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Conformational and Structural Analysis of Methyl Hydrazinocarboxylate by Microwave Spectroscopy and ab Initio Geometry Refinements

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Abstract: The microwave spectrum of methyl hydrazinocarboxylate has been studied in the frequency range 26–40 GHz. The assigned rotational spectrum is consistent with various conformers of the system, but most likely it corresponds to a structure with a symmetry plane and with a bifurcated internal hydrogen bond between the amino hydrogens of the outer nitrogen and the carbonyl oxygen. The H—N—C═O arrangement involving the inner nitrogen is planar like in a peptide group. From several A–E doublet lines measured in the ground state, the barrier hindering the rotation of the methyl group has been determined as $V_3 = 980 \pm 30$ cal/mol. The spectroscopic assignment was guided by ab initio gradient geometry refinements on the 4-21G level. The calculations made it possible to assign the spectrum of the N_2-d_3 isotopic species and allow the inference that a second conformer, so far undetected, is also significantly populated in the vapors of this compound.

Few molecules with a possible bifurcated hydrogen bond between the hydrogen atoms of an amino group and the oxygen atom of a carbonyl group have been investigated in the gas phase. One of them is glycine, for which this kind of interaction characterizes the most abundant species.[1-4] Ab initio calculations on glycine were useful in prompting the assignment of the most abundant conformer,[4] whose dipole moment (and therefore the intensity of the microwave transitions) was smaller than that of the second conformer. The methyl ester of glycine also was investigated by microwave spectroscopy[5] and electron diffraction,[6] and only the conformer with the internal bifurcated hydrogen bond was observed in good agreement with ab initio gradient optimizations.[7,8]

Methyl hydrazinocarboxylate (MHC) has, with respect to the methyl ester of glycine, an N–H group replacing a CH_2 group. Its most plausible conformations are shown in Figure 1. Replacing a methylene group by an imino group has interesting structural consequences. For example, it can be reasonably expected that MHC does not possess a plane of symmetry (except in the enolic form), and as the C–N bond is shorter than the C–C bond, the molecular situation is markedly different from that of the methyl ester of glycine. In spite of these considerations our analysis forced us, as described below, to select a most likely structure for MHC which shares with the methyl ester of glycine the common feature of a molecular symmetry plane.

Experimental Section

MHC was supplied by Aldrich Chemical Co. It is a solid (white crystals) with a vapor pressure of about 20 μtorr at 15 °C, and for this reason almost all the experiments were carried out at this temperature.

In order to take away an impurity which was originating an unknown spectrum, but a stronger one than that of MHC, it was necessary to completely melt the compound while pumping over, until its vapors were spectroscopically pure.

The spectra were obtained with a computer-controlled spectrometer partially based on an 8400 C Hewlett-Packard instrument.

A number of radio-frequency-microwave double-resonance measurements of the type described by Wodarczyk and Wilson[9] were made during the assignment of the spectrum.

Results

Microwave Spectrum of the Normal Isotopic Species. Model calculations with structural parameters from ref 5 and 10 (formamide) gave roughly the same set of rotational constants for conformers I–VI of Figure 1, with the Ray asymmetry parameter κ in the range −0.90 to −0.92. For the corresponding conformers with the methyl group anti to the carbonyl oxygen, values of $\kappa = -0.56$ to −0.58 were calculated.

With respect to the rotational spectrum the most relevant differences between the proposed conformers are (i) conformer I must have an inertial defect corresponding to five hydrogen atoms out of the plane of the heavy atoms, whereas in conformers II–VI only four hydrogen atoms are out of plane; (ii) conformers II and IV should possess a large μ_c dipole moment component, while for conformers I and VI μ_c is zero by symmetry and for conformers III and V it is close to zero; (iii) conformer I could show a doubling of the rotational lines due to imino hydrogen tunneling between two equivalent potential energy minima. Conformers II–V, too, have two equivalent minima, but with higher barriers to inversion, as two hydrogens have to move in a concerted manner.

