBAA. The internal rotation constant  $F$  was fixed to the value determined with

*XIAM*. The rms deviation of all 250 hyperfine components is 3.0 kHz, which is very close to the measurement accuracy. Parameters which can be transformed into the principal axis system are given as Fit *BELGI* in Table 1. The *BELGI-C<sub>1</sub>-hyperfine* parameters in the rho axis system are summarized in Table 2.

The *BELGI-C<sub>1</sub>-hyperfine* code also shows its efficiency for fitting the microwave spectrum of EAA. As reported in Ref. 9, four E species transitions ( $2_{11} \leftarrow 1_{11}$ ,  $2_{12} \leftarrow 1_{01}$ ,  $3_{03} \leftarrow 2_{12}$ ,  $3_{13} \leftarrow 2_{02}$ ) were excluded in a fit using the program *XIAM* because of their large observed-minus-calculated values (see the frequency list given in the SI of Ref. 9). Using the *BELGI-C<sub>1</sub>-hyperfine* code, the same data set as in Ref. 9, but including these four transitions, were fitted to a rms deviation of 2.7 kHz, much better than that of the *XIAM* fit. In the *BELGI* fit of EAA we floated 20 parameters, which are also listed in Table 2. It should be noted that the out-of-plane  $D_{aci}$  and  $D_{acji}$  parameters, which multiply the  $P_aP_c+P_cP_a$  and  $P^2(P_aP_c+P_cP_a)$  terms, respectively, are well determined, while the  $D_{bci}$  parameter (multiplying the  $P_bP_c+P_cP_b$  terms) could not be fitted and was set to zero. All fitted transitions of EAA along with their residuals are available in Table S-3; parameters transformed into the principal axis system in Table S-4.

**Discussions.** The rotational constants  $A$ ,  $B$ ,  $C$  deduced from the *XIAM* and *BELGI-C<sub>1</sub>-hyperfine* fits are of high accuracy and in excellent agreement with the values calculated at the MP2/6-311++G(d,p) level of theory. The centrifugal distortion constants calculated using anharmonic frequency calculations are also close to the experimental values. The NQCCs determined in both fits are essentially the same, and are as expected very well calculated using the method given in section *<sup>14</sup>N nuclear quadrupole coupling constants*.

The barrier to internal rotation of the acetyl methyl group in TBAA was fitted by the program *XIAM* to be 65.5668(1) cm<sup>-1</sup>, which is close to the barrier of 64.91548(41) cm<sup>-1</sup> obtained with *BELGI-C<sub>1</sub>-hyperfine*. In comparison to the values of 73.468(51) cm<sup>-1</sup> and 73.4782(1) cm<sup>-1</sup> found

for N-methylacetamide<sup>28</sup> and EAA,<sup>9</sup> respectively, the barrier in TBAA decreases by about 8  $\text{cm}^{-1}$ . This is strange, because we expect that the bulky *tert*-butyl group increases the acetyl methyl barrier height because of the sterical effect, as already observed in esters by comparing methyl acetate ( $102.413(20) \text{ cm}^{-1}$ )<sup>29</sup> and ethyl acetate ( $101.606(23) \text{ cm}^{-1}$ )<sup>11</sup> with *tert*-butyl acetate ( $112.983(13) \text{ cm}^{-1}$ ).<sup>30</sup> However, since electronic effects might have a much stronger influence on the barrier to internal rotation of the acetyl methyl group than the sterical hindrance, as discussed in Ref. 9, we suspect that sizable electronic effects occurring from the orientation of the *tert*-butyl group connected to the amide bond lead to the decrease of the potential barrier in TBAA. On the other hand, it is interesting that the barrier to internal rotation of the acetyl methyl group in TBAA is almost the same as those of two conformers of ethylacetamidoacetate ( $63.695(61) \text{ cm}^{-1}$  and  $64.756(63) \text{ cm}^{-1}$ )<sup>31</sup> and that of  $64.96(4) \text{ cm}^{-1}$  found for N-acetyl alanine methyl ester.<sup>32</sup> Unfortunately, not like in the case of acetates,<sup>33</sup> the limited number of data points is not sufficient to give any definitive statement on the acetyl internal rotation barrier in acetamides.

The *ab initio* barrier height of  $119 \text{ cm}^{-1}$  was obtained by rotating the acetyl methyl group in a grid of  $10^\circ$ , and the structure was optimized except for the frozen dihedral angle  $\gamma$  defining the torsional coordinate. The *ab initio* barrier is almost twice the experimental value. Many previous investigations have shown that calculating the potential barriers is a difficult task. The predicted values vary in a wide range and depend strongly on the level of theory in use.<sup>33,34</sup> Considering the zero point energy correction might improve the results.<sup>31</sup> Nevertheless, it requires frequency calculations for the transition states, which cannot be performed at high level of theory due to the limitation of our computational resources. Furthermore, a level that yields reasonable value for a methyl group may fail for another methyl group, even in the same molecule (for example see Table VII in Ref. 31). High level quantum chemical methods such as diffusion quantum Monte

Carlo and coupled cluster are not forcedly in best agreement with the experiments.<sup>10</sup> Currently, no general methods exist to calculate the methyl barrier height. However, results from quantum chemical calculations often give the correct order of magnitude (low, intermediate, or high) of the barrier heights, which is sufficient to hint the authors in the spectral assignment step.

