The Structural and Conformational Properties of Formic Hydrazide (Formylhydrazine) Studied by Microwave Spectroscopy and Quantum Chemical Calculations

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Formic hydrazide (formylhydrazine) has been investigated by microwave spectroscopy in the 8−62 GHz spectral range, as well as by quantum chemical ab initio and density functional theory calculations made at several levels of theory. Both the ab initio and the density functional theory calculations predict that two stable forms exist for this compound, a more stable conformer having a *syn-periplanar* arrangement for the heavy atoms, and a less stable form where these atoms are *anti-periplanar*. The latter rotamer is calculated to be 10−14 kJ/mol less stable than the former, depending on the theoretical approach. The barrier height separating the two forms is calculated to be 92.2 kJ/mol at the B3LYP/cc-pVTZ level. The microwave spectra of the ground and four vibrationally excited states of the lowest torsional mode of the *syn-periplanar* conformer were assigned. The lowest torsional frequency was determined to be 77(15) cm^{-1} by relative intensity measurements. The variation of the rotational constants upon excitation of this mode and the lowest torsional frequency were fitted to a potential function of the form $V(z) = 15.6(\langle z^4 \rangle + 4.9\langle z^2 \rangle)$ cm^{-1}, indicating that the heavy atoms are effectively planar at the equilibrium conformation. The dipole moment was determined to be $\mu_a = 1.54(2)$, $\mu_b = 1.85(2)$, $\mu_c = 0$ (assumed), and $\mu_{tot} = 2.41(3)$ D [$8.04(8) \times 10^{-30}$ C m] by Stark effect measurements.

Introduction

This work is a continuation of our interest in the molecular structures and conformational properties of gaseous amides[1−11] that we have studied by electron diffraction and microwave (MW) spectroscopy as well as by quantum chemical calculations. Our studies are now extended to include the closely related hydrazides. Formic hydrazide (formylhydrazine), HC(=O)-NHNH$_2$, which is the prototype of this class of compounds, was selected for the present study.

The structural properties of this compound are likely to be a complicated compromise of several effects, e. g., electron resonance along the O=C−N chain of atoms, intramolecular hydrogen (H) bonding between the hydrogen atoms attached to the nitrogen atoms and the oxygen atom, as well as repulsion between the lone pairs of the nitrogen and oxygen atoms.

Resonance is rather important in amides giving the C−N bond some double bond character resulting in a rather high barrier to internal rotation around this bond and an effectively planar conformation of the amide group. A similar situation is expected to occur in hydrazides. Two conformers are thus expected to exist for formic hydrazide. These two forms are drawn in Figure 1.

In Conformer I, the O=C−N−N link of atoms has a *syn-periplanar* conformation; in II it is *anti-periplanar*. Resonance should roughly be the same in both of these rotamers. However, intramolecular hydrogen bonding would be different in the two forms. Conformer I is stabilized by two weak five-membered intramolecular hydrogen bonds from H7 and H8 to the bifurcated oxygen atom, O1, whereas just one weak four-membered hydrogen bond between H4 and O1 exits in II. The geometry

of the hydrogen bond should thus be less favorable in II than in I. Interaction between the lone electron pairs on O1 and on N5 are quite different in the two conformers and might influence the conformational properties.

Although the conformational composition is a central problem of this work, one interesting question remains: how coplanar are the O=C−N−N chain of atoms in the conformer(s) that it is possible to identify in the MW spectrum?

No gas-phase studies of the physical properties of formic hydrazide have to the best of our knowledge been made, but some solution studies have been reported. The dipole moment of the compound dissolved in dioxane was reported in 1958 to be 2.72 D.[12] A ^{1}H NMR study of the conformational properties in dimethyl sulfoxide (DMSO) solution appeared 14 years later.[13] The conformational properties in the DMSO solution were reinvestigated more recently by ^{1}H, ^{13}C, and ^{15}N NMR spectroscopy. A mixture of 75% of Conformer I and 25% of Conformer II was found to exist in this solution.[13,14]

Our methods of study are MW spectroscopy and high-level quantum chemical calculations. MW spectroscopy is ideal because of its high resolution and specificity. Thus, it is possible by this method to make a unique identification of low-energy conformers, to determine their dipole moments, and to derive accurate information about the torsional potential function about the C−N bond. Modern high-level quantum chemical calculations predict a number of molecular properties not available from spectroscopy rather accurately, thus complementing MW spectroscopy in an ideal manner.

There is an additional important reason for making a MW study of the title compound. Formic hydrazide is composed of a total of eight atoms of four elements (H, C, N, and O). MW spectra are the basis for the identification of nearly 100 small organic compounds found in interstellar space, many of which are composed of about 8 atoms.[15] The chemistry of this exotic

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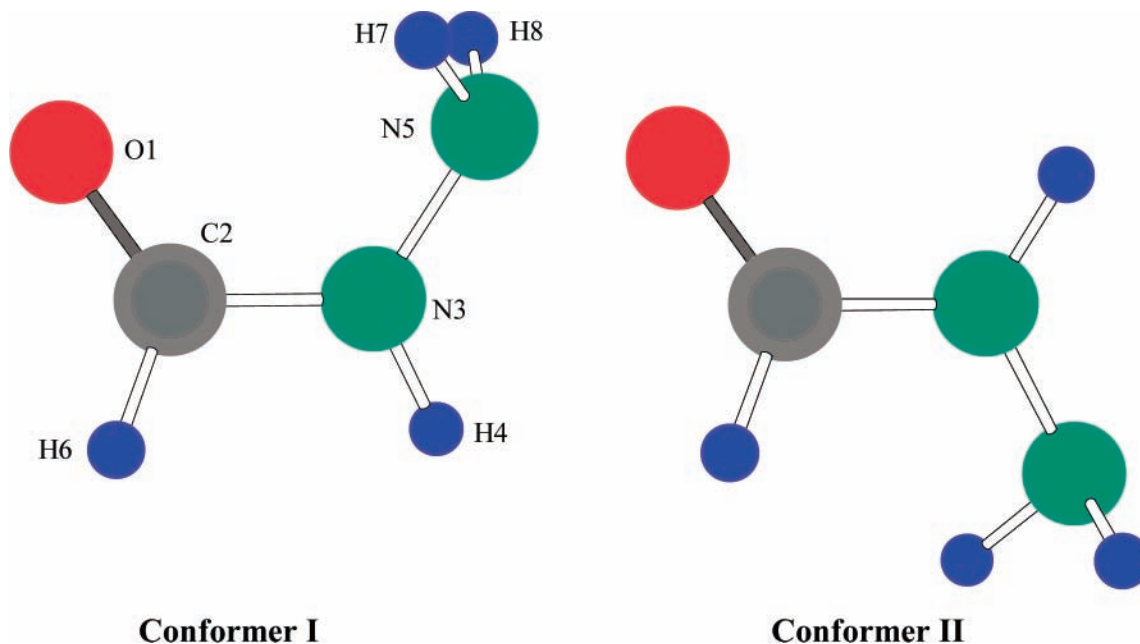
Figure 1. Two conformations of formic hydrazide. Atom numbering is indicated on Conformer I, which was assigned in this work.

environment is poorly understood, but several compounds already identified contain the same elements as formic hydrazide.[15] The MW spectrum should for this reason not be without interest for radio astronomy.

Experimental Section

Formic hydrazide was obtained from Aldrich and used as received. Ammonia was the only impurity seen. The vapor pressure is only a few Pascal at room temperature. The MW spectrum was recorded at this temperature at a pressure of roughly 2−4 Pa using the Oslo Stark spectrometer. This instrument is described briefly in ref 16. Brass cells of 2 and 3 m lengths were utilized. Radio frequency microwave double resonance (RFMWDR) experiments were carried out as described in ref 17 using the equipment mentioned in ref 18. The whole 8−62 GHz spectral region available in this laboratory was investigated in order to assign as many transitions as possible for later possible use in radio astronomy. The spectrum was recorded and stored electronically using the program written by Waal.[19] The accuracy of the spectral measurements is no better than ±0.15 MHz in this case because of quadrupole interaction of the two nitrogen nuclei of formic hydrazide. The maximum resolution was about 0.5 MHz.