The spectrum of a conformer with rotational constants similar to those of I–V was possible to assign. By using the microwave radio-frequency technique,[9] the K doublets $9_4 \leftarrow 8_4$ and $9_3 \leftarrow 8_3$ were assigned first. Then a number of ^aR, ^bR, and ^bQ transitions were measured with the conventional Stark modulation technique.

Several lines were split into doublets due to methyl group internal rotation (see next section). No effect of the nuclear quadrupole moments of the two ^{14}N nuclei was observed. A careful search for μ_c-type transitions was performed in wide ranges at lower and higher frequencies with respect to precise calculated values but without success.

The A-component line frequencies are reported in Table I. They have been fitted with the Watson semirigid Hamiltonian.[11] The obtained molecular parameters are shown in Table II.

The weakness of the spectrum did not allow a straightforward analysis of the rotational spectra of the vibrational satellites. For

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(1) Suenram, R. D.; Lovas, F. J. *J. Am. Chem. Soc.* **1980**, *102*, 7180–7184.

(2) Brown, R. D.; Godfrey, P. D.; Storey, J. W. V.; Bassez, M. P. *J. Chem. Soc., Chem. Commun.* **1978**, 547–548.

(3) Suenram, R. D.; Lovas, F. J. *J. Mol. Spectrosc.* **1978**, *72*, 372–382.

(4) Schäfer, L.; Sellers, H. L.; Lovas, F. J.; Suenram, R. D. *J Am. Chem. Soc.* **1980**, *102*, 6566–6568.

(5) Caminati, W.; Cervellati, R. *J. Am. Chem. Soc.* **1982**, *104*, 4748–4752.

(6) Klimkowski, V. J.; Ewbank, J. D.; Van Alsenoy, C.; Scarsdale, J. N.; Schafer, L. *J. Am. Chem. Soc.* **1982**, *104*, 1476–1480.

(7) Klimkowski, V. J.; Scarsdale, J. N.; Schäfer, L. *J. Comp. Chem.* **1983**, *4*, 494–498.

(8) Klimkowski, V. J.; Schäfer, L.; van den Enden, L.; Van Alsenoy, C.; Caminati, W. *J. Mol. Struct.* **1983**, *105*, 169–174.

(9) Wodarczyk, F. J.; Wilson, E. B. *J. Mol. Spectrosc.* **1971**, *37*, 445–463.

(10) Hirota, E.; Sugisaki, R.; Nielsen, C. J.; Sörensen, G. O. *J. Mol. Spectrosc.* **1974**, *49*, 251–267.

(11) Watson, J. K. G. *J. Chem. Phys.* **1967**, *46*, 1935–1949.

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Table I. "A" Component Line Frequencies of the Measured Transitions of MHC