It is worth noting that almost all lines observed in the broadband scan could be assigned to the *trans* conformer of TBAA. The *trans* conformer is thus the only conformer, which can be observed under our measurement conditions.

## CONCLUSION

The microwave spectrum of N-*tert*-butylacetamide was measured between 2 and 26.5 GHz using a molecular beam Fourier transform microwave spectrometer with a measurement accuracy of 2 kHz. Only one conformer with *trans* configuration and  $C_s$  symmetry was observed in the spectrum. The data set was fitted using the programs *XIAM* and *BELGI-C<sub>1</sub>-hyperfine* to rms deviations of 16.9 kHz and 3.0 kHz, respectively. Both *XIAM* and *BELGI* fits included 26 A and 35 E species transitions with a total of 250 hfs components, determining 14 and 17 molecular parameters, respectively. All comparable fitted parameters were in excellent agreement. The barrier to internal rotation of the acetyl methyl group was approximately  $65\text{ cm}^{-1}$ , surprisingly lower than that of about  $73\text{ cm}^{-1}$  found in N-methylacetamide and N-ethylacetamide, but close to that found in ethylacetamidoacetate and N-acetyl alanine methyl ester. The *BELGI-C<sub>1</sub>-hyperfine* code was also used to refit the microwave spectrum of N-ethylacetamide reported in Ref. 9 to measurement accuracy.

## ASSOCIATED CONTENT

**Supporting Information.** Cartesian coordinates of the *trans* and *cis* conformers, lists of fitted frequencies along with their residuals of *trans* N-*tert*-butylacetamide and N-ethylacetamide, *BELGI-C<sub>1</sub>-hyperfine* parameters in the principal axis system of N-ethylacetamide. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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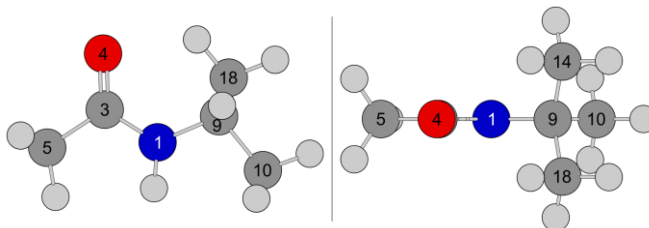
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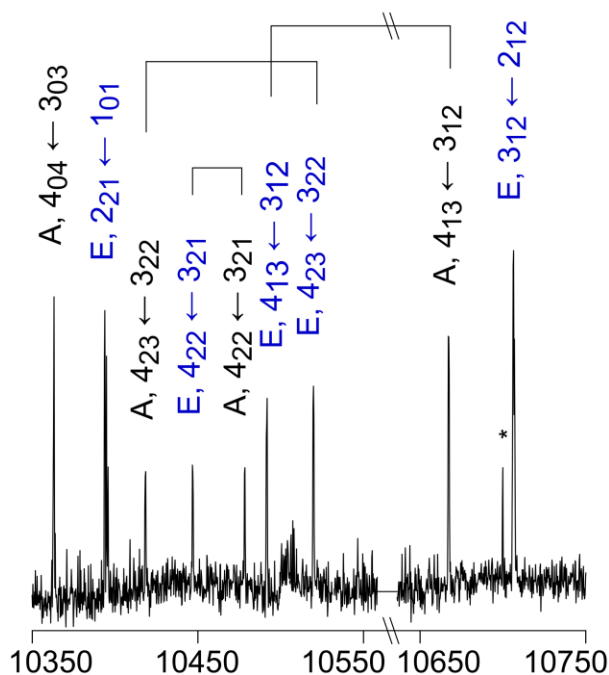
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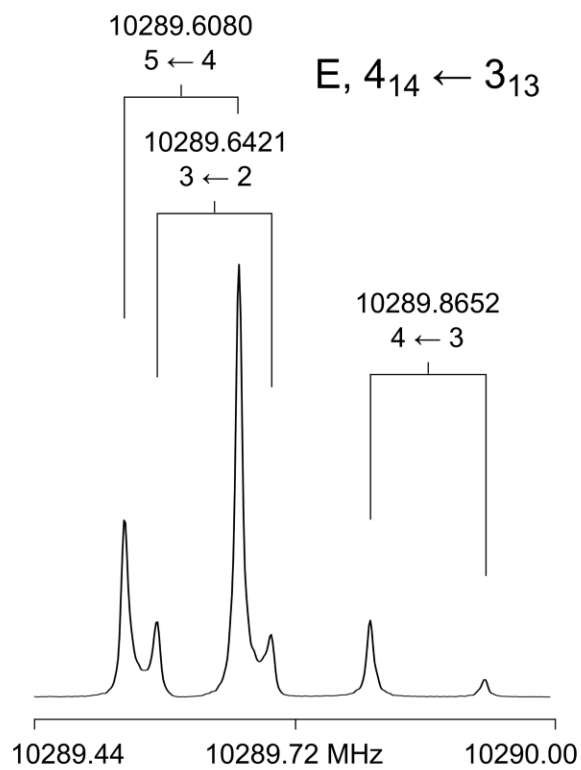
FIGURES



