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The Acetyl Methyl Torsion in N-Ethylacetamide – A Challenge for Microwave Spectroscopy and Quantum Chemistry

Raphaela Kannengießer,^[b] Marcel J. Lach,^[b] Wolfgang Stahl,^[b] and Ha Vinh Lam Nguyen^{*[a]}

Abstract: The gas phase structures and parameters describing the acetyl methyl torsion of N-ethylacetamide were determined with very high accuracy using a combination of molecular beam Fourier-transform microwave spectroscopy and quantum chemical calculations. Conformational studies at the MP2 level of theory yielded four minima on the energy surface. The most energetically favorable conformer, which possesses a C_1 symmetry, was experimentally observed and assigned. The torsional barrier of the acetyl methyl group was obtained to be $73.4782(1) \text{ cm}^{-1}$. Due to this rather low barrier, fine splittings up to 4.9 GHz were found in the spectrum. The conformational structure was not only confirmed by the rotational constants but also by the orientation of the internal rotor. The ^{14}N quadrupole hyperfine splittings were analyzed and compared with theoretical calculations.

Introduction

The amide bond is of inevitable importance in the description of proteins, their reactions, their structural preferences, and many other characteristics. It remains, however, surprisingly unexplored in biology, chemistry, and spectroscopy: While amide bonds are found in virtually all metabolites, enzymes, and hormones as well as being important in drug design and medical applications, still very little quantitative information on their impact in metabolism processes is available. Chemically, amides participate in a lot of classical reactions such as Hofmann rearrangement and amide reduction. Described by two limiting mesomeric structures, they exhibit a complicated electronic configuration due to a conjugation between the carbonyl π -electrons and the lone electron pair of the nitrogen, which forces the C-(C=O)-N subunit to planarity. Consequently, the motif of the amide bond is the origin of a characteristic behavior in chemical reactions as well as biological processes.

Acetamides form a sub-class of amides, which contain an acetyl group $\text{CH}_3\text{-(C=O)-N}$. Besides mostly unrevealed structural preferences of substituted amides in general, acetamides are especially interesting due to their internal dynamics. The methyl group undergoes internal rotation with an intermediate or low barrier. The observation of its large amplitude motion does not only contain information on the intramolecular orientation of the

methyl group and in consequence on the molecular structure, but also on the electronic configuration: The methyl group can be considered as a sensitive probe, whose torsional barrier varies significantly upon changes of the electronic environment readily induced by structural changes at the other side of the amide bond.

In the family of secondary acetamides, the rotational structure of only one molecule, N-methylacetamide,^[1] was reported. This molecule exists as a *cis* and a *trans* conformer, whereby the *cis* conformer possesses a very high energy. In the rotational spectrum, only the *trans* conformer could be observed as the singly possible structure, and no discussion of structural preferences is thus necessary. This becomes an important question in the structure and dynamics of N-ethylacetamide, since the torsion of the ethyl group around the σ -bond allows different conformations. For the acetyl methyl torsion, it is known from a series of saturated acetates that the barrier is largely invariant.^[2-4] However, in unsaturated acetates like vinyl acetate^[5] and isopropenyl acetate,^[6] π -electron conjugation becomes possible and the barrier increases significantly. This leads to the question what situation might be found in acetamides, where complex electronic conjugation between π -electrons and the lone electron pair is present? Using internal rotation as a sensitive probe, this question can be answered by comparing the torsional barrier in N-methyl- and N-ethylacetamide.

N-ethylacetamide is found in alcoholic beverages, tea, and wine. It is also a chemical motif in melatonins, for example, the hormone 6-hydroxymelatonin. Its structural properties are therefore of underlying nature to the characteristics observed in larger bio-functional molecules. For the structure determination, a combination of microwave spectroscopy and quantum chemistry has lately developed into a powerful and reliable tool. With 14 atoms, N-ethylacetamide is a relatively small biomimetic substance, at the same time being a medium-sized molecule in the realm of precise spectroscopic studies. Determining its structure in a multi-isotopologue study, the atom-by-atom substitution structure method, is already becoming a tedious task for the heavy atom backbone while – in natural abundance – not providing the hydrogen positions. Combining the experimentally deduced molecular parameters with quantum chemical results, a detailed and precise statement on the three-dimensional structure of N-ethylacetamide becomes possible.