transition $J_{K_{-1}',K_1'}' \leftarrow J_{K_{-1},K_1}$	obsd, MHz	diff,[a] MHz
$7_{0,7} \leftarrow 6_{0,6}$	28 672.50	0.02
$7_{1,7} \leftarrow 6_{1,6}$	27 887.29	0.00
$7_{1,6} \leftarrow 6_{1,5}$	30 468.01	−0.02
$7_{2,6} \leftarrow 6_{2,5}$	29 247.03	0.03
$7_{2,5} \leftarrow 6_{2,4}$	29 920.67	−0.09
$8_{0,8} \leftarrow 7_{0,7}$	32 567.90	−0.08
$8_{1,8} \leftarrow 7_{1,7}$	31 820.75	0.00
$8_{1,7} \leftarrow 7_{1,6}$	34 741.09	−0.02
$8_{2,7} \leftarrow 7_{2,6}$	33 382.60	−0.04
$8_{2,6} \leftarrow 7_{2,5}$	34 352.27	0.06
$8_{3,6} \leftarrow 7_{3,5}$	33 660.09	0.06
$8_{3,5} \rightarrow 7_{3,4}$	33 728.40	−0.02
$8_{5,4} \leftarrow 7_{5,3}$	33 601.02	−0.16
$8_{6,3} \leftarrow 7_{6,2}$	33 586.50	0.04
$8_{3,5} \leftarrow 8_{2,6}$	39 036.34	−0.09
$8_{1,8} \leftarrow 7_{0,7}$	35 955.52	0.09
$8_{0,8} \leftarrow 7_{1,7}$	28 433.43	0.13
$9_{0,9} \leftarrow 8_{0,8}$	36 416.20	0.06
$9_{1,9} \leftarrow 8_{1,8}$	35 738.56	−0.09
$9_{1,8} \leftarrow 8_{1,7}$	38 976.85	−0.07
$9_{2,8} \leftarrow 8_{2,7}$	37 501.66	0.03
$9_{2,7} \leftarrow 8_{2,6}$	38 813.00	−0.08
$9_{3,7} \leftarrow 8_{3,6}$	37 886.28	0.18
$9_{3,6} \leftarrow 8_{3,5}$	38 009.98	−0.11
$9_{4,6} \leftarrow 8_{4,5}$	37 852.63	0.04
$9_{4,5} \leftarrow 8_{4,4}$	37 856.37	−0.09
$9_{5,5} \leftarrow 8_{5,4}$	37 814.86	−0.04
$9_{6,3} \leftarrow 8_{6,2}$	37 794.09	0.05
$9_{7,3} \leftarrow 8_{7,2}$	37 781.54	0.07
$9_{3,6} \leftarrow 9_{2,7}$	38 233.54	0.10
$9_{1,9} \leftarrow 8_{0,8}$	39 126.15	0.05
$9_{0,9} \leftarrow 8_{1,8}$	33 028.68	−0.01
$10_{2,9} \leftarrow 10_{1,10}$	35 092.05	−0.11
$10_{3,7} \leftarrow 10_{2,8}$	37 267.45	0.05
$10_{0,10} \leftarrow 9_{1,9}$	37 519.43	0.05
$11_{1,10} \leftarrow 10_{2,9}$	32 302.83	−0.04
$12_{3,9} \leftarrow 12_{2,10}$	35 020.03	0.01
$13_{3,10} \leftarrow 13_{2,11}$	33 870.87	−0.04
$14_{3,11} \leftarrow 14_{2,12}$	32 812.16	−0.04
$15_{2,13} \leftarrow 15_{1,14}$	26 863.54	0.17
$15_{3,12} \leftarrow 15_{2,13}$	31 929.12	0.03
$16_{2,14} \leftarrow 16_{1,15}$	29 455.51	0.06
$16_{3,13} \leftarrow 16_{2,14}$	31 303.07	0.02
$17_{3,14} \leftarrow 17_{2,15}$	31 007.12	−0.01
$18_{2,16} \leftarrow 18_{1,17}$	35 924.44	−0.02
$18_{3,15} \leftarrow 18_{2,16}$	31 103.40	−0.02
$19_{3,16} \leftarrow 19_{2,17}$	31 642.42	0.01
$20_{3,17} \leftarrow 20_{2,18}$	32 663.25	−0.03
$21_{3,18} \leftarrow 21_{2,19}$	34 193.71	0.03
$22_{3,19} \leftarrow 22_{2,20}$	36 248.21	−0.11
$23_{3,20} \leftarrow 23_{2,21}$	38 826.36	0.04

[a] Diff = obsd − calcd.

Table II. Molecular Constants for Methyl Hydrazinocarboxylate Obtained from the Data of Table I

A, MHz	10 242.62 (3)	Δ_J, kHz	0.15 (3)
B, MHz	2 283.022 (5)	Δ_{JK}, kHz	2.04 (6)
C, MHz	1 909.410 (5)	Δ_K, kHz	11 (3)
Δ_c, uÅ^2	−6.0268 (2)	δ_J, kHz	0.030 (2)
		δ_{JK}, kHz	0.08 (14)

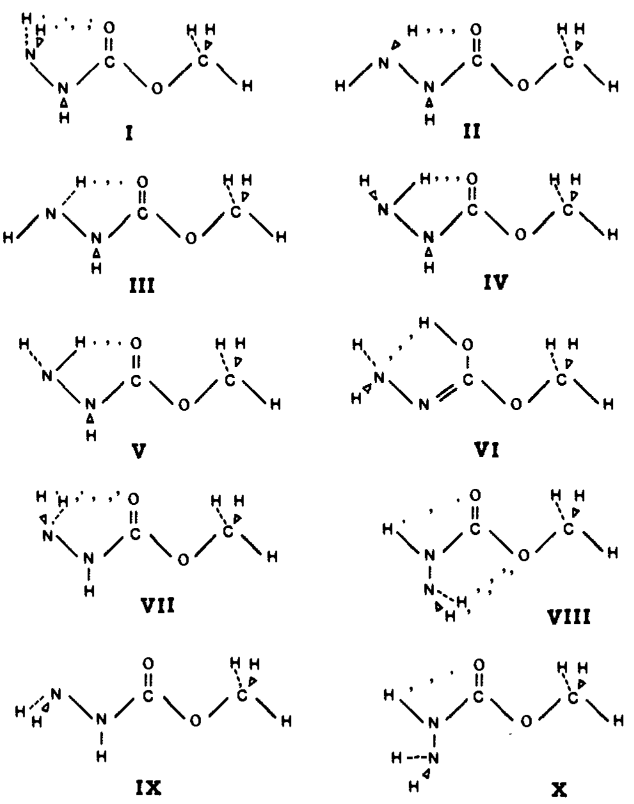

Figure 1. Conformations I-X of methyl hydrazinocarboxylate.

Table III. Measured E–A splittings for MHC

transition $J_{K_{-1},K_1} \leftarrow J_{K_{-1},K_1}$	$\nu_E - \nu_A$, MHz obsd	$\nu_E - \nu_A$, MHz diff[a]
$7_{1,6} \leftarrow 6_{1,5}$	−0.73	0.10
$8_{2,6} \leftarrow 7_{2,5}$	−3.18	0.06
$8_{2,7} \leftarrow 7_{2,6}$	2.50	0.05
$8_{1,7} \leftarrow 7_{1,6}$	−0.86	0.09
$8_{0,8} \leftarrow 7_{0,7}$	−0.64	0.14
$8_{0,8} \leftarrow 7_{1,7}$	4.00	−0.07
$9_{2,7} \leftarrow 8_{2,6}$	−1.71	0.23
$9_{2,8} \leftarrow 8_{2,7}$	1.02	0.01
$9_{1,8} \leftarrow 8_{1,7}$	−0.86	0.24
$9_{0,9} \leftarrow 8_{0,8}$	−0.86	0.02
$9_{1,9} \leftarrow 8_{0,8}$	−4.48	0.17
$9_{0,9} \leftarrow 8_{1,8}$	3.57	0.13
$10_{0,10} \leftarrow 9_{1,9}$	3.00	0.18
$15_{3,12} \leftarrow 15_{2,13}$	−20.87	0.06
$15_{2,13} \leftarrow 15_{1,14}$	−8.81	−0.23
$16_{3,13} \leftarrow 16_{2,14}$	−20.65	0.18
$16_{2,14} \leftarrow 16_{1,15}$	−8.06	−0.24
$17_{3,14} \leftarrow 17_{2,15}$	−19.90	0.03
$18_{3,15} \leftarrow 18_{2,16}$	−18.63	−0.15
$19_{3,16} \leftarrow 19_{2,17}$	−16.79	−0.11
$20_{3,17} \leftarrow 20_{2,18}$	−14.72	−0.05
$\sigma = 0.15$		

[a] Diff = obsd. − calcd.