Results and Discussion

Quantum Chemical Calculations. A series of quantum chemical calculations were made using the Gaussian 98 program package[20] running on the HP superdome in Oslo. Ab initio calculations at the Hartree−Fock (HF), Møller−Plesset second-order perturbation theory (MP2),[21] quadratic configuration interaction with single and double substitutions (QCISD)[22] as well as couple cluster theory using single and double substitutions including triplets (CCSD(T))[22] were made. Becke's B3LYP functional[23] were employed in the density functional theory (DFT) calculations. The 6-31G*, 6-311++G**, and Dunning's correlation consistent triple-ζ with polarized valence electrons (cc-pVTZ)[24] wave functions were employed.

Calculations were first carried out for Conformers I and II. The starting geometries were selected to be near the *syn-periplanar* or near the *anti-periplanar* conformations (see Figure

1 where the atom numbering is also given). No symmetry restrictions were imposed. Calculations of quadratic force fields were made only in some selected cases for economic reasons. Positive values of all the vibrational fundamental frequencies were found in all these cases indicating that the Conformers I and II are indeed minima on the potential energy hyper surface. The barrier height separating the two forms was calculated in one case at the B3LYP/cc-pVTZ level.

The B3LYP/cc-pVTZ geometries of the two stable conformers as well as of the transitions state are shown in Table 1 together with some other parameters of interest. Similar results obtained at several other levels of theory are given in Table 1S (Conformer I) and 2S (Conformer II) in the Supporting Information.

Some of the results in these tables warrant comments. It is seen that the B3LYP calculations predict that the heavy atoms O1−C2−N3−N5 fall in a symmetry plane both for Conformer I and II. The ab initio calculations vary on this point. A planar arrangement of these atoms is predicted in the MP2(full)/cc-pVTZ calculations, whereas the remaining ab initio calculations yield mixed results with deviation from symmetry up to about 10°. cc-pVTZ is the largest basis set employed. It is quite likely that the nonplanarity predicted for this chain of atoms would have disappeared if basis sets larger than the ones (6-31G* or 6-311++G**) used in the QCISD and CCSD(T) had been employed.

It is further noted that the bond distances and angles differ little in the various theoretical approaches. The ab initio dipole moments tend to be a bit larger than their DFT counterparts. Only the three lowest vibrational fundamentals are listed in these tables. Interestingly, the lowest harmonic frequency, ν_1, assumed to be the torsion around the C2−N3 bond varies quite a lot form 33 (Table 1) to 164 cm^{-1} (Table 1S) in the cases where it has been calculated.

The energy difference between the two forms is predicted to be between 10.0 (B3LYP/pVTZ) and 13.7 kJ/mol (QCISD/6-31G*) with Conformer I as the preferred form, depending on the method used (Tables 1S and 2S). The B3LYP/pVTZ barrier height is 92.2 kJ/mol above the energy of Conformer I. A barrier as high as this indicates that electron resonance is rather

Microwave Spectrum of Formic Hydrazide

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TABLE 1: Selected B3LYP/cc-pVTZ Parameters[a] of Conformers I, II, and of the Transition State