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Supporting information for this article is given via a link at the end of the document.

Results and Discussion

QUANTUM CHEMICAL CALCULATIONS

Since the last years, with the rapid development of computer technique, quantum chemical calculations receive an irreplaceable position in the assignment process with the aim to determine initial molecular parameters. All calculations throughout the present work were carried out at the MP2/6-

311++G(d,p) level of theory using the program *GAUSSIAN*⁷ unless otherwise stated. This combination of method and basis set was used, since it produced reasonable agreement with experimental values in many previous studies on nitrogen containing molecules.^[8-10]

In total, 36 different starting geometries were created by varying two dihedral angles $\alpha_1 = \angle(\text{H}_2\text{-N}_1\text{-C}_3\text{-C}_5)$ and $\alpha_2 = \angle(\text{H}_2\text{-N}_1\text{-C}_9\text{-C}_{12})$ from -120° to 180° in a grid of 60° (for atom numbers see Figure 1). Optimizations yielded four conformers, which were confirmed as stable minima by frequency calculations. Their energy values, rotational constants, and dipole moment components are given in Table 1. In the most stable conformers I and II, the oxygen atom is distant from the proton attached to the nitrogen atom. Conversely, the oxygen atom and the proton are in a more hindered *cis* orientation in conformer III and IV. These conformers are thus higher in energy (see Figure S-1 in the supporting information (SI)).

Table 1. Relative energy values (in $\text{kJ}\cdot\text{mol}^{-1}$), rotational constants (in GHz), and dipole moment components (in D) of four stable conformers of N-ethylacetamide calculated at the MP2/6-311++G(d,p) level of theory.

	<i>E</i>	<i>A</i>	<i>B</i>	<i>C</i>	$ \mu_a $	$ \mu_b $	$ \mu_c $
I	0.0	7.093	2.213	1.969	0.43	3.98	0.68
II	2.8	8.294	1.952	1.643	1.62	3.79	0.60
III	11.0	6.353	2.243	1.962	4.13	1.83	0.90
IV	11.4	7.756	1.994	1.651	3.83	2.65	0.37

The most stable conformer I, shown in Figure 1, is most likely to be observed under molecular beam conditions. Its coordinates in the principal axis system are available in the SI (Table S-1). Conformer II is $2.8 \text{ kJ}\cdot\text{mol}^{-1}$ higher in energy and might also be identifiable. In contrast, conformer III and IV with much higher relative energies (11.0 and $11.4 \text{ kJ}\cdot\text{mol}^{-1}$) are not expected to be seen in the spectrum.

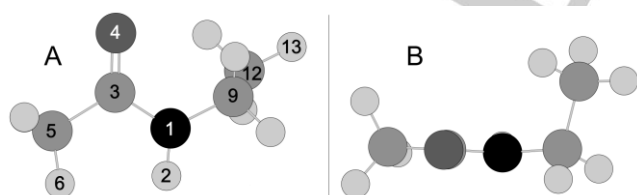


Figure 1. The optimized geometry of the most stable conformer I of N-ethylacetamide in the front view (A) and the top view (B). The ethyl group is tilted out of the $\text{C}_5\text{-C}_3\text{-O}_2\text{-N}_1$ plane by a small angle of approximately 6° , the ethyl methyl group by 67° .

Due to the nuclear spin $I = 1$ of the ^{14}N nucleus, all transitions in the microwave spectrum show a quadrupole hyperfine structure.

For initial values of the quadrupole coupling constants (QCCs), single point electric field gradient (EFG) calculations at the B3PW91/6-311+G(d,p) level of theory were carried out based on the structure optimized at the MP2/6-311++G(d,p) level and a calibration factor of eQ/h of $4.5617(43) \text{ MHz/a.u.}$ introduced by Bailey.^[11] This combination often yields QCCs in almost exact agreement with experimental values for nitrogen containing molecules,^[12] which significantly simplified the spectrum assignment in some cases.^[13]

The acetyl methyl $\text{CH}_3\text{-C=O}$ and ethyl methyl group $\text{-CH}_2\text{CH}_3$ in N-ethylacetamide undergo internal rotation and cause splittings of all rotational transitions.^[14] To estimate the order of magnitude of these splittings, the barrier heights were calculated by varying the dihedral angles $\beta_1 = \angle(\text{O}_4\text{-C}_3\text{-C}_5\text{-H}_6)$ and $\beta_2 = \angle(\text{N}_1\text{-C}_9\text{-C}_{12}\text{-H}_{13})$ in a grid of 10° . Due to the C_{3v} symmetry of the methyl group, a rotation of 120° was sufficient.