Table IV. Internal Rotation Parameters for Methyl Hydrazinocarboxylate

$s^a = 27.54$ (14)	I_α, uÅ^2 = 3.2^b
θ, deg = 24.9 (4)	Δ_0,^{c} MHz = 773 (20)
γ, deg = 0^b	V_3, cal·mol^{-1} = 980 (30)

[a] Reduced barrier. [b] Fixed. [c] $\Delta_0 = E_E - E_A$ (vibrational energy difference between the two sublevels in the ground state).

the strongest one, the $9_4 \leftarrow 8_4$ doublet has been observed (at higher frequencies with respect to the ground state). From relative intensity measurements,[12] its vibrational energy with respect to the ground state has been estimated to be 100 ± 50 cm^{-1}. By analogy with the methyl ester of glycine[5] and glycine itself,[1] it has been assigned to the O=C—N—N torsion.

Methyl Group Internal Rotation. Several A–E splittings were measured and fitted to the internal rotation parameters underlying the Herschbach PAM model.[13] They are reported in Table III

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(12) Esbitt, A. S.; Wilson, E. B., Jr. *Rev. Sci. Instrum.* **1963**, *34*, 901–907.

(13) Herschbach, D. R. *J. Chem. Phys.* **1959**, *31*, 91–108.

Table V. Methyl Barrier to Internal Rotation for Substituted Methyl Formates

compd	formula	V_3, cal·mol^{-1}	ref.
methyl formate	$HCOOCH_3$	1190 ± 40	14
methyl fluoroformate	$FCOOCH_3$	1077 ± 30	15
methyl cyanoformate	$NCCOOCH_3$	1172 ± 30	15
methyl acetate	CH_3COOCH_3	1215 ± 30	15
cis-methyl acrylate	$CH_2{=}CHCOOCH_3$	1220 ± 30	15
methyl propiolate	$HC{\equiv}CCOOCH_3$	1266 ± 30	15
methyl chloroformate	$ClCOOCH_3$	1250 ± 30	16
methyl glycolate	$HOCH_2COOCH_3$	1131 ± 30	17
glycine methyl ester	$H_2NCH_2COOCH_3$	1177 ± 30	5
methyl hydrazinocarboxylate	$H_2NNHCOOCH_3$	980 ± 30	this work

Table VI. 4-21G Optimized Geometries (Bond Distances in Å, Angles in deg) for Conformations VII–X of Methyl Hydrazinocarboxylate[a]

	VII	VIII	IX	X
		Bond Distances		
2–1	1.4211	1.4237	1.4066	1.4086
7–1	1.0026	1.0021	0.9980	0.9984
3–2	1.3489	1.3514	1.3556	1.3571
9–2	0.9908	0.9914	0.9944	0.9955
4–3	1.2145	1.2141	1.2059	1.2181
5–3	1.3574	1.3598	1.3689	1.3462
6–5	1.4582	1.4587	1.4554	1.4584
10–6	1.0757	1.0758	1.0761	1.0755
11–6	1.0779	1.0778	1.0782	1.0779
		Angles		
7–1–2	109.82	109.64	112.66	112.23
8–1–7	111.04	110.80	115.04	114.73
3–2–1	120.66	124.17	119.37	122.70
9–2–1	117.79	116.79	122.12	121.36
9–2–3	121.55	119.04	118.52	115.94
4–3–2	125.55	125.67	128.74	122.86
5–3–2	110.44	110.96	107.91	113.84
5–3–4	124.01	123.38	123.35	123.30
6–5–3	116.93	116.50	116.64	116.37
10–6–5	104.93	104.97	105.08	104.71
11–6–5	110.03	109.97	110.14	110.13
11–6–10	111.11	111.16	111.01	111.20
12–6–11	109.57	109.51	109.41	109.44
		Torsions		
3–2–1–7	–61.3	–60.8	113.9	114.5
9–2–1–7	118.9	119.0	–66.2	–65.7
4–3–2–1	0.1	180.0	–0.1	179.9
4–3–2–9	179.9	0.1	180.0	0.1
5–3–2–1	–179.9	–0.1	179.9	–0.1
5–3–2–9	–0.1	–179.9	0.0	–180.0
6–5–3–2	–180.0	180.0	179.9	–180.0
6–5–3–4	0.0	–0.0	–0.1	–0.0
10–6–5–3	–179.8	179.8	–179.8	–179.6
11–6–5–3	–60.2	–60.5	–60.2	–60.0

[a] The total energy of VII in 4-21G space is –337.03772 au. The 4-21G energy differences of VIII, IX, and X, relative to VII, are (in kcal/mol) 1.4, 4.7, and 6.4, respectively.

along with the standard deviation of the fit. The internal rotation parameters, that is, the reduced barrier s, the angles θ and γ between the internal rotation axis and the principal axes a and c, respectively, the moment of inertia of the top I_α, the vibrational energy difference Δ_0 between the sublevels E and A, and the V_3 barrier are reported in Table IV.

This barrier is the lowest one observed within the CH_3OCOX series investigated, as shown in Table V. It seems that V_3 decreases as the electronegativity of X increases and as X can give resonance forms of the type CH_3—O—C(—O$^-$)=X$^+$.

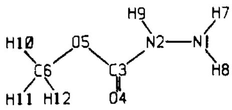

Figure 2. Atom numbering for methyl hydrazinocarboxylate.

Table VII. Rotational Constants (MHz) Calculated for Various Model Geometries of Conformations VII–X of Methyl Hydrazinocarboxylate and the Differences, Theory Minus Experiment

	calcd	% diff
VII[a]		
A	10327.93	0.8
B	2235.35	–2.1
C	1877.77	–1.7
VIII[a]		
A	6341.61	–38.1
B	2859.25	25.2
C	2016.85	5.6
IX[a]		
A	10225.71	–0.2
B	2217.88	–2.9
C	1862.75	–2.4
X[a]		
A	6650.66	–35.1
B	2731.98	19.7
C	1981.85	3.8
VII[b]		
A	10316.69	0.7
B	2276.72	–0.3
C	1906.50	–0.2
IX[b]		
A	10247.38	0.0
B	2255.06	–1.2
C	1889.64	–1.0
VII[c]		
A	10241.97	0.0
B	2281.75	–0.1
C	1907.44	–0.1
IX[d]		
A	10246.47	0.0
B	2281.99	0.0
C	1908.48	0.0

[a] Constants calculated with the unmodified 4-21G geometries, Table VII. [b] Constants calculated with the 4-21G geometries, Table VII, with C3–O5–C6, N1—N2–C3, H9–N2–C3, and H9–N2–N1 adjusted by –2°, –2.45°, +1.23°, and +1.23°, respectively, to reduce the differences between theory and experiment. [c] Constants calculated with the 4-21G geometry of VII including the following parameter changes: C3–N2–N1 (–2.45°); O4–C3–N2 (+0.45°); O5–C3–N2 (–0.89°); O5–C3–O4 (+0.45°); C6–O5–C3 (–2.0°); H9–N2–N1 (+1.23°); H9–N2–C3 (+1.23°). [d] Constants calculated with the 4-21G geometry of IX including the following parameter changes: C3–N2–N1 (–2.45°); C6–O5–C3 (–2.0°); H9–N2–N1 (+1.23°); H9–N2–C3 (+1.23°); N2–N1 (–0.02 Å); C6–O5 (–0.02 Å).

Conformation and Structure. The experimental rotational constants can fit any of the conformers I–VI of Figure 1. However, from the values of the inertial defect, $\Delta_c = I_c - I_a - I_b$ (see Table II), we can rule out I, the conformer with the bifurcated hydrogen bond, since it has a model value of Δ_c which is about 1 uÅ^2 higher (absolute value) than the observed one. As in the case of the methyl ester of glycine, the experimental value is larger than the model value probably because of large out of plane amplitude motions.