**Figure 1.** Optimized geometry of the *trans* conformer of N-*tert*-butylacetamide calculated at the MP2/6-311++G(d,p) level of theory. Right hand side: view along the O<sub>4</sub>-C<sub>3</sub> bond, left hand side: front view.



**Figure 2.** A portion of the broadband scan of N-*tert*-butylacetamide in the frequency range from 10350 to 10750 MHz. The transitions are marked with their respective quantum numbers and LAM symmetry species; the asterisk marks an unassigned line. A-E splittings are indicated by brackets. Additional splittings arise from the quadrupole coupling of the <sup>14</sup>N nucleus.



**Figure 3.** A high resolution spectrum of the  $4_{14} \leftarrow 3_{13}$  E species transition of N-*tert*-butylacetamide. The Doppler doublets are marked by brackets. Hyperfine transitions are given by the respective  $F' \leftarrow F$  quantum numbers. For this spectrum, 380 decays were co-added.

TABLES

**Table 1.** Molecular parameters of the observed *trans* conformer of N-*tert*-butylacetamide in the principal axis system obtained from fits using the programs *XIAM* and *BELGI-C<sub>1</sub>-hyperfine* and from quantum chemical calculations.

Parameter <sup>a</sup>	Unit	Fit <i>XIAM</i> <sup>b</sup>	Fit <i>BELGI</i> <sup>c</sup>	Calc. <sup>d</sup>
<i>A</i>	MHz	3302.4457(46)	3304.8012(16)	3307.1
<i>B</i>	MHz	1365.5902(17)	1364.2402(14)	1365.5
<i>C</i>	MHz	1238.8312(14)	1238.48089(62)	1237.8
<i>D<sub>J</sub></i>	kHz	0.1042 (81)	0.1016(20)	0.0872
<i>D<sub>JK</sub></i>	kHz	0.529(80)		0.4594
<i>d<sub>l</sub></i>	kHz	-0.0169(66)		-0.0055
$\chi_{aa}$	MHz	2.0129(72)	2.0118(35)	1.9833 <sup>e</sup>
$\chi_{bb}-\chi_{cc}$	MHz	5.827(18)	5.8278(58)	6.0342 <sup>e</sup>
$\chi_{ab}$	MHz	-0.144(28)	-0.1395(37)	-0.1255 <sup>e</sup>
<i>V<sub>3</sub></i>	cm <sup>-1</sup>	65.5668(1)	64.91548(41)	119.
<i>F<sub>0</sub></i>	GHz	158.0 <sup>f</sup>	158.062356(27)	
<i>D<sub>pi2J</sub></i>	kHz	-52.27(17)		
<i>D<sub>pi2K</sub></i>	kHz	529.1(12)		
<i>D<sub>pi2-</sub></i>	kHz	-28.01(35)		
$\angle(i,a)$	deg	32.4448(1)	32.56356(15)	34.95
$\angle(i,b)$	deg	57.5552(1)	57.43644(15)	55.05
$\angle(i,c)$	deg	90.0 <sup>f</sup>	90.0 <sup>f</sup>	90.00
rms <sup>g</sup>	kHz	16.9	3.0	
N <sub>A</sub> / N <sub>E</sub> / N <sub>q</sub> <sup>h</sup>		110/140/250	110/140/250	

<sup>a</sup> All parameters refer to the principal axis system. Statistical uncertainties are given as one standard uncertainty in the last digit. <sup>b</sup> Watson's S reduction and I' representation were used, with *d<sub>2</sub>* set to zero. <sup>c</sup> Obtained by transformation from the rho axis system to the principal axis system (for details see Ref. 11). <sup>d</sup> Calculated at the MP2/6-311++G(d,p) level of theory. <sup>e</sup> Electric field gradient single point calculation at the B3PW91/6-311+(df,pd) level of theory. <sup>f</sup> Fixed value. <sup>g</sup> Root-mean-square deviation of the fit. <sup>h</sup> Number of A and E species transitions as well as hyperfine components, respectively.