	Conformer I	Conformer II	transition state
	Bond Length/Å		
C1=O2	1.2118	1.2096	1.1941
C2−N3	1.3566	1.3607	1.4396
N3−H4	1.0055	1.0080	1.0144
N3−N5	1.4047	1.4009	1.4421
C2−H6	1.1047	1.1067	1.1121
N5−H7	1.0154	1.0122	1.0124
N5−H8	1.0155	1.0122	1.0211
	Angle/deg		
O1−C2−N3	124.79	124.78	123.58
O1−C2−H6	123.60	123.60	121.23
N3−C2−H6	111.61	111.62	115.09
C2−N3−N5	123.51	125.25	109.33
C2−N3−H4	120.68	118.68	110.46
H4−N3−N5	115.81	116.07	106.48
N3−N5−H7	108.07	110.75	106.84
N3−N5−H8	108.06	110.75	111.69
H7−N5−H8	106.49	109.48	107.86
	Dihedral Angle[b]/deg		
O1−C2−N3−H4	179.80	0.00	−133.11
O1−C2−N3−N5	0.12	180.00	110.03
H6−C2−N3−H4	−0.20	180.00	50.50
C2−N3−N5−H7	−57.51	-60.00	-80.03
C2−N3−N5−H8	56.81	60.83	37.69
	Rotational Constants/MHz		
A	20550.5	48844.6	26572.2
B	6418.5	4471.6	5058.8
C	5019.8	4190.1	4817.2
Δ^c/u Å^2	2.65	2.75	14.01
	Dipole Moment/D		
μ_a	1.60	3.32	1.51
μ_b	1.93	1.15	0.19
μ_c	0.0	0.0	2.32
μ_{tot}	2.51	3.51	2.77
	Vibrational Frequencies[d]/cm^{-1}		
ν_1	33	122	
ν_2	278	327	
ν_3	307	355	
	Energy Difference[d]/kJ mol^{-1}		
	0.0	10.0	92.2

[a] Atom numbering is given in Figure 1. [b] Measured from *synperiplanar* = 0°. [c] $\Delta = I_a + I_b - I_c$ (moments of inertia). Conversion factor: 505379.05 MHz u Å^2. [d] Of the "stable" conformers. [e] Total energy of Conformer I is −59 537.5 kJ/mol.

important in this case. It is noted that the O1−C2−N3−N5 dihedral angle is 110° in the transition state, and that the N3 atom is pyramidal in this conformation, presumably because resonance is lost here.

Microwave Spectrum and Assignment of Conformer I. The B3LYP/pVTZ rotational constants and the *a*- and *b*-axis components of the dipole moments shown in Table 1 were used to predict the MW spectrum. Survey spectra revealed a comparatively strong and rich spectrum, just as predicted. The large majority of lines would be of the *b*-type variety. Low-*J* key spectral lines of the *a*- and *b*-type were first searched for and soon found. Their assignments were in many cases confirmed by their more or less resolved Stark effects and fit to Watson's Hamiltonian (*A* reduction *I*^{r} representation).[25] The frequencies of medium-*J* lines were predicted next and readily assigned. The assignment procedure was gradually extended to high-*J* *b*-type transitions (up to *J* = 52). Transitions including even higher values of *J* were searched for but were not assigned, presumably because of insufficient intensity owing to an unfavorable Boltzmann factor in the intensity expression.

c-type transitions were also looked for. Their hypothetical frequencies should be very accurately predicted from the material now available. However, none could be assigned with certainty, presumably because of insufficient, if not zero intensities. A dipole moment component along the *c* inertial axis larger than 0.3 D is thus ruled out.

Formic hydrazide has two nitrogen nuclei. Quadrupole coupling occurs for the ^{14}N isotope, which makes up 99.6% of the total. Each line therefore has a complicated hyperfine structure, which is completely unresolved in most cases, especially for the *a*-type lines and intermediate and high-*J* *b*-type transitions. However, several low- and medium-*J* *b*-type transitions were broad or apparently split by up to about 1 MHz in some cases. Unfortunately, the split lines did not furnish sufficient information to determine the quadrupole coupling constants of the two ^{14}N nuclei.

Accurate spectroscopic constants are important in order to predict transitions that have not been assigned in this work, but may be of radio astronomical interest. Lines whose frequencies were suspected of being perturbed significantly by quadrupole coupling effects, were therefore omitted from the final fit (278 transitions; Table 3S) used to determine the spectroscopic constants displayed in Table 2.

The experimental rotational constants in this table agree with the B3LYP/cc-pVTZ (Table 1) to within better than about 2%. A difference of this order of magnitude is to be expected because the experimental and theoretical rotational constants are defined differently.

