

Measurements of Microwave and NMR Spectra for ^{15}N Substituted Formamidinium Formate

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Abstract

A sample of doubly-substituted ^{15}N formamidinium formate was synthesized and the microwave spectrum was measured in the 5.6-14.2GHz frequency range using a Flygare-Balle type pulsed beam Fourier transform microwave (MW) spectrometer. A total of 13 a-type rotational transitions were measured and fitted to obtain the rotational constants and centrifugal distortion constants for the ^{15}N substituted isotopologue. The rotational constants and centrifugal distortion constants determined have the following values: $A=5808.02(18)\text{MHz}$, $B=2127.008(2)\text{MHz}$, $C=1557.615(2)\text{MHz}$, $D_J=0.60(11)\text{kHz}$, $D_{JK}=4.95(71)\text{kHz}$ and $\delta_J=-0.138(24)\text{kHz}$. Tunneling splittings were searched for, but not observed. NMR spectra for this compound are reported including values of δ_C , δ_N , $^1J_{\text{CH}}$, $^1J_{\text{CN}}$ and $^2J_{\text{NH}}$ in CD_3SOCD_3 , CD_3OD and D_2O . The occurrence of NH to ND exchange in D_2O allowed the fortuitous measurement of $^1J_{\text{ND}}$.

I. INTRODUCTION

Formamidinium and formic acid readily form the cyclic, doubly hydrogen-bonded complex formamidinium formate, shown in Figure 1. The microwave spectrum, rotational constants, quadrupole coupling parameters and structure calculations for the normal isotopologue were published previously.^{1,2} Spectra for the normal isotopologue were congested owing to quadrupole hyperfine structure from the two ^{14}N nitrogen atoms and possible tunneling splittings were not found. Spectra for the doubly substituted ^{15}N compound are much simpler and possible tunneling splittings were searched for, but not found.

Doubly hydrogen bonded complexes can provide simple models for the hydrogen bonding in DNA base pairs. The DNA base pair A-T, with two hydrogen bonds and G-C, with three hydrogen bonds, both have N-H hydrogen bonds. Microwave measurements on formamidinium formate provide the opportunity to study the structure and the dynamics of a doubly H-bonded complex with N-H bonds and $C_{2v}(m)$ symmetry. Doubly hydrogen bonded carboxylic acids with $C_{2v}(m)$ symmetry³ can exhibit interesting tunneling dynamics. The $C_{2v}(m)$ symmetry for the GROUND tunneling state makes the two N atoms, and the two O atoms in the complex equivalent. The simpler carboxylic acid complexes, propionic acid – formic acid,^{4,5,6} and acetic acid – formic acid⁷ have the $C_{2v}(m)$ symmetry and have been shown to exhibit resolvable concerted proton tunneling splittings in microwave spectra. Without the $C_{2v}(m)$ symmetry, the tunneling splittings have not been observed. No tunneling splittings were reported for formic acid-formamide,⁸ 1,2-cyclohexanedione-formic acid⁹ or cyclopropanecarboxylic acid-formic acid,¹⁰ or the maleimide – formic acid complex.¹¹

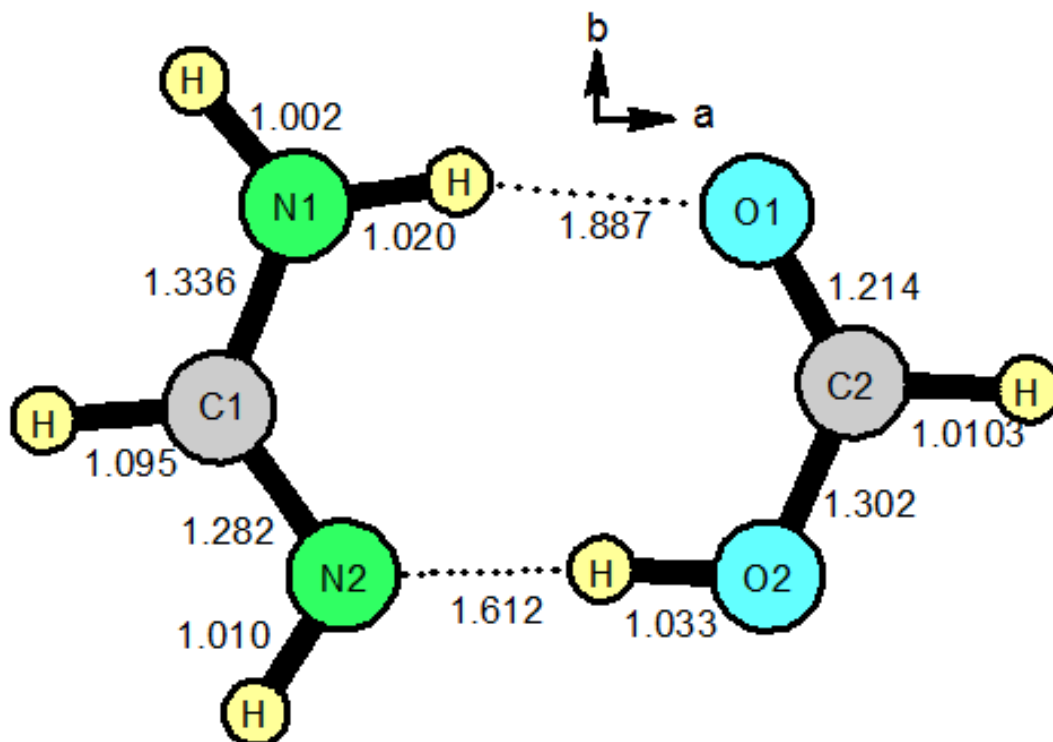


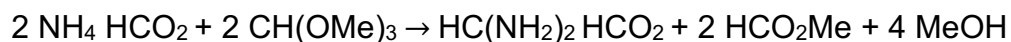
Figure 1. Calculated structure of the formamidinium formate complex from and MP2/cc-pVQZ calculation¹.

For the present measurements, doubly substituted ^{15}N formamidinium formate was synthesized in St Andrews and the microwave spectrum measured in the 5-15 GHz frequency range using a a Flygare-Balle type pulsed-beam Fourier transform microwave spectrometer at the University of Arizona. The ^{15}N atoms have nuclear spin of $\frac{1}{2}$ and so the ^{15}N substituted formamidinium formate spectra do not have the complications from quadrupole coupling splittings. Additional splittings were searched for, but not observed in the present microwave measurements of ^{15}N formamidinium formate isotopologue.

II. EXPERIMENTAL

A. Sample Synthesis

The preparation of formamidinium formate dimer based on a patent report¹² was documented in the previous study.² The synthesis was conducted by heating ammonium formate with an excess amount of trimethyl orthoformate to generate the targeted product and can be summarized in the following equation:



In order to obtain ¹⁵N substituted formamidinium formate, a concentrated ¹⁵N substituted aqueous ammonia solution was used and neutralized to pH4 with formic acid to give crystals of ¹⁵N substituted ammonium formate after evaporation. The ¹⁵N ammonia was obtained in previous experiments at MIT.¹³ Subsequently reactants ammonium formate (7.68 g) and trimethyl orthoformate (30 mL) were heated to 100°C in the flask of a distillation setup for 8h. After the distillate was discarded, the solvent in the mixture was evaporated under reduced pressure and the leftover solid was washed with cold dry diethyl ether for further purification. The final product in colorless crystal form (2.90 g, 53%) was obtained after being sucked dry on a sintered glass funnel.

B. Microwave Measurements

The microwave spectrum was measured for ¹⁵N substituted formamidinium formate, synthesized by the methods described above, in the 5 -15 GHz frequency range using a Flygare-Balle type pulsed beam Fourier transform microwave spectrometer at University of Arizona. The instrumentation and operation of the spectrometer have been described

previously.^{14,15} The synthesized sample was loaded into a glass cell inside a nitrogen dry box in order to prevent water molecules in the atmosphere from contaminating the sample. The sample cell has two openings and while one end of the cell was connected to the pulsed valve of the microwave spectrometer, the other end was connected to a carrier gas passing through the system. The sample molecules were carried by argon gas, purified by a suppelco OMI-1 purifier from Sigma-Aldrich with a backing pressure of 1atm and this pressure was maintained throughout the duration of the measurement. The sample was heated up 96°C and this temperature was maintained to generate a few torr vapor pressure for the sample. The vaporized sample was pulsed into the chamber through a General Valve pulsed valve at a frequency of 2Hz during the collection of the spectrum. The chamber of the microwave spectrometer was kept at 10^{-6} to 10^{-7} torr, with a diffusion pump to substantially reduce possible collisions of the sample molecules and to enhance the rotational cooling from the expansion of argon-sample mixture. Under these conditions, a single pulsed beam cycle can produce a 5 to 1 signal to noise ratio signal for an a-type $2_{02}-1_{01}$ transition centered at 7308.1348 MHz.

To make predictions for rotational transitions for ^{15}N substituted isotopologue of formamidinium formate, the Cartesian coordinates from the previous calculation¹ were used to calculate scale factors (A for ^{15}N /A for ^{14}N), etc. and these scale factors were applied to the previous experimental A(^{14}N), B(^{14}N), C(^{14}N).¹ These corrected rotational constants for ^{15}N were used in Pickett's SPCAT¹⁶ program to give predictions of rotational transitions for ^{15}N substituted formamidinium formate.

A total of 13 a-type rotational transitions were measured and they are listed in Table 1 with their quantum number assignments. B-type transitions were searched for but not

observed. These observed a-type transitions are assigned using only three quantum numbers J, K_a and K_c since ¹⁵N has a nuclear spin of ½ and does not give rise to quadrupole coupling splitting. Additional transitions near where a-type 1₀₁-0₀₀ and 5₁₄-5₁₅ transitions were expected, were observed and recorded at 3684.5535 MHz and 8428.0859MHz during the measurement but not used in the fitting due to their more significant deviations. The 13 rotational transitions were used in the SPFIT program in the Pickett program suite to give three rotational constants and three centrifugal distortion constants. The b-dipole transitions were searched for but not found. The calculated dipole moments are μ_a = 3.4 D and μ_b = 0.23 D. The values of these fitted parameters are shown in Table 2. The fit to these 13 rotational transitions fit yields a standard deviation of 10.3kHz, which is greater than the experimental error of about 5kHz but in comparison to the magnitudes of rotational transitions and constants, this fit is considered to be reasonably accurate.

Table 1. Measured rotational transitions for ¹⁵N substituted formamidinium formate and deviations from the fit values (ν_{0-c}). Values shown are in MHz.

J' K _a ' K _c '	J'' K _a '' K _c ''	ν _{obs}	ν _{0-c}
4 1 3	4 1 4	5665.3511	-0.0101
2 1 2	1 1 1	6799.7954	-0.0120
2 0 2	1 0 1	7308.1348	-0.0095
2 1 1	1 1 0	7938.6133	0.0109

3 1 3	2 1 2	10163.3242	-0.0179
3 0 3	2 0 2	10814.0049	0.0011
3 2 2	2 2 1	11053.6850	0.0023
3 2 1	2 2 0	11293.4892	0.0087
6 1 5	6 1 6	11625.6757	0.0011
3 1 2	2 1 1	11867.4453	0.0179
4 1 4	3 1 3	13488.7188	-0.0003
4 0 4	3 0 3	14165.6084	0.0049
4 2 3	3 2 2	14690.5235	-0.0084

Table 2. Rotational and centrifugal distortion constants of ^{15}N substituted formamidinium formate, determined from the fit to the measured transitions. The standard deviation for the fit is 10.3 kHz.

	Experimental
<i>A</i> /MHz	5808.02(18)
<i>B</i> /MHz	2127.0076(24)
<i>C</i> /MHz	1557.6145(24)
<i>D_J</i> /kHz	0.5988(1104)
<i>D_{JK}</i> /kHz	4.9549(7143)

D_K/kHz	-0.1380(237)
N	13
σ/kHz	10.3

C. NMR Measurements

Spectra were obtained on a Bruker AV instrument at 300 MHz (^1H) and 75 MHz (^{13}C) and a Bruker AVIII-HD at 50.7 MHz (^{15}N). Chemical shift values are referenced to Me_4Si (H, C) and MeNO_2 (N). To investigate any possible solvent effects, spectra were run in three different solvents: CD_3SOCD_3 , CD_3OD and D_2O , and for each of these ^1H , ^1H -decoupled ^{13}C , undecoupled ^{13}C , and ^{15}N spectra were run. The data obtained are summarized numerically in Table 3 and typical spectra are shown (in CD_3OD) in Figure 2. As discussed later, recording the ^{15}N spectrum in D_2O revealed that complete D/H exchange had taken place and the resulting 1:2:3:2:1 quintet (Figure 3) allowed measurement of $^1J_{\text{N-D}}$.

Table 3. NMR chemical shifts (δ , ppm) and coupling constants (J , Hz) for ^{15}N -substituted formamidinium formate in three different solvents

	CD_3SOCD_3	CD_3OD	D_2O
$\delta_{\text{H}} \text{HCO}_2$	8.38	8.51	8.44
$\delta_{\text{H}} \text{HCN}_2$	7.83	7.83	7.80
$^2J_{\text{H-N}}$	3.3	3.6	—
$\delta_{\text{C}} \text{HCO}_2$	166.8	170.1	170.6
$^1J_{\text{H-CO}}$	189.5	191.7	196.4
$\delta_{\text{C}} \text{HCN}_2$	158.2	158.8	156.8

$^1J_{\text{H-CN}}$	188.1	189.6	191.2
$^1J_{\text{C-N}}$	16.7	17.7	18.4
$\delta_{\text{N HCN}_2}$	-267.2	-274.4	-274.4

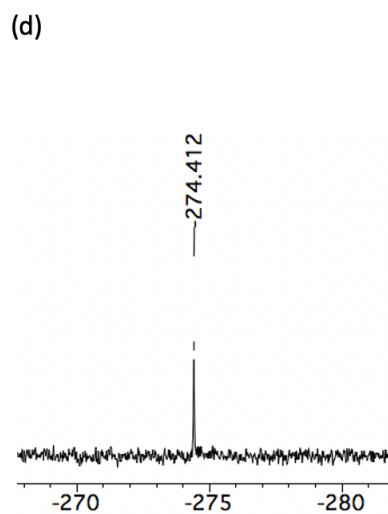
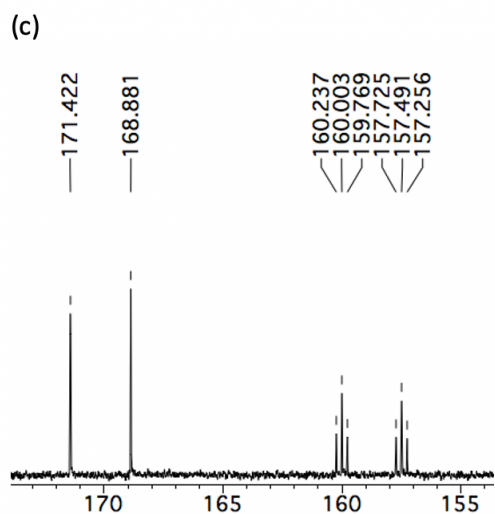
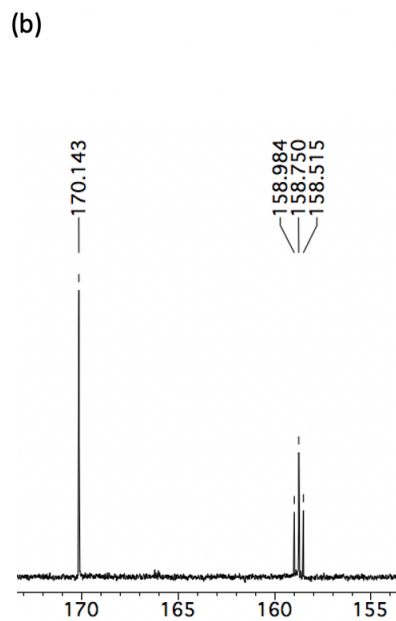
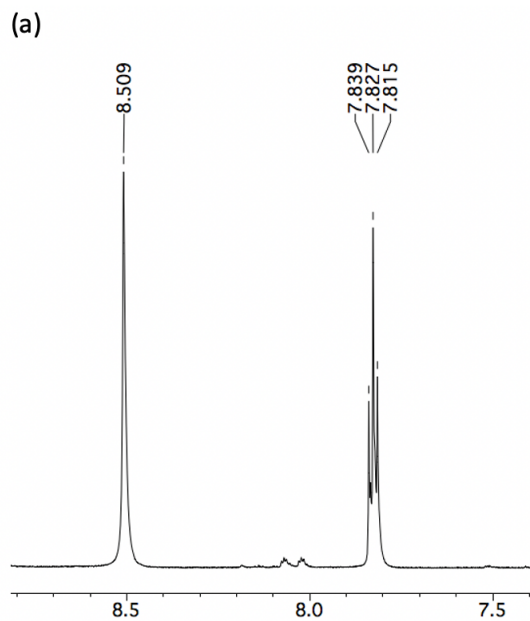


Figure 2. NMR spectra in CD₃OD: (a) ¹H spectrum; (b) ¹H decoupled ¹³C spectrum; (c) undecoupled ¹³C spectrum; (d) ¹⁵N spectrum

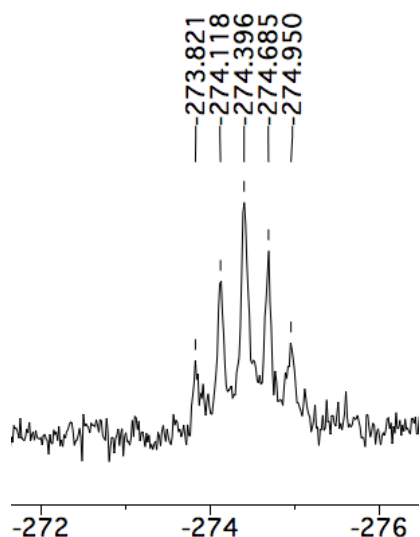


Figure 3. ¹⁵N NMR signal in D₂O showing N–D coupling

III. DISCUSSION

The calculated structure and measured rotational constants for the previous paper¹ can be used to obtain rotational constants for the doubly substituted ¹⁵N formamidinium formate isotopologue. The calculated cartesian coordinates and a rotational constant program are used to generate predicted A, B, and C values for the ¹⁵N substituted formamidinium formate using A, B, and C for the normal isotopologue. When these are applied to A = 5880.05(2)MHz, B = 2148.7710(2)MHz, C = 1575.2347(1)MHz from the normal isotopologue, we would predict, A = 5712.13MHz, B = 2114.29MHz, C = 1544.58MHz. These values, for B and C, are 0.6% different from the experimental values (above) in Table 2. This discrepancy could be due to large amplitude vibrational motions of the complex. In the first paper,² a large discrepancy

between measured and calculated ^{14}N quadrupole coupling strengths was observed. This was attributed to vibrational averaging effects over large amplitude motions of the hydrogen-bonding protons in the complex, but a much better agreement between measured and calculated quadrupole coupling parameters was obtained in the most recent paper.¹ Tunneling splittings of spectral lines were not observed in this work.