**Table 2.** Spectroscopic constants of N-*tert*-butylacetamide ( $C_s$  symmetry) and N-ethylacetamide ( $C_1$  symmetry) in the rho axis system obtained with the program *BELGI-C1-hyperfine*.

Parameter <sup>a</sup>	Unit	TBAA	EAA	Operator
$A$	MHz	3178.6949(12)	7158.6153(12)	$P_a^2$
$B$	MHz	1490.34657(62)	2277.9833(32)	$P_b^2$
$C$	MHz	1238.48091(62)	1961.4748(10)	$P_c^2$
$D_{ab}$	MHz	478.3453(24)	715.186(18)	$\{P_a, P_b\}$
$D_{aci}$	MHz	0.0 <sup>b</sup>	-291.1414(50)	$\{P_a, P_c\}$
$D_{ac,ji}$	kHz	0.0 <sup>b</sup>	2.611(85)	$P^2\{P_a, P_c\}$
$\Delta_J$	kHz	0.1016(20)	1.2533(45)	$-P^4$
$\Delta_{JK}$	kHz	0.0 <sup>c</sup>	-0.885(21)	$-P^2P_a^2$
$\Delta_K$	kHz	2.00(13)	17.23(19)	$-P_a^4$
$\delta_J$	kHz	0.0254(21)	0.0724(42)	$-2P^2(P_b^2 - P_c^2)$
$\delta_K$	kHz	-0.468(59)	-7.136(69)	$-\{P_a^2, (P_b^2 - P_c^2)\}$
$\chi_{aa}$	MHz	4.1477(60)	3.8943(62)	
$\chi_{bb}$	MHz	3.6919(67)	3.6666(62)	
$\chi_{cc}$	MHz	-7.8396 <sup>d</sup>	-7.5609 <sup>d</sup>	
$\chi_{ab}$	MHz	-0.1916(80)	-1.257(19)	
$V_3$	cm <sup>-1</sup>	64.91548(41)	73.08159(26)	$(1/2)(1 - \cos 3\gamma)$
$\rho$	unitless	0.01795553(18)	0.04082824(25)	$P_a P_\gamma$
$F$	cm <sup>-1</sup>	5.3641 <sup>e</sup>	5.4845 <sup>e</sup>	$P_\gamma^2$
$d_{ab}$	MHz	-3.6271(58)	-7.383(48)	$(1 - \cos 3\gamma)\{P_a, P_b\}$
$k_1$	MHz	0.0 <sup>c</sup>	0.1512(25)	$(P_a P_\gamma)P_a^2$
$c_1$	MHz	0.0 <sup>c</sup>	-0.01642(30)	$P_\gamma^2(P_b^2 - P_c^2)$
$c_4$	MHz	-0.00140(24)	0.0 <sup>c</sup>	$(1 - \cos 3\gamma)P_a^2$
$F_v$	MHz	0.5748(15)	0.0 <sup>c</sup>	$(1 - \cos 3\gamma)P^2$
$G_v$	MHz	0.0 <sup>c</sup>	-0.02219(55)	$P_\gamma^2 P^2$
$L_v$	MHz	0.00233(12)	0.0 <sup>c</sup>	$(P_a P_\gamma)P^2$
$N_A / N_E / N_q^f$		110/140/250	150/125/275	
rms A / E <sup>g</sup>	kHz	2.5 / 3.3	1.7 / 3.5	

<sup>a</sup> All parameters refer to the rho-axis system and cannot be directly compared to those referred to the principal axis system.  $P_a$ ,  $P_b$ , and  $P_c$  are the components of the overall rotation angular momentum,  $P_\gamma$  is the angular momentum of the internal rotor rotating about the internal rotor axis by an angle  $\gamma$ .  $\{u, v\}$  is the anti-commutator  $uv + vu$ . The product of the parameter and

operator from a given row yields the term actually used in the vibration-rotation-torsion Hamiltonian, except for  $F$ ,  $\rho$ , and  $A$ , which occur in the Hamiltonian in the form  $F(\mathbf{P}_\gamma - \rho \mathbf{P}_a)^2 + A P_a^2$ . Statistical uncertainties are shown as one standard uncertainty in the last digit. <sup>b</sup> These parameters are not allowed for a  $C_s$  symmetry molecule, and therefore are set to zero. <sup>c</sup> Not fitted parameters, set to zero. <sup>d</sup> Derived from the linear combination  $\chi_{cc} = -(\chi_{aa} + \chi_{bb})$ . <sup>e</sup> Fixed to the value from a *XIAM* fit. <sup>f</sup> Number of A and E species transitions as well as hyperfine components. <sup>g</sup> Root-mean-square deviations of the A and E species.

### Graphical abstract:

