Short Communication

Structural and Conformational Properties of Methoxyacetamide as Studied by Microwave Spectroscopy and *Ab Initio* Computations

K.-M. Marstokk, Harald Møllendal and Svein Samdal*

Department of Chemistry, The University of Oslo, PO Box 1033 Blindern, N-0315 Oslo, Norway

Marstokk, K.-M., Møllendal, H. and Samdal, S., 1996. Structural and Conformational Properties of Methoxyacetamide as Studied by Microwave Spectroscopy and *Ab Initio* Calculations. – Acta Chem. Scand. 50: 845–847. © Acta Chemica Scandinavica 1996.

In previous communications from this laboratory structural and conformational properties of gaseous acetamides, XCH_2CONH_2, with $X = F$,[1] Cl,[1b] I,[2] and CH_3,[3] have been reported. These compounds display interesting and varied conformational behaviour.[1-3] Methoxyacetamide, $CH_3OCH_2CONH_2$, was chosen for study as the next member of this series. Rotational isomerism is possible around the C2–C6 and C6–O7 bonds (Fig. 1), and several rotamers may thus exist for this compound. Intramolecular hydrogen (H) bonding between one of the H atoms of the amide group and the oxygen atom of the methoxy group may stabilize some of these conformations. No studies of this particular kind of internal H bond in gases have previously been reported, and this was another reason for studying the title compound as a continuation of our studies of internal H bonding.[4] A combined investigation by reasonably high-level *ab initio* quantum mechanical computations and microwave (MW) spectroscopy has proved rather effective, and this approach was therefore chosen in the present case.

Ab initio computations employing the Gaussian 92 program package[5] were first made in order to locate minima, i.e. 'stable' rotamers, on the conformational energy surface. The rather high-level 6–311+G** basis set was used in these computations. Three minima were located. The structures as well as some other parameters of interest of the corresponding three stable rotamers are listed in Table 1. They are depicted in Fig. 1, where the atom numbering is also given.

The *ab initio* computations predict that *Conformer I*, which has a symmetry plane, is considerably more stable than the other two conformations by 6.7 and 15.0 kJ mol^{-1}, respectively (Table 1). This rotamer is

---

* To whom correspondence should be addressed.

undoubtedly stabilized by a five-membered intramolecular H bond formed between the nearest H atom of the amide group (H4) and the oxygen atom of methoxy group (O7), as the non-bonded H4···O7 distance is calculated to be 221 pm from the structure in Table 1. This is 40 pm shorter than the sum of the van der Waals radii of hydrogen and oxygen.[6] The N3–H4···O7 angle is 103.5°, far from the ideal linear arrangement.

Conformer II is also stabilized by an internal H bond between H4 and O7, but the non-bonded distance is calculated to be 233 pm in this case, so the H bond interaction is presumed to be less here than in *Conformer I*. However, the differences of the H bonds in *Conformers I* and *II* are too small to explain all the energy difference between these rotamers, which is predicted to be 6.7 kJ mol^{-1}(Table 1). Steric and electronic effects other than H bonding are thus presumed to stabilize *Conformer I* relative to other forms.

The rotational constants computed for *Conformer I* (Table 1) indicate that this rotamer is quite prolate with the asymmetry parameter $\kappa \approx -0.8$. The largest component of the dipole moment is calculated to be as large as 12×10^{-30} C m and to lie along the a-inertial axis (Table 1). Characteristic ^aR-branch pile-ups of transitions should thus occur for this rotamer at frequencies given approximately by $(B + C)(J + 1)$.

The microwave spectra of a commercial sample were taken in the 20–39 GHz spectral range at room temperature using the Oslo spectrometer.[7] The sublimation pressure of methoxyacetamide is marginal (*ca.* 1 Pa) for a MW study at room temperature. The ^aR-pile-ups, which were immediately noted, were remarkably weak for a compound with such a large dipole moment as this one (*ca.* 12×10^{-30} C m), as the strongest transitions had peak absorption coefficients of only roughly

τ(2-6-7-10) = 180°
τ(3-2-6-7) = 0°
r(H4 ··· O7) = 221 pm
ΔE = E$_I$ - E$_I$ = 0 kJ mol^{-1}

Conformer I

τ(2-6-7-10) = 89°
τ(3-2-6-7) = 16°
r(H4 ··· O7) = 233 pm
ΔE = E$_{II}$ -E$_I$ = 6.7 kJ mol^{-1}