The harmonic force field obtained in the MP2(full)/cc-pVTZ calculations were used to predict the quartic centrifugal distortion constants as $\Delta_J = 6.44$, $\Delta_{JK} = -22.5$, $\Delta_K = 82.7$, $\delta_J = 1.96$, and $\delta_K = 0.835$ kHz, respectively, using the ASYM40 program.[26,27] It is seen that these values agree reasonably well with the experimental ones in Table 2.

Vibrationally Excited States. The ground-state transitions were accompanied by several lines that have very similar Stark patterns but are considerably weaker than the ground-state transitions. The lowest vibrational mode was predicted above to be the C2−N3 torsional fundamental. Four excited states assumed to be successively excited states of this mode were ultimately assigned as seen in Table 2. Their spectra are found in the Supporting Information; Tables 4S−7S.

The frequency of the first excited state was determined by relative intensity measurements following the recommendations of ref 28. A value of 77(15) cm^{-1} was found.

The theoretical force field calculations predict that the two lowest bending modes (ν_2 and ν_3) fall in the 270−335 cm^{-1} range (Tables 1 and 1S). The first excited states of each of these two modes should have sufficient intensity to be assigned. The intensities, Stark effects, and double resonance patterns of several candidates have been investigated, and it is quite likely that some of them have indeed been identified. However, it was not possible to fit them to Watson's Hamiltonian to the desired precision (about 0.15 MHz). It is possible that these two states are perturbed by Coriolis interaction. Further details are not given here because of the tentative nature of these observations.

Searches for Conformers II. About 1000 transitions were assigned as described above. This includes all the strongest lines found in the MW spectrum as well as the majority of the lines of intermediate intensities. Many weak transitions were also identified. Extensive searches were made among the unassigned transitions in an attempt to assign Conformer II. This rotamer is predicted to be 10−14 kJ/mol less stable than I in the theoretical calculations above (Tables 1 and 2S). These numbers

TABLE 2: Spectroscopic Constants[a,b] of the Ground and Excited States of the Torsion around the C2−N3 Bond of Formic Hydrazide

vib. state:	ground	first ex.	second ex.	third ex.	fourth ex.
A/MHz	20130.567(11)	20067.811(10)	20053.957(12)	20074.060(17)	20091.597(37)
B/MHz	6544.6687(30)	6580.8443(32)	6596.4878(35)	6595.1655(48)	6595.1258(93)
C/MHz	5064.9140(39)	5079.8564(33)	5085.0561(48)	5082.9984(58)	5081.5701(96)
Δ_J/kHz	5.934(37)	6.018(19)	5.637(35)	5.921(17)	5.98(14)
Δ_{JK}/kHz	−22.67(24)	−28.00(15)	−29.65(26)	−27.27(15)	−31.08(80)
Δ_K/kHz	78.972(61)	83.339(47)	82.453(66)	84.221(73)	83.4(41)
δ_J/kHz	2.0813(87)	1.9917(60)	2.0075(65)	1.8126(81)	1.933(35)
δ_K/kHz	−1.11(25)	6.14(19)	5.00(28)	5.86(31)	8.3(11)[c]
Φ_J/Hz	−0.879(76)	−1.184(50)	−0.974(77)	−0.0330(28)[c]	
Φ_{JK}/Hz	−4.9(12)	−11.69(70)	−15.2(12)		
Φ_{KJ}/Hz	−20.4(11)	−20.9(10)	−14.8(12)[c]		
Φ_K/Hz	8.04(49)	4.10(61)			
ϕ_J/Hz	0.151(11)	0.120(14)			
ϕ_{JK}/Hz	−9.74(30)	−7.74(58)			
ϕ_K/Hz	32.0(12)	21.2(25)			
Δ^d/u Å^2	2.544636(48)	2.492162(42)	2.429169(65)	2.379061(85)	2.32960(25)
no of trans.	278	251	191	92	31
max J^e	52	48	42	33	14
rms/MHz	0.124	0.124	0.130	0.166	0.152

[a] A reduction I^r representation.[25] [b] Uncertainties represent one standard deviation. [c] Further sextic constants preset at zero in the least-squares fit. [d] $\Delta = I_a + I_b - I_c$ (principal moments of inertia). Conversion factor 505379.05 MHz u Å^2. [e] Maximum value of the J quantum number.

