

Microwave Spectrum, Conformation and Intramolecular Hydrogen Bonding of 3-Methoxypropanol

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Marstokk, K.-M. and Møllendal, H., 1989. Microwave Spectrum, Conformation and Intramolecular Hydrogen Bonding of 3-Methoxypropanol. – *Acta Chem. Scand.* 43: 715–719.

The microwave spectra of $\text{CH}_3\text{OCH}_2\text{CH}_2\text{CH}_2\text{OH}$ and one deuterated species $\text{CH}_3\text{OCH}_2\text{CH}_2\text{CH}_2\text{OD}$ have been investigated in the 26.5–38.0 GHz spectral region at about -20°C . One conformer with a six-membered intramolecular hydrogen bond formed between the hydroxyl group hydrogen atom and the oxygen atom of the methoxy group was assigned. There is no indication of the presence of large fractions of any further rotameric forms.

3-Substituted propanol derivatives may form six-membered ring structures with intramolecular hydrogen (H) bonds provided a suitable proton acceptor is available in the 3-position. Several such molecules have been studied in recent years in the gaseous state by electron diffraction (ED) and microwave (MW) spectroscopy. In an ED study¹ of 3-chloropropanol it was found that three different rotamers are present in the gas phase for this compound. One of these conformers present to the extent of approximately 16% possesses an internal H bond, while the other two forms do not have intramolecular H bonds. Later, the same two non-H-bonded conformers were assigned by MW spectroscopy.² The H-bonded form was searched for extensively, but not assigned.² It can thus be concluded from these two studies that the H-bonded conformation of 3-chloropropanol has a rather high energy, and is consequently present in relatively small concentrations. This finding has been taken as an indication that the chlorine atom is a rather weak acceptor.²

The situation for 3-fluoropropanol³ is different from that found for 3-chloropropanol.^{1,2} In an elegant MW study,³ three different conformers were assigned for 3-fluoropropanol. Two of these rotamers have no intramolecular H bonds, while the third has this kind of stabilizing interaction. The H-bonded form was, however, found to be about 1.6 kJ mol^{-1} less stable than the most abundant non-H-bonded species.³ This was taken as evidence that the fluorine atom is a weak proton acceptor.³

π -Electrons are also rather weak acceptors. However, in recent ED studies by Trættemberg *et al.* of 4-pentenol^{4a} and 4-pentynol^{4b} there is clear evidence for the occurrence of H-bonded conformers of these compounds in considerable concentrations.

Hydroxyl groups may act as proton donors or proton acceptors. In diols, one of the hydroxyl groups is donor and the other acceptor, as shown beyond doubt in recent MW

studies of ethylene glycol.⁵ Butane-1,3-diol is closely related to 3-substituted propanols. One conformer with an internal six-membered H bond was found in a MW investigation⁶ of this molecule.

The amino group is a much better acceptor for H bonds than fluorine and chlorine atoms, π -electrons or hydroxyl groups. As a consequence of this, only the H-bonded conformation showed up in the MW spectrum of 3-aminopropanol.⁷

The acceptor properties of ether oxygen atoms are probably similar to those of hydroxyl groups. With 3-methoxypropanol it is possible to investigate the intramolecular H-bonding interaction between a hydroxyl group hydrogen atom and an ether oxygen in 3-position. Is this interaction so strong that the H-bonded conformation predominates just as in the case of 3-aminopropanol, or are several forms present in appreciable concentrations as for 3-fluoropropanol? It has been the aim of this work to answer this question.

There have been some solution studies of the intramolecular H-bonding properties of 3-methoxypropanol. Kuhn and Wires⁸ found that the H-bonded conformer is stabilized by about 9 kJ mol^{-1} in dilute carbon tetrachloride solution, while Prabhumirashi⁹ found a value of 15 kJ mol^{-1} . Although conformational equilibria in the gas phase may differ from those observed in solution, these solution studies nevertheless demonstrate that the H-bonded conformer is stabilized to a remarkable degree in solution. A model of this rotamer is shown in Fig. 1.

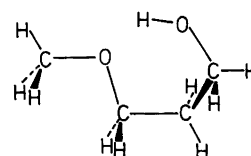


Fig. 1. The assigned H-bonded conformation of 3-methoxypropanol.

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Experimental

The sample used in this work was purchased from ICN Pharmaceuticals, Inc., K & K Labs Division, New York. It was examined by vapour phase chromatography and found to be practically 100 % pure. The microwave spectrum was studied in the 26.5–38.0 GHz spectral region at a temperature of about -20°C . Lower temperatures could not be used due to insufficient vapour pressure of the compound. The pressure was between 1 and 2 Pa during the recording of the spectra. The spectrometer is an improved version of the one described briefly in Ref. 10, employing klystrons

as radiation sources. The radio-frequency microwave frequency double resonance technique (RFMWDR) was used as described in Ref. 11, employing the equipment mentioned in Ref. 12. The deuterated species $\text{CH}_3\text{OCH}_2\text{CH}_2\text{CH}_2\text{OD}$ was produced by conditioning the cell with D_2O and then introducing the normal sample.

Results

Microwave spectrum and assignment. Survey spectra revealed a relatively weak, but dense MW spectrum for 3-methoxypropanol. The strongest lines of the spectrum have

Table 1. Selected transitions of the ground-state MW spectrum of 3-methoxypropanol.

Transition	Observed frequency ^a /MHz	Obs. – calc. frequency/MHz	Centrifugal dist./MHz
7 _{1,7} ← 6 _{0,6}	26983.57	0.00	-0.39
7 _{2,6} ← 6 _{1,5}	35657.76	-0.01	-0.38
7 _{1,6} ← 6 _{1,5}	28568.36	0.01	-1.07
7 _{3,4} ← 6 _{3,3}	27979.56	-0.11	-0.95
7 _{5,2} ← 6 _{5,1}	27709.42	-0.03	-0.51
7 _{5,3} ← 6 _{5,2}	27709.42	0.11	-0.51
8 _{0,8} ← 7 _{0,7}	29561.85	0.08	-0.84
8 _{0,8} ← 7 _{1,7}	28681.00	-0.01	-1.04
8 _{2,7} ← 7 _{2,6}	31112.75	-0.02	-1.19
8 _{4,4} ← 7 _{4,3}	31782.63	0.01	-1.21
8 _{4,5} ← 7 _{4,4}	31760.43	0.02	-1.19
8 _{7,1} ← 7 _{7,0}	31635.34	0.04	-0.36
8 _{7,2} ← 7 _{7,1}	31635.34	0.04	-0.36
9 _{0,9} ← 8 _{0,8}	33017.10	0.02	-1.16
9 _{1,9} ← 8 _{0,8}	33381.22	0.00	-0.97
9 _{1,8} ← 8 _{2,9}	30296.89	-0.01	-2.93
9 _{4,5} ← 8 _{4,4}	35829.73	0.01	-1.88
9 _{6,3} ← 8 _{6,2}	35639.89	-0.11	-1.23
9 _{6,4} ← 8 _{6,3}	35639.89	-0.08	-1.23
9 _{8,1} ← 8 _{8,0}	35589.23	0.04	-0.46
9 _{8,2} ← 8 _{8,1}	35589.23	0.04	-0.46
10 _{0,10} ← 9 _{0,9}	36479.62	0.03	-1.56
10 _{1,10} ← 9 _{0,9}	36704.85	-0.04	-1.40
10 _{1,10} ← 9 _{1,9}	36340.75	0.00	-1.58
9 _{4,5} ← 9 _{3,6}	28090.33	-0.07	0.12
11 _{4,8} ← 11 _{3,9}	29795.86	-0.05	-0.74
13 _{5,9} ← 13 _{4,10}	37231.80	-0.03	-0.64
16 _{3,14} ← 16 _{2,15}	35947.25	-0.05	-9.46
17 _{2,15} ← 17 _{1,16}	36077.60	-0.06	-16.93
18 _{3,15} ← 18 _{2,16}	28548.15	-0.07	-23.31
18 _{5,13} ← 18 _{4,14}	29356.00	0.13	11.95
20 _{5,15} ← 20 _{4,16}	26742.91	-0.02	10.28
22 _{4,18} ← 22 _{3,19}	30946.37	0.05	-41.83
22 _{6,16} ← 22 _{5,17}	36550.56	-0.03	26.06
24 _{5,19} ← 24 _{4,20}	28084.98	-0.02	-27.58
24 _{6,18} ← 24 _{5,19}	32969.16	-0.10	27.77
26 _{5,21} ← 26 _{4,22}	33122.34	-0.16	-63.58
27 _{5,22} ← 27 _{4,23}	36585.15	-0.02	-82.71
27 _{6,21} ← 27 _{5,22}	30782.64	-0.03	-4.11
29 _{6,23} ← 29 _{5,24}	33000.99	0.01	-52.44
29 _{7,22} ← 29 _{6,23}	37881.51	0.03	53.88
30 _{6,24} ← 30 _{5,25}	35336.72	0.07	-82.92
31 _{7,24} ← 31 _{6,25}	35544.53	-0.06	21.87
33 _{7,26} ← 33 _{6,27}	36196.38	-0.10	-45.72
34 _{7,27} ← 34 _{6,28}	37835.53	0.09	-90.91

^a ± 0.10 MHz.

peak absorption coefficients of roughly $1.5 \times 10^{-7} \text{ cm}^{-1}$. It turned out later that these transitions are high- J b -type Q -branch, or intermediate- J a -type R -branch lines.