For the acetyl methyl group, a barrier of 108.64 cm^{-1} was obtained, which is rather low. We thus expected torsional fine splittings of a few hundreds of MHz. The results for the ethyl methyl group show a much higher barrier of 1187.36 cm^{-1} . From many previous investigations we know that, splittings arising from such barriers are very small and cannot be resolved with our spectrometers.^[15]

MICROWAVE SPECTROSCOPY

Two broadband spectra were recorded in the frequency ranges from 10 to 17 GHz and 27 to 38 GHz. All lines appear as multiplets due to the quadrupole coupling of the ^{14}N nucleus. Figure 2 illustrates a typical spectrum in the scan mode, where some A-E splittings can be recognized.

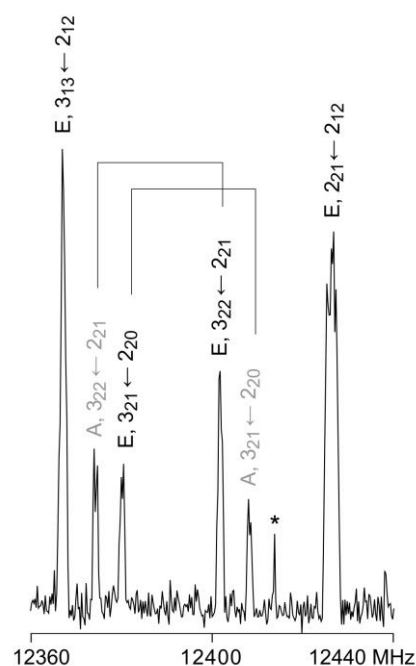


Figure 2. A typical spectrum of N-ethylacetamide. The transitions are marked with their respective species and quantum numbers J, K_a, K_c , an unassigned line with an asterisk. A-E splittings are indicated by brackets.

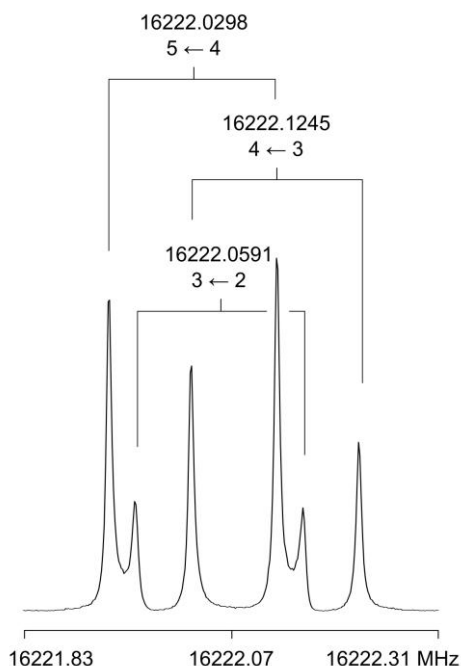


Figure 3. Three quadrupole components of the E species $4_{04} \leftarrow 3_{03}$ transition of conformer I. The experimental accuracy is 2 kHz. The Doppler doublets are marked by brackets. The hyperfine transitions are given by $F' \leftarrow F$. For this spectrum, 404 decays were co-added.

Afterwards, measurements in the high resolution mode were carried out with an intrinsic experimental line width of 2-3 kHz and an experimental accuracy of 0.1 kHz for isolated lines.^[16] The experimental accuracy often rises to 2 kHz when the lines are broadened by overlapping transitions due to unresolved splittings from highly hindered internal rotations as well as spin-spin or spin-rotation couplings. Figure 3 shows a typical spectrum in the high resolution mode. Quadrupole hyperfine structure and Doppler splittings can be clearly recognized.

SPECTRUM ASSIGNMENT

The assignment was carried out in three steps. In a first step, the internal rotation and quadrupole coupling effects were neglected and the molecule was treated as a rigid rotor. Using the calculated $A, B,$ and C rotational constants, a first prediction was performed using the program *XIAM*.^[17] The prediction showed a characteristic b -type Q-branch, which was shifted by approximately 1 GHz in the experimental spectrum, but could be assigned by trial and error. Subsequently, further R-branches were included. In total, 6 a - and 16 b -type transitions were fitted using the rigid-rotor model. No c -type lines could be found.

As a second step, the model was extended by considering the quadrupole hyperfine splittings, which are expected to be much

smaller than the fine splittings from internal rotation. Using the calculated QCCs, the quadrupole hyperfine components of all rigid rotor signals could be easily assigned.

In the last step, the internal rotation of the acetyl methyl group was taken into account. Quantum chemical calculations suggested a barrier height of 108.64 cm^{-1} , which is in the same order of magnitude of the value found for N-methylacetamide ($73.468(51) \text{ cm}^{-1}$). In cases with such low barriers to internal rotation, the fine splittings might change dramatically by varying the barrier slightly. To assign the torsional splittings, several *XIAM* predictions were performed, whereby the V_3 potential was first varied in steps of 5.0 cm^{-1} from 70.0 cm^{-1} to 110.0 cm^{-1} . In the region between 70.0 cm^{-1} and 75.0 cm^{-1} , reasonable agreement between the calculated E species and the remaining lines in the spectrum could be found. Afterwards, a much finer step width of 0.067 cm^{-1} (2 GHz) was used in this region, as illustrated in Figure 4. At $V_3 \approx 73.48 \text{ cm}^{-1}$, the calculated spectrum matched the experimental one best. It should be noted that by varying the V_3 potential, the A-E splittings of a -type transitions changed much less than those of b -type. Thus, we first included a - and subsequently b -type lines in the fit. Finally, 150 A and 121 E-species torsional and hyperfine components were assigned. The fit results are given in Table 2, the frequency list of all fitted transitions is available in Table S-2 in the SI.

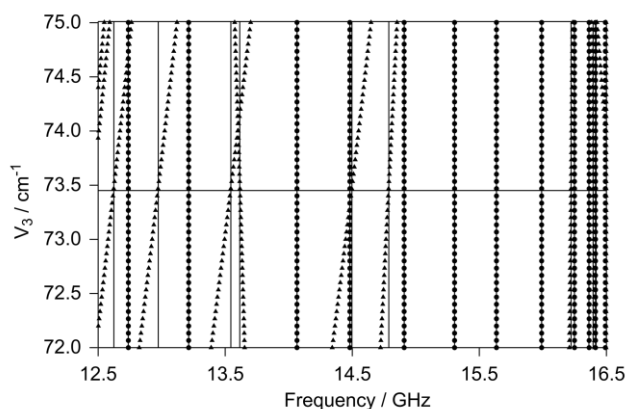


Figure 4. Calculated frequencies of the A and E species between 12.5 and 16.5 GHz depending on the V_3 potential. Observed A species transitions were fitted at different values of V_3 , while all other internal rotation parameters were fixed. Based on this fit, the A (dots) and E (triangles) species frequencies were predicted. All measured transitions are represented by black vertical lines. The black dots are located exactly on the measured A species lines. The observed and predicted E species transitions match best at 73.48 cm^{-1} (indicated by the horizontal line).

Using the program *XIAM*, 271 hyperfine components could be assigned to conformer I of N-ethylacetamide by fitting 18 molecular parameters: the rotational constants A, B, C , the centrifugal distortion constants $\Delta_J, \Delta_{JK}, \Delta_K, \delta_J, \delta_K$, the V_3 potential, the polar coordinates of the internal rotor axis in the principal axis system δ and ϵ , the effective parameters $D_{pi2J}, D_{pi2K},$ and D_{pi2-} , and the QCCs $\chi_{aa}, \chi_{bb}-\chi_{cc}, \chi_{ac},$ and χ_{bc} . The QCC

χ_{ab} was fixed to a value of 0.1686 MHz, the rotational constant of the methyl rotor F_0 to 158 GHz, corresponding to a moment of inertia of $I_a = 3.2 \text{ u}\text{\AA}^2$. The correlation matrix can be found in Table S-3 in the SI.

Table 2. Molecular parameters of conformer I of N-ethylacetamide deduced from the program XIAM (obs.) and parameters calculated at the MP2/6-311++G(d,p) level of theory (calc.).