TABLE 3: Comparison of Calculated and Observed Rotational Constants (MHz)[a,b]

Vib. state	A_v calc.[c]	A_v calc.-obs.	B_v calc.[d]	B_v calc.-obs.	C_v calc.[e]	C_v calc.-obs.
0	20129.98	−0.59	6544.80	0.14	5065.02	0.11
1	20069.83	2.02	6580.47	−0.39	5079.53	−0.33
2	20052.56	−1.40	6596.56	0.07	5085.23	0.17
3	20073.29	−0.77	6595.66	0.60	5083.23	0.23
4	20092.51	0.91	6594.81	−0.32	5081.37	−0.20

[a] Using the potential function $V(z) = 15.6(\langle z^4 \rangle + 4.9\langle z^2 \rangle)$ cm^{-1}. [b] Uncertainties represent one standard deviation. [c] $A_v = 20173.9(31) - 279.4(95)\langle z^2 \rangle + 105.4(39)\langle z^4 \rangle$. [d] $B_v = 6520.62(83) + 145.8(25)\langle z^2 \rangle - 44.8(10)\langle z^4 \rangle$. [e] $C_v = 5054.92(56) + 62.2(17)\langle z^2 \rangle - 20.77(69)\langle z^4 \rangle$.

are assumed to be accurate to within ±6 kJ/mol. Conformer II was therefore expected be present in a very small proportion. Extensive searches including the use of the powerful and sensitive RFMWDR technique[17] were made in a futile attempt to find it. Intensity considerations of unassigned transitions lead us to conclude that Conformer II is likely to be at least 4 kJ/mol less stable than Conformer I. This estimate is considered to be conservative and in agreement with the theoretical predictions.

The conformational composition in the gas is thus very different from the composition in DMSO solution (25% of Conformer II).[13,14] It is possible that this can at least partly be ascribed to the fact that Conformer II is predicted to be considerably more polar (higher dipole moment) than Conformer I (Table 1) and would be stabilized in a polar solvent such as DMSO.

Planarity of the O=C−N−N Chain of Atoms. The quantum chemical calculations above do not unequivocally indicate that O1−C2−N3−N5 link atoms form a plane, and that the molecule thus has C_s symmetry. However, there are several pieces of evidence that should be considered in an attempt to settle this question.

In molecules possessing a plane of symmetry, the principal moments of inertia (I_a, I_b, and I_c) are related to the out-of-plane atoms by $\Delta = I_a + I_b - I_c = 2\Sigma m_i c_i^2$, where m_i is the mass of the ith atom and c_i is the corresponding out-of-plane coordinate, respectively. It is seen in Table 2 that $\Delta = 2.54$ u Å^2 for the ground vibrational state. This value is nearly the same as 2.59 u Å^2 found for H_2NOH.[29] A value of 2.66 u Å^2 is calculated in

the case of CH_3NH_2 when the contributions from the H atoms of the methyl group are subtracted.[30] These compounds are known to have a symmetry plane (C_s symmetry) and two out-of-plane H atoms attached to N.

The second information can be obtained from the lack of c-type lines in the spectrum as noted above, and the dipole moment (next paragraph). The third piece of evidence is obtained from the variation of the rotational constants upon excitation of the C2−N3 torsional mode.

The changes of the rotational constants upon successive excitation of a typical harmonic torsional mode are nearly constant. Inspection of the rotational constants in Table 2 shows that this is not the case for formic hydrazide. Obviously a more complicated potential function than harmonic governs C2−N3 torsion in this case. Following Gwinn and co-workers,[31] a reduced potential function of the form

$$V(z) = A(\langle z^4 \rangle + B\langle z^2 \rangle) \tag{1}$$

can be employed to describe the torsion. A and B (not to be confused with the rotational constants) are parameters to be fitted. A may have the dimension cm^{-1}. B and z are dimensionless. The molecule will have C_s symmetry as its equilibrium conformation provided B is positive. A double minimum potential with a hump at the planar form will exist if B is negative, resulting in C_1 symmetry for the equilibrium conformation of the compound.