Conformer II

τ(2-6-7-10) = 78°
τ(3-2-6-7) = 187°
r(H4 ··· O7) = 254 pm
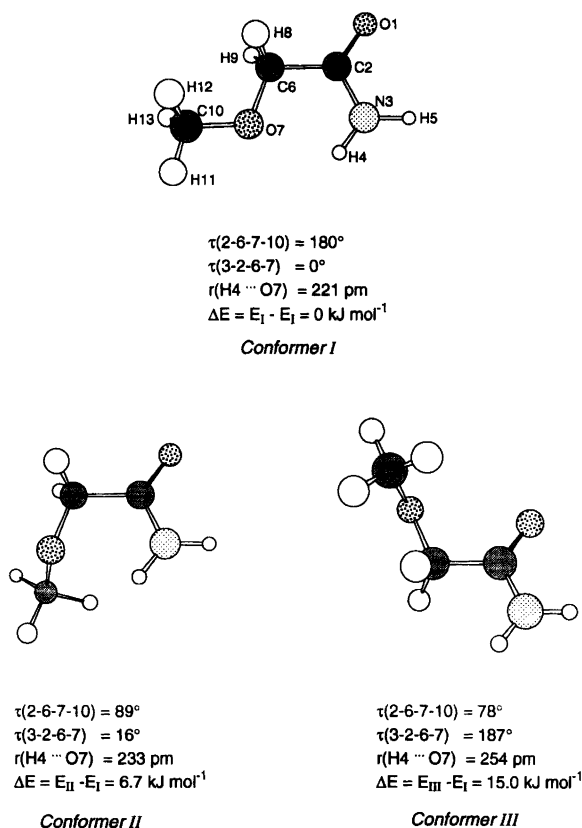ΔE = E$_{III}$ -E$_I$ = 15.0 kJ mol^{-1}

Conformer III

Fig. 1. The three conformers that were found to be minima on the potential energy surface in the 6–311+G** computations. Atom numbering is indicated on *Conformer I*. This rotamer which was the only one found in the MW spectrum, is calculated to be more stable than the other two forms by the values indicated on this figure. The dihedral angles which are important for rotational isomerism are shown on this figure.

4×10^{-8} cm^{-1}. The reasons for this weakness are presumed to be the large partition function and low sublimation pressure.

The assignments started with the pile-ups; the ground and four vibrationally excited states were ultimately assigned.* The spectroscopic constants (*A*-reduction, I^r-representation[8]) are listed in Table 2. Only $^a R$-lines were assigned for the vibrationally excited states, whereas several very weak $K_{-1} = 4 \leftarrow 3$ $^b Q$-branch transitions were also assigned for the ground vibrational state. Four of the quartic centrifugal distortion constants were fitted for the ground vibrational state, while only two (Δ_J and Δ_{JK}) were fitted for the vibrationally excited states where δ_J and δ_K were held constant at the values found for the ground vibrational state.

It is seen in Table 2 that the rotational constants of the ground vibrational state agree with those calculated for *Conformer I* (Table 1) to within better than about

* The complete spectra are available from the authors upon request, or from the Molecular Spectra Data Center, National Institute of Standards and Technology, Molecular Physics Division, Bldg. 221, Rm. B265, Gaithersburg, MD, USA, where they have been deposited.

Table 1. Structure,[a] rotational constants, dipole moments and energy differences of the three rotamers of methoxyacetamide found to be minima on the potential energy surface in the *ab initio* computations at the 6–311+G** level.