The synthesis of doubly ^{15}N -labelled formamidine chloride was reported at an early date,¹⁷ where it was used to prepare ^{15}N -labelled adenine, but this was before the advent of NMR. A later study of the ^{14}N -decoupled ^1H NMR spectrum of formamidine chloride allowed separate observation of a 16 Hz 3-bond coupling between CH (δ 7.81) and the (*E*)-NH (δ 8.45) with 6 Hz coupling to the (*Z*)-NH (δ 8.34) with the patterns appearing, respectively, as triplet of triplets, doublet and doublet.¹⁸ In our earlier paper,² we reported values of δ_{H} , δ_{C} and $^1J_{\text{CH}}$ for formamidine formate in CD_3SOCD_3 . Since the incorporation of two spin- $\frac{1}{2}$ ^{15}N nuclei allows determination of several further NMR parameters for this fundamental system, we obtained a range of spectra in three separate solvents (Table 3). As shown in Figure 2 for CD_3OD solution, the incorporation of ^{15}N results in observation of a triplet for HC^{15}N_2 in both ^1H and ^{13}C spectra with the values of $^2J_{\text{H-N}}$ and $^1J_{\text{C-N}}$ available directly. It is rather difficult to find good literature values for comparison, but the spectrum of 8-hydroxyadenine labelled with ^{15}N at positions 1 and 3 is reported to give a value of 14 Hz for the 2-bond coupling to 2-H,¹⁹ significantly higher than our values of 3.3 and 3.6 Hz. For the magnitude of $^1J_{\text{C-N}}$ there is more literature precedent and our values of 16.7–18.4 Hz can be compared with 9.7 Hz for C-2 of 1,3-di(^{15}N)-labelled 8-hydroxyadenine,¹⁹ 7.2 Hz for C-2 of 1,3-di(^{15}N)-labelled 4,6-diamino-5-formamidopyrimidine,¹⁹ 17.8 Hz for C-5 of 5-formyl(^{15}N)-amino-labelled 4,6-diamino-5-

formamidopyrimidine,¹⁹ 10.7 Hz for $^1J_{N3-C4}$ of an *N*-acetylsydnonimine,²⁰ and 23.7 Hz for $^1J_{N6-C5}$ of its hydrochloride salt.²⁰

As we noted previously,² the magnitude of $^1J_{C-H}$ is known to show some correlation with the bond order and degree of hybridization.²¹ In addition it may be subject to significant solvent effects, as indeed may the other coupling constants determined here.^{21,22} In fact, all the coupling constants show a progressive increase in magnitude in going from CD₃SOCD₃ to CD₃OD to D₂O, something that does not quite correlate with the dielectric constants of the solvents (46, 33.6, 80).²² The effect is fairly small however with a maximum of 10% for $^1J_{C-N}$ and $^2J_{N-H}$. As mentioned previously,² the values of $^1J_{C-H}$ for H-CO₂ of 189–196 Hz compare well with 194.8 Hz for sodium formate in D₂O,²³ while a good comparison with the values of $^1J_{C-H}$ for H-CN₂ of 188–191 Hz is the 199 Hz reported for $^1J_{C-H}$ at C-2 of 1,3-di(¹⁵N)-labelled 8-hydroxyadenine.¹⁹

Importantly, the observation of just a single ¹⁵N chemical shift environment in all three solvents provides further support for the equivalence of the two nitrogens on the NMR timescale and thus the existence of formamidinium formate as a fully ionic salt in solution, consistent with the form we previously observed in the solid state by X-ray diffraction.² Finally in the current NMR study, examination of the ¹⁵N signal run in D₂O showed a 1:2:3:2:1 quintet (Figure 3) corresponding exactly to the pattern expected for ND₂ with coupling to the spin-1 deuterium of 14.3 Hz. It appears that $^1J_{N-D}$ is a rarely observed parameter and we have been unable to locate any reported values for comparison.

ACKNOWLEDGEMENTS

This material is based upon work supported by the National Science Foundation under Grant Nos. CHE-1057796 and CHE-1952289 at the University of Arizona.

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