It is possible to expand the rotational constants in a power series involving the expectation value of the dimensionless coordinate z

$$\beta_v = \beta_0 + \beta_2\langle z^2 \rangle_v + \beta_4\langle z^4 \rangle_v \tag{2}$$

where β_v is the A_v, B_v, or C_v rotational constants in the vth state of the torsional mode. β_0, β_2, and β_4 are empirical parameters adjusted to give the best fit. The values of $\langle z^2 \rangle_v$ and $\langle z^4 \rangle_v$ in eq 1 depend only on the value of B.[31]

The computer program described in ref 32 based on these ideas was utilized. The rotational constants of successively excited states of the torsion were fitted to eq 2 using the least-squares method for a range of values of B. It was found that the value $B = 4.9$ yielded the best overall fit. All rotational
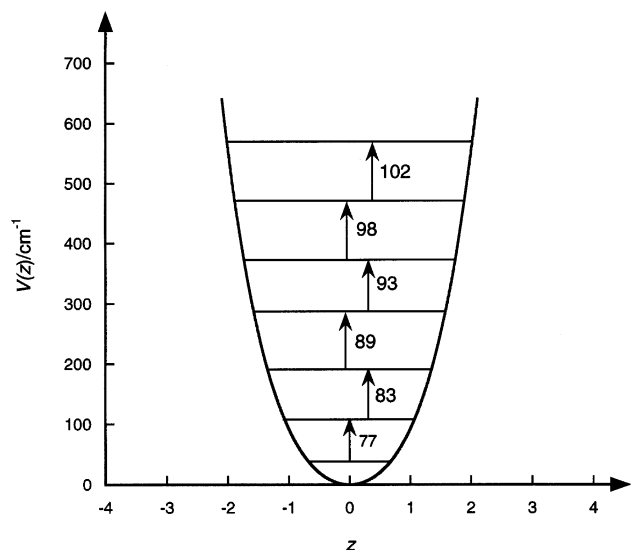
Figure 2. Potential function $V(z) = 15.6(\langle z^4 \rangle + 4.9\langle z^2 \rangle)$ cm^{-1} describing the torsional vibration around the C–N bond. The first eigenstates are indicated.

constants were given the same weight in the fit. The results of the fitting procedure are given in Table 3.

It is seen in this table that a fit with a *positive B* is able to reproduce the rotational constants fairly well. This is another indication that the equilibrium conformation of the O1–C2–N3–N5 link of atoms is indeed effectively planar.

Finally, the *A* constant of eq 1 was adjusted to reproduce the observation that the first excited state is 77 cm^{-1} higher in energy than the ground state. A value of $A = 15.6$ cm^{-1} was found. The potential function is thus

$$V(z) = 15.6(\langle z^4 \rangle + 4.9\langle z^2 \rangle) \text{ cm}^{-1} \qquad (3)$$

The function is drawn in Figure 2. The first few eigenstates calculated from this potential function are indicated on this figure.

Dipole Moment of Conformer I. The Stark shifts are functions of the components of the dipole moment along the principal inertial axes. The *c*-axis component would be nonzero if formic hydrazide were nonplanar. Transitions whose Stark effects are strongly dependent on the *c*-component of the dipole moment were looked for in order to determine this component accurately. Unfortunately, none that could be used had the desired strong dependence of this component.

The dipole moment was determined in a least-squares fit using the second-order Stark coefficients shown in Table 4. The cell was calibrated using OCS whose dipole moment was taken to be 0.71521(20) D.[33] The weight of each Stark coefficient was taken to be the inverse square of its standard deviation shown in Table 4. A small nonzero value with a large standard deviation was initially found for μ_c when all three dipole moment components were allowed to vary in the fit. It is thus not possible to decide conclusively from the material in Table 4 that this component is indeed different from zero, or if this component is slightly different from zero. However, μ_c was preset to zero in the final fit with the results shown in Table 4.