Rotamer:	Conformer I	Conformer II	Conformer III
Distances/pm			
C2–O1	119.6	119.5	119.0
C2–N3	134.3	138.8	136.0
N3–H4	99.2	99.2	99.2
N3–H5	99.3	99.4	99.4
C2–C6	151.8	152.4	137.6
C6–O7	139.1	139.2	137.6
C6–H8	108.8	108.4	108.5
C6–H9	108.8	108.5	109.2
O7–C10	139.6	140.1	140.2
C10–H11	108.1	108.1	108.1
C10–H12	108.2	108.7	109.1
C10–H13	108.8	108.8	108.3
Angles/°			
O1–C2–N3	124.2	123.9	122.7
C2–N3–H4	120.7	120.5	121.5
C2–N3–H5	118.7	118.4	117.6
H4–N3–H5	120.7	119.9	117.8
O1–C2–C6	119.7	120.4	123.6
C6–C2–N3	116.1	115.7	113.7
C2–C6–H8	107.1	106.7	108.3
C2–C6–H9	107.1	107.6	107.8
O7–C6–H8	111.4	107.8	107.2
O7–C6–H9	111.4	112.2	111.7
O7–C6–C2	111.6	114.4	114.2
C6–O7–C10	114.5	115.2	116.2
O7–C10–H11	107.5	107.3	106.8
O7–C10–H12	111.1	110.9	110.7
O7–C10–H13	111.1	111.6	111.5
H11–C10–H12	109.1	109.0	108.8
H11–C10–H13	109.1	109.1	109.3
H12–C10–H13	108.9	108.9	109.7
Dihedral angles[b]/°			
O1–C2–N3–H4	180.0	187.2	167.6
O1–C2–N3–H5	0.0	−5.4	7.7
C6–C2–N3–H4	0.0	5.8	−14.3
C6–C2–N3–H5	180.0	173.1	185.8
O1–C2–C6–O7	180.0	194.4	−9.4
O1–C2–C6–H8	57.8	75.3	−128.8
O1–C2–C6–H9	−57.8	−40.3	−244.7
N3–C2–C6–O7	0.0	15.8	187.5
N3–C2–C6–H8	−122.2	−103.3	53.2
N3–C2–C6–H9	122.2	141.1	−62.7
C2–C6–O7–C10	180.0	89.1	78.0
C6–O7–C10–H11	180.0	180.9	176.6
C6–O7–C10–H12	60.8	61.9	58.3
C6–O7–C10–H13	−60.8	−59.7	−64.0
Rotational constants[c]/MHz			
A	9275.2	7244.7	7986.6
B	2084.5	2362.8	2358.0
C	1738.8	2067.6	1984.7
Dipole moment[d]/10^{-30} C m			
μ_a	11.97	9.24	5.60
μ_b	6.14	7.34	10.67
μ_c	0.0[e]	0.80	5.54
Energy difference[e,f]/ kJ mol^{-1}	0.0	6.7	15.0

[a] See Fig. 1 for definition. [b] Measured from *syn*=0°. [c] Calculated from the structures given above in this table. [d] 1 D=3.335 64 × 10^{-30} C m. [e] The total energy of *Conformer I* was calculated as −845 287.33 kJ mol^{-1} (−321.952 928 0 hartree). [f] Energy difference between *Conformer I* and each of the two other conformations.

2.5%, and are widely different from those of *Conformers II* and *III*. There is thus no doubt that *Conformer I* has indeed been assigned.

The frequencies of the three lowest fundamental modes

Table 2. Spectroscopic constants[a,b] the ground and vibrationally excited states of methoxyacetamide.

Vibrational state:	Ground	1st ex. C2–C6 tors.	2nd ex. C2-C6 tors.	1st ex. C2-O7 tors.	1st ex. in-plane bend.
No. of transitions:	83	61	46	48	45
R.m.s. dev.[c]/MHz:	0.12	0.14	0.22	0.21	0.21
A_v/MHz	9047.595(54)	8968.16(69)	8896.5(13)	8974.1(12)	9010.6(13)
B_v/MHz	2065.0450(47)	2067.1794(67)	2069.317(14)	2066.192(12)	2065.211(12)
C_v/MHz	1719.5353(48)	1723.2504(74)	1726.871(14)	1722.480(13)	1717.667(12)
Δ_J/kHz	0.249(21)	0.281(30)	0.195(49)	0.304(44)	0.318(52)
Δ_{JK}/kHz	1.465(49)	1.179(58)	0.76(12)	2.435(92)	0.86(11)
Δ_K/kHz	0.0[e]	0.0[e]	0.0[e]	0.0[e]	0.0[e]
δ_J/kHz	0.1449(45)	0.145[e]	0.145[e]	0.145[e]	0.145[e]
δ_K/kHz	2.18(34)	2.18[e]	2.18[e]	2.18[e]	2.18[e]
$(I_a+I_b-I_c)^d/10^{-20}$ m^2 u	6.6837(13)	7.5593(57)	8.375(11)	7.5080(98)	6.5737(88)

[a] A-reduction, I^r-representation.[8] [b] Uncertainties represent one standard deviation. [c] Root-mean-square deviation. [d] Conversion factor $505\,379.05 \times 10^{-20}$ m^2 u MHz. [e] Pre-set at this value.

could not be determined experimentally in this case because the spectral lines were so weak that quantitative measurements of relative intensities could not be made properly.