Models II and IV of Figure 1 should have a high μ_c dipole moment component ($\mu_c \geqslant 2$ D). Since we did not observe any μ_c-type transitions, these two conformers should also be excluded. Since VI can be expected to be energetically unfavorable, it was also excluded from further consideration. Thus, only III and V of the forms without a symmetry plane were left to assign the observed spectrum. For these two conformers it is, indeed, possible to obtain satisfactory agreement between the observed and calculated inertial defects when the H–N–N–H torsion is correctly adjusted. Furthermore, V is a plausible model, because it is

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(14) Curl, R. F. *J. Chem. Phys.* **1959**, *30*, 1529–1536.

(15) Williams, G.; Owen, N. L.; Sheridan, J. *Trans Faraday Soc.* **1971**, *67*, 922–949.

(16) Lister, D. G.; Owen, N. L. *Trans. Faraday Soc.* **1973**, *69*, 1036–1042.

(17) Caminati, W.; Cervellati, R. *J. Mol. Struct.* **1982**, *81*, 143–145.

Table VIII. Measured Transitions and Molecular Parameters of the N2-*d*, N1-d_2 Trideuterated Species of MHC

measured transitions

transition $J_{K_{-1}',K_1}{}' \leftarrow J_{K_{-1},K_1}$	obsd, MHz	diff,[a] MHz	transition $J_{K_{-1}',K_1}{}' \leftarrow J_{K_{-1},K_1}$	obsd, MHz	diff,[a] MHz
$8_{4,5} \leftarrow 7_{4,4}$	31 647.29	0.00	$9_{4,6} \leftarrow 8_{4,5}$	35 622.74	−0.15
$8_{4,4} \leftarrow 7_{4,3}$	31 648.87	−0.02	$9_{4,5} \leftarrow 8_{4,4}$	35 626.86	0.16
$8_{5,3} \leftarrow 7_{5,2}$	31 621.81	−0.01	$9_{5,5} \leftarrow 8_{5,4}$	35 587.35	0.01
$8_{6,2} \leftarrow 7_{6,1}$	31 607.87	0.00	$9_{6,3} \leftarrow 8_{6,2}$	35 567.62	0.01
$9_{2,8} \leftarrow 8_{2,7}$	35 291.45	−0.10	$10_{2,9} \leftarrow 9_{2,8}$	39 150.42	0.08

molecular parameters, MHz[b]

		exptl.	calcd[f]
$A = 9346.80$[c]	ΔB[e]		
$B = 2145.452$[d] (18)	ΔB[e]	137.570 (23)	136.498
$C = 1799.994$ (18)	ΔC[e]	109.416 (23)	109.385

[a] Diff = obsd − calcd. [b] Centrifugal distortion constants fixed to the values of the normal species. [c] Fixed to the calculated value. [d] Errors quoted are one standard deviation. [e] Difference between the normal and N-d_3 isotopic species values. [f] Using the parameters of VII[c] of Table VII.

stabilized by internal hydrogen bonds between N1–H8 and the lone pair on N2, between N1–H7 and a lone pair on O4, and between N2–H9 and the lone pair on N1 (atom numbering, Figure 2). However, since the structure of V derived in this way was not in agreement with the rotational constants of the N2-*d*,N1-d_2 trideuterated isotopic species (see below), we decided to perform an ab initio conformational analysis of the system.

For this analysis, Pulay's gradient method[18] and program[19] were used with the 4-21G basis set,[19] and approximate locations of potential energy minima were determined by a grid search. Geometries of MHC were partially refined, with torsional angles τ_1 (4–3–2–1) and τ_2 (7–1–2–9) constrained at 60-deg intervals, until the calculated energies of each form could be expected to be within a few kilocalories/mole of the true 4-21G minima. The results showed that local conformational energy minima for MHC can be expected in the vicinity of $(\tau_1,\tau_2) = (0,60)$, (0,240), (180,60), and (180,240).