Par.	Unit	Obs. ^[a]	Calc. ^[b]	Obs.-Calc.
A	GHz	7.2702759(93)	7.093	0.177
B	GHz	2.1835536(24)	2.213	-0.029
C	GHz	1.9387113(18)	1.969	-0.030
Δ_J	kHz	1.0227(89)	2.57 ^[c]	1.54
Δ_{JK}	kHz	1.387(90)	3.88 ^[c]	2.5
Δ_K	kHz	10.66(96)	13.22 ^[c]	2.56
δ_J	kHz	0.1101(74)	0.04 ^[c]	-0.07
δ_K	kHz	-6.37(44)	-33.23 ^[c]	-26.86
χ_{aa}	MHz	1.7508(32)	1.7713	-0.0205
χ_{bb-cc}	MHz	5.4174(83)	5.5303	-0.1125
χ_{ab}	MHz	0.1686 ^[d]	0.1686	
χ_{ac}	MHz	-1.651(71)	-1.4352	-0.2158
χ_{bc}	MHz	0.595(59)	1.0657	-0.4707
V_3	cm^{-1}	73.4782(1)	108.64	-35.16
F_0	GHz	158.0 ^[d]		
D_{pi2J}	kHz	-33.59(33)		
D_{pi2K}	MHz	1.4506(19)		
D_{pi2-}	kHz	-91.06(88)		
$\angle(i,a)$	$^\circ$	27.7216(2)	30.10	-2.38
$\angle(i,b)$	$^\circ$	67.2076(5)	65.67	1.54
$\angle(i,c)$	$^\circ$	75.0772(6)	73.38	1.70
σ^{fit}	kHz	9.8		
N_A/N_E^{fit}		150/121		

[a] Parameters are given with one standard uncertainty in parentheses. Watson's A reduction and I' representation were used. [b] See section quantum chemical calculations. [c] Anharmonic frequency calculations at the B3LYP/6-311++G(d,p) level of theory [d] Fixed. [e] Standard deviation of the fit. [f] Number of lines.

The fitted rotational constants B and C are quite close to the calculated values. Contrarily, the calculated and experimental A rotational constants differ by 177 MHz. This difference is very high compared to many other studies where the same method and basis set were used for molecules of a similar size^[18,19] and causes the large shift of approximately 1 GHz between the predicted and experimental b -type Q-branch transitions. We additionally optimized the structure of conformer I using various method/basis set combinations. The results are summarized in Table S-4 in the SI. In all calculations, the A rotational constant is not satisfactorily close to the experimental value, except in the calculation at the MP2/6-311++G(2df,2pd) level. The B and C rotational constants are both well calculated in all cases.

In the upper diagram of Figure 5, the experimentally determined rotational constants A , B , and C are plotted as straight horizontal lines. These can be compared with the calculated values of the four stable conformers found in our quantum chemical calculations, which are given as dots. Conformer I and III possess similar B and C rotational constants, but the A rotational constant of conformer III does not match the experimental value as well as that of conformer I. However, since the calculated A rotational constant varies in a wide range, depending on the used method and basis set, it is still possible that conformer III is the assigned one.

By considering the calculated energies indicated in the middle of Figure 5, this assumption seems unlikely since conformer III is much higher in energy ($11 \text{ kJ}\cdot\text{mol}^{-1}$). Finally, the calculated angles of the internal rotor axis with respect to the principal axes of inertia illustrated in the lower part of Figure 5 confirms unambiguously that the assigned conformer is conformer I. The calculated angles of conformer I match perfectly the experimental values, whereas those of conformer III show a completely different orientation of the acetyl methyl rotor.

Conformer II is calculated to be only $2.8 \text{ kJ}\cdot\text{mol}^{-1}$ higher in energy than conformer I and might also exist in the spectrum. However, almost all measured lines found in the scan belong to conformer I, and only some weak lines remained unassigned. Therefore, we conclude that only the most stable conformer I could be observed.

The experimental V_3 potential of $73.4782(1) \text{ cm}^{-1}$ is quite low and accordingly, large A-E splittings up to 4.9 GHz occurred in the spectrum. Contrarily, the hyperfine splittings from the ^{14}N nucleus are only in the order of a few hundreds of kHz. Therefore, the fit was much more sensitive to variation in the internal rotation parameters than in the QCCs. Since the quadrupole coupling effect is negligible if compared to the effect of internal rotation, only the absolute line positions of the quadrupole components with the highest predicted intensity^[20] were fitted. For the other quadrupole components, we fitted the splittings relative to these transitions.

The diagonal QCCs χ_{aa} and $\chi_{bb}-\chi_{cc}$ could be calculated almost exactly, as found in many other investigations on nitrogen containing molecules where Bailey's approach was applied.^[14] Additionally, the two off-diagonal elements of the quadrupole coupling tensor χ_{ac} and χ_{bc} could be determined while the third element χ_{ab} was fixed to the calculated value. The deviations between the observed and calculated values are therefore

slightly higher than those of the diagonal elements. Fitting all three off-diagonal elements simultaneously led to high correlations.

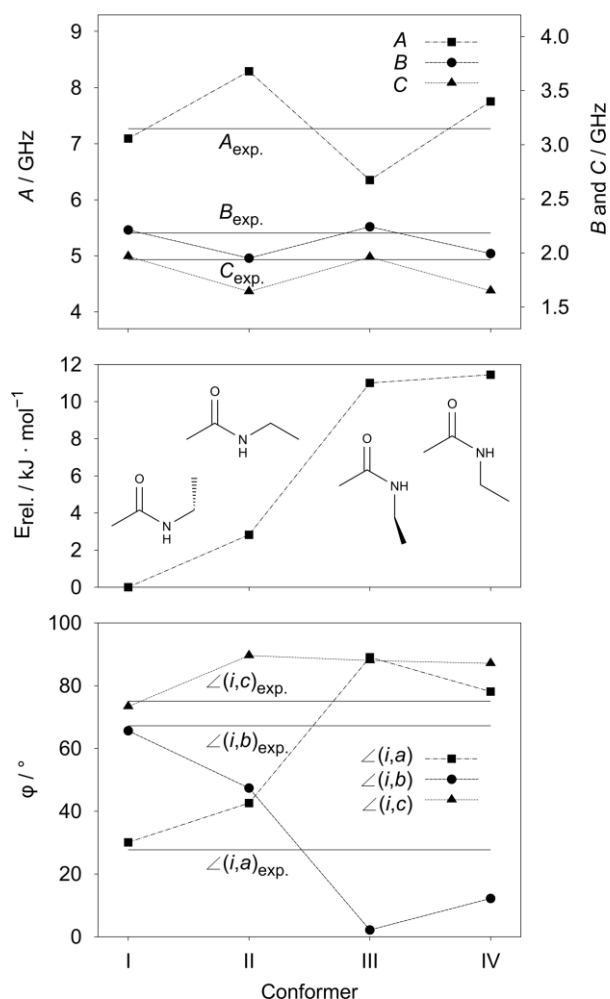


Figure 3. Comparison of quantum chemical calculation and experimental results to identify the assigned conformer of N-ethylacetamide. The experimental rotational constants ($A_{\text{exp.}}$, $B_{\text{exp.}}$, and $C_{\text{exp.}}$) are indicated as horizontal lines in the upper diagram, the calculated values as separated points connected by dashed or dotted lines, which are only present for a better tracing. The energy values are shown in the middle together with the structural formulas. In the lower part, the angles between the internal rotor axis and the principal axes $\varphi = \angle(i, n)$, $n = a, b, c$ are plotted, where the directions of the principal axes were chosen in a way to assure angles between 0° and 90° .

Not only the V_3 potential and the polar coordinates of the internal rotor axis δ and ε , where δ is the angle between the internal rotation axis and the principal a axis and ε the angle between the principal b axis and the projection of the internal rotation axis onto the bc -plane, but also three higher order terms $D_{\text{pi}2J}$, $D_{\text{pi}2K}$, and $D_{\text{pi}2}$ were needed to reproduce the spectrum. The standard deviation of the fit is about 10 kHz, five times larger than our experimental resolution. However, since only few parameters

can be fitted with the program *XIAM* and the barrier to internal rotation is quite low, the fit is already much better than in many other cases with comparably low barriers.^[21,22]