The value of $I_a+I_b-I_c = 6.683\ 7(13) \times 10^{-20}$ u m^2 (I_a, I_b and I_c being the principal moments for inertia) for the ground vibrational state is typical for a molecule with C_s symmetry and 4 sp^3 hybridized out-of-plane H atoms and a low-frequency out-of-plane torsional motion (calculated to be 67 cm^{-1} for the torsion around C2–C6 bond; not given in Table 1). This value is practically the same as that of the one assigned conformer of methoxyacetic acid,[9] which is similar to *Conformer I* and has a *planar* acid group that is *proton donor* in the internal H bond formed with the oxygen atom of the methoxy group.

$I_a+I_b-I_c$ is seen to *increase* for the first and second excited states of the C2–C6 torsional fundamental, as well as for the first excited state of the C2–O7 torsion (calculated frequency: 94 cm^{-1}). This is typical for out-of-plane motions.[10] The increases are again found to be very similar to what was found for the corresponding excited states of methoxyacetic acid.[9] In the fourth excited state given in Table 2, $I_a+I_b-I_c$ is *decreasing*. This is typical for an in-plane bending[10] vibration (calculated frequency 220 cm^{-1}).

The following conclusions can be drawn from the present study: methoxyacetamide prefers *Conformer I* as its most stable form. The five-membered internal H bond between H4 of the amide group and O7 of the methoxy group which is stabilizing this rotamer, is the first one of its kind studied in the gas phase. *Conformer I* has a symmetry plane (C_s symmetry) with four out-of-plane hydrogens. The amide group is planar, or very nearly so, in agreement with the 6–311+G** computations. The vibrational dynamics of *Conformer I* is very similar to what was found for the corresponding conformer of methoxyacetic acid. The experimental structure that may

be determined in the future is presumed to be close to 6–311+G** structure shown in Table 1.

References

1. (a) Marstokk, K.-M. and Møllendal, H. *J. Mol. Struct. 22* (1974) 287; (b) Samdal, S. and Seip, R. *J. Mol. Struct. 52* (1979) 195.
2. Samdal, S. and Seip, R. *J. Mol. Struct. 62* (1980) 131.
3. Marstokk, K.-M., Møllendal, H. and Samdal, S. *J. Mol. Struct. 376* (1996) 11.
4. (a) Wilson, E. B. and Smith, Z. *Acc. Chem. Res. 20* (1987) 257; (b) Møllendal, H. *J. Mol. Struct. 97* (1983) 303; (c) Møllendal, H. *Structures and Conformations of Non-Rigid Molecules*, Ed. Laane, J., Dakkouri, M., van der Veken, B. and Oberhammer, H., Kluwer Academic Publishers, Dordrecht, Netherlands 1993, p. 277.
5. Frisch, I. M., Trucks, G. W, Head-Gordon, M., Gill, P. M. W., Wong, M. W., Foresman, J. B., Johnson, B. G., Schlegel, H. B., Robb, M. A., Replogle, E. S., Gomperts, R., Andres, J. L., Raghavachari, K., Binkley, J. S., Gonzalez, C., Martin, R. L., Fox, D. J., Defrees, D. J., Baker, J., Stewart, J. J. P. and Pople, J. A., *Gaussian 92*, Revision C, Gaussian, Inc., Pittsburgh PA 1992.
6. Pauling, L. *The Nature of the Chemical Bond*, 3rd Edn., Cornell University Press, New York 1960, p. 260.
7. Guirgis, G. A., Marstokk, K.-M. and Møllendal, H. *Acta Chem. Scand. 45* (1991) 482.
8. Watson, J. K. G. In: Durig, J. R., Ed., *Vibrational Spectra and Structure*, Elsevier, Amsterdam 1977, Vol. 6, p 1.
9. Marstokk, K.-M. and Møllendal, H. *J. Mol. Struct. 18* (1973) 247.
10. Herschbach, D. R. and Laurie, V. W. *J. Chem. Phys. 40* (1960) 3142.