When geometries in these regions were optimized completely, the parameters for forms VII to X were obtained which are listed in Table VI. Largest residual Cartesian forces in each of these forms are <0.001 mdyn. Rotational constants calculated with these structures are compared with the constants observed in Table VII. It is seen that the rotational constants of VII and IX both agree with the microwave spectrum, and both have only four out-of-plane hydrogen atoms, which corresponds to the observed inertial defect, Δ_c. In 4-21G space, VII is more stable than IX by more than 4 kcal/mol (see Table VI).

Microwave Spectrum of the N2-*d*, N1-d_2 Trideuterated Species. Prior to executing the ab initio calculations, we tried to analyze the spectrum of the N2-*d*,N1-d_2 triply deutrated species, in order to make the conformational assignment. Due to the weakness of the spectrum and to the complexity of the mixture of eight isotopic species when D_2O and H_2O coexist, it was difficult to be sure of the success of the deuteration. Attempts at deuterating the compound by direct exchange of the protons with D_2O adsorbed in the cell were not successful. Therefore, the compound was mixed with D_2O in a tube, and the excess of D_2O was pumped away. After several attempts of this kind some weak lines were measured and fitted with a semirigid Hamiltonian.[11] Somewhat to our disappointment, the additional data were not helpful in solving the conformational problem, because the obtained rotational constants were not in agreement with any of the conformers I–VI of Figure 1. Since in addition the measured lines were extremely weak, at this point we could neither be sure of the success of the deuteration nor of the general conformational assignment. In constrast to this, when the results of the ab initio calculations were available, it was easy to assign the spectrum described above to conformer VII.

The measured transitions are reported in Table VIII, along with the observed molecular constants and the experimental and calculated differences of the rotational constants of the two isotopic species.

Conclusions

It is a distinctive feature of the 4-21G minimim energy structures that they possess a molecular symmetry plane and a planar H—N—C═O peptide-like unit. (The final geometries reported are negligibly nonplanar, because they were approached from asymmetric starting geometries.) The 4-21G basis set is not really adequate reliably to determine conformational energies for N–N-type systems. In a complete ab initio conformational analysis of MHC, calculations with polarization functions would be a necessity. However, similar calculations were successful in the past in conformational analyses of such molecules. For example, they were essential in guiding the electron diffraction and microwave analyses of 1,2-dimethylhydrazine.[20–22] The agreement achieved here between theory and experiment also renders superfluous any additional calculations.

It seems significant that the most stable form of MHC in 4-21G space, VII, represents one of two conformations whose uncorrected ab initio geometries are in good agreement with the experimental microwave spectrum (Table VII). Of the other forms, it seems that VIII and X can be clearly ruled out as the observed rotational constants. IX is ruled out because its structure is not compatible with the variation of the rotational constants observed upon deuteration. It is seen from Table VII that slight changes in the 4-21G geometries of VII and IX will engender rotational constants which are practically identical with the experimental data of the normal species.

We think that the combined results presented above will support the conclusion that form VII is the most probable observed conformation and maybe the only one possible. This form is characterized by a molecular symmetry plane, with a planar peptide-like H—N—C═O unit and by a bifurcated hydrogen bond.

Furthermore, the calculations allow the expectation that a second conformer, VIII, so far unobserved, may also be populated significantly in vapors of this compound. Its dipole moment is slightly larger than that of conformer VII, but because of its low concentration, its detection is below our available instrument sensitivity.

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(18) Pulay, P. *Mol. Phys.* **1969**, *17*, 197–204.

(19) Pulay, P.; Fogarasi, G.; Pang, F.; Boggs, J. E. *J. Am. Chem. Soc.* **1979**, *101*, 2550–2560.

(20) Kohata, K.; Fukuyama, T.; Kuchitsu, K. *Chem. Lett.* **1979**, 257–259.

(21) Chiu, N. S.; Sellers, H. L.; Schafer, L.; Kohata, K. *J. Am. Chem. Soc.* **1979**, *101*, 5883–5889.

(22) Nakata, M.; Takeo, H.; Matsumura, C.; Yamanouchi, K.; Kuchitsu, K.; Fukuyama, T. *Chem. Phys. Lett.* **1981**, *83*, 246–249.