In the case of N,N-diethylacetamide, two conformers were assigned, whose structures differed only by the orientations of the two ethyl groups. Quite different V_3 potentials of $517.04(13) \text{ cm}^{-1}$ and $619.48(91) \text{ cm}^{-1}$ were observed. In N,N-dimethylacetamide, a barrier of 677 cm^{-1} was reported,^[23] which is significantly higher than in N,N-diethylacetamide. Therefore, we expected a similar situation in N-methyl- and N-ethylacetamide. Surprisingly, the obtained V_3 potential of $73.4782(1) \text{ cm}^{-1}$ of N-ethylacetamide is essentially the same value of $73.468(51) \text{ cm}^{-1}$ found for N-methylacetamide. Furthermore, these barriers are one order of magnitude lower than those found in the tertiary acetamides, which seems mainly influenced by a change in the electronic environment, introduced by the presence of a proton at the nitrogen atom in the secondary acetamides.

In a series of saturated acetates from methyl acetate up to n-hexyl acetate, the barrier to internal rotation of approximately 100 cm^{-1} was found, even in cases where the alkyl chain is branched.^[24] Only for *tert*-butyl acetate, the steric effect of the bulky *tert*-butyl group caused a slightly higher barrier of 112 cm^{-1} .^[25] In vinyl acetate⁵ and isopropenyl acetate,⁶ where the vinyl group is bound directly to the ester group and a π -electron conjugation, extending from the vinyl double bond to the ester group, is possible, the barrier heights increase significantly to $151.492(34) \text{ cm}^{-1}$ and $135.3498(38) \text{ cm}^{-1}$, respectively. Obviously, the electronic effect has a much stronger influence on the barrier to internal rotation than the steric hindrance, which is, again, supported by this investigation.

Conclusions

The microwave spectrum of the lowest energy conformer of N-ethylacetamide was studied using a combination of molecular beam technique and quantum chemistry. The ethyl methyl group is tilted out of the molecular plane by an angle of 67° . Hyperfine splittings were found for all transitions due to the electric quadrupole coupling of the ^{14}N nucleus. The acetyl methyl group undergoes internal rotation, which causes large fine splittings up to 4.9 GHz. The torsional barrier is approximately 73 cm^{-1} , exactly the value found for N-methylacetamide, whereas a significantly different barrier was expected. A fit including both, the internal rotation and the quadrupole coupling effect, was carried out and yielded molecular parameters with very high accuracy. The structure and internal dynamics of the title compound is an important step towards understanding larger biological systems with amide bonds.

Experimental Section

The microwave spectra were recorded using two molecular beam Fourier transform microwave spectrometers operating in the frequency ranges of 2 – 26.5 GHz^[26] and 26.5 – 40 GHz.^[27] N-Ethylacetamide was purchased

from Alfa Aesar GmbH & Co KG, Karlsruhe, Germany. The purity was stated to be 99%, the vapor pressure 0.341 hPa at 298 K. No further purification was carried out. Since the vapor pressure is rather low, a few drops of the substance were placed on a piece of a pipe cleaner^[28] and inserted into a stainless steel tube in front of the nozzle, which was heated to approximately 343 K. Helium at a pressure of 150 to 175 kPa was flowing over the sample and the helium-substance mixture was expanded into a vacuum chamber containing the Fabry-Pérot resonator.

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Keywords: molecular beam Fourier transform microwave spectroscopy • ethylacetamide • internal rotation • quadrupole coupling • conformational analysis

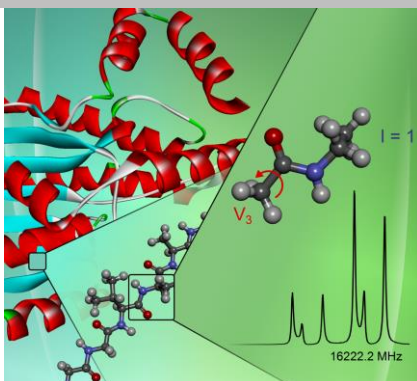
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Entry for the Table of Contents

ARTICLE

Molecular structure and internal dynamics of N-ethylacetamide:

The gas phase structures and parameters describing the acetyl methyl torsion of N-ethylacetamide were determined with very high accuracy using a combination of molecular beam Fourier-transform microwave spectroscopy and quantum chemical calculations. The most energetically favorable conformer was experimentally observed and assigned.



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The Acetyl Methyl Torsion in N-Ethylacetamide – A Challenge for Microwave Spectroscopy and Quantum Chemistry