The experimental values of the components being $\mu_a = 1.54(2)$, $\mu_b = 1.85(2)$, and $\mu_c = 0.0$ (assumed), and $\mu_{tot} = 2.41(3)$ D [$8.04(8) \times 10^{-30}$ C m] (Table 4) agree very well with the B3LYP/cc-pVTZ values $\mu_a = 1.60$, $\mu_b = 1.93$, and $\mu_c = 0$ D (Table 1). The agreement with the ab initio calculations

TABLE 4: Second-Order Stark Coefficient[a] and Dipole Moment[a,b] of Formic Hydrazide

		$\Delta\nu$ E^{-2}/10^{-6} MHz V^{-2} cm^2	
transition		obs.	calc.
$6_{2,4} \leftarrow 6_{1,5}$	$|M| = 6$	13.6	13.0
	$|M| = 5$	10.5	10.0
	$|M| = 4$	7.44	7.54
	$|M| = 3$	5.57	5.64
	$|M| = 2$	4.32	4.31
$5_{2,3} \leftarrow 5_{1,4}$	$|M| = 5$	20.1	18.8
$3_{0,3} \leftarrow 2_{0,2}$	$|M| = 1$	1.00	1.03
$3_{1,2} \leftarrow 2_{1,2}$	$|M| = 1$	3.30	3.53
	$|M| = 0$	−1.24	−1.25

[a] Uncertainties represent one standard deviation. [b] $\mu_a = 1.54(2)$, $\mu_b = 1.85(2)$, and $\mu_c = 0.0$ (assumed) and $\mu_{tot} = 2.41$ D [$8.04(8) \times 10^{-30}$ C m]; 1 D = 3.33564 × 10^{-30} C m.

(Table 1S) is somewhat poorer. The gas-phase value is not very different from value obtained in dioxane solution, 2.72 D.[12]

Conclusions

The preferred form of formic hydrazide, Conformer I, has C_s symmetry with the heavy atoms effectively in one plane in a *syn-periplanar* arrangement. The torsional potential around the C2–N3 bond is not purely harmonic. A potential function consisting of quadratic and quartic terms reproduces the rotational constants satisfactorily and in addition indicates that the molecule indeed has C_s symmetry.

Extensive searches for the *anti-periplanar* Conformer II were futile. This rotamer is assumed to be considerably less stable (over 4 kJ/mol) than Conformer I.

It is interesting to compare the findings for formic hydrazide with those of the isoelectronic compounds methyl formate (HCO$_2$CH$_3$),[34] methyl nitrite (CH$_3$ONO),[34] and *N*-methylformamide (CH$_3$NHCHO).[35] Each of these three compounds prefers a *syn-periplanar* conformation similar to that of Conformer I.[34,35] The energy differences between the *anti-* and the *syn-periplanar* forms are about 20, 3, and 5 kJ/mol, respectively.[34,35] None of them are stabilized by intramolecular hydrogen bonding.

The general tendency to prefer a *syn-periplanar* conformer for this series of isoelectronic compounds is augmented by internal hydrogen bonding in Conformer I of formic hydrazide. The two hydrogen bonds of the bifurcated O atom are definitely not strong since the nonbonded distance between the O atom and the two H atoms of the amino group is calculated to be about 2.78 Å, a bit longer than the sum of the van der Waals radii of O (1.40 Å) and of H (1.20 Å) totaling 2.60 Å.[36] The high-level ab initio and DFT calculations indicating that Conformer II is less stable than Conformer I by 10−14 kJ/mol higher thus seems reasonable in light of the results obtained for the three other isoelectronic species.

Supporting Information Available: Tables 1S−2S contain further quantum chemistry results and Tables 3S−7S contain the assigned MW spectra used to obtain the spectroscopic constants given in Table 2. This material is available free of charge via the Internet at http://pubs.acs.org.

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