A preliminary set of rotational constants was predicted for the H-bonded conformer shown in Fig. 1. The dipole moment components along the principal inertial axes were predicted to be approximately $\mu_a = 6.9$, $\mu_b = 5.6$, $\mu_c = 3.2$ (in units of 10^{-30} C m) using the bond-moment method.¹³ The rotational constants predicted that the high- K_{-1} transitions of the $7 \leftarrow 6$, $8 \leftarrow 7$, and $9 \leftarrow 8$ a -type R -branch transitions falling in the investigated spectral range should coalesce two by two. This was exploited in a RFMWDR search¹¹ for these transitions, which were readily found close to their predicted frequencies using this mode of operation. Extension of the assignments to include the lower K_{-1} a -type R -branch transitions was then made using normal MW spectroscopy. The b -type transitions were found next. No c -type transitions were positively identified, although their hypothetical frequencies could be very accurately predicted, presumably because they are too weak as a result of a small dipole-moment component along the c -axis. A total of about 120 transitions were assigned for the ground vibrational state. Table 1 shows a portion of this spectrum.⁸

The spectroscopic constants (A -reduction I' -representation¹⁴) derived from 108 transitions are shown in Table 2.

Unfortunately, the spectrum was too weak to allow a determination of the dipole moment of 3-methoxypropanol.

Vibrationally excited states. The ground-state transitions were accompanied by a relatively strong spectrum presumably belonging to vibrationally excited states of the molecule. As shown in Table 3, these excited states are attributed to the two lowest heavy-atom torsional modes as well

Table 2. Spectroscopic constants^{a,b} for the ground vibrational state of $\text{CH}_3\text{OCH}_2\text{CH}_2\text{CH}_2\text{OH}$ and $\text{CH}_3\text{OCH}_2\text{CH}_2\text{CH}_2\text{OD}$.

Species	Parent	Deuterated
No. of transitions	108	54
R.m.s./MHz	0.061	0.076
A_0/MHz	6181.5927(47)	6039.050(12)
B_0/MHz	2190.9382(26)	2189.8796(61)
C_0/MHz	1750.0461(25)	1738.2239(61)
Δ_J/kHz	0.750(17)	0.674(39)
Δ_{JK}/kHz	-1.654(14)	-1.667(31)
Δ_K/kHz	8.60(16)	10.03(37)
δ_J/kHz	0.20487(68)	0.1967(13)
δ_K/kHz	1.409(21)	1.741(38)

^a A -reduction I' -representation. ^bUncertainties represent one standard deviation. ^cRoot-mean-square deviation.

⁸The complete spectra are available from the authors upon request, or from the Molecular Spectra Data Center, Bldg. 221, Room B 268, National Bureau of Standards, Gaithersburg, Maryland 20899, U.S.A., where they have been deposited.

as to the lowest bending mode. These assignments are only tentative, because it is possible that the second lowest torsional vibration and the bending vibration should be interchanged. Relative intensity measurements performed largely as described in Ref. 15 yielded $82(30) \text{ cm}^{-1}$ for the lowest torsional mode, $102(30) \text{ cm}^{-1}$ for the second lowest torsional mode and $179(40) \text{ cm}^{-1}$ for what is presumed to be the lowest bending mode. No split transitions caused by methyl-group tunnelling could be seen for any excited-state lines, and it is assumed that the first excited state of the methyl-group torsional vibration was not identified, although a search for it was made. It is presumed that the absolute weakness of the spectrum is the reason why this excited state escaped being assigned.

Searches for further conformations. The assignments reported above include all the strongest lines of the spectrum, a large majority of the intermediate intensity transitions as well as many of the weakest lines. Moreover, the absolute intensities of the assigned transitions are roughly what one would predict for 3-methoxypropanol if it were the only conformation present.

Many hypothetical conformations other than the assigned one are of course possible for 3-methoxypropanol. Most of these hypothetical forms should possess sizable dipole moments. Searches for further hypothetical conformations among the unassigned, weak lines using normal MW as well as RFMWDR spectroscopic techniques were negative. It is concluded that it is unlikely that further rotamers coexist in relatively high concentrations with the identified H-bonded form shown in Fig. 1. The remaining unassigned weak or very weak lines are presumed to belong to unassigned vibrationally excited states.

Structure. The six rotational constants of Table 2 furnish insufficient information for a full structure determination of the identified H-bonded conformer of 3-methoxypropanol. Assumptions have to be made in order to derive structural parameters of interest. The heavy-atom dihedral angles and the H-O-C1-C2 (atom numbering is given in Table 4) dihedral angle were chosen for fitting because they are chemically interesting and can be obtained with considerable accuracy. The remaining structural parameters were kept fixed at the values shown in Table 4. These fixed parameters were selected from recent accurate structural studies of closely related compounds. It is to be noted that the methyl group is *anti* to the C2-C3 bond, just as in the case of methoxyethanol which has been subject to several MW studies.¹⁶

The heavy-atom dihedral angles O-C1-C2-C3 and C1-C2-C3-O were fitted in steps of 1° to the rotational constants. The O-C1-C2-C3 dihedral angle was found to be $75(4)^\circ$ from *syn*, and the C1-C2-C3-O dihedral angle was determined as $60(4)^\circ$ from *syn*. The uncertainties are estimated to be about three standard deviations.

An alternative approach was used to derive the H-O-C1-C2 dihedral angle. The substitution (or Kraitchman's)

Table 3. Spectroscopic constants^{a,b} for vibrationally excited states of CH₃OCH₂CH₂CH₂OH.

Vib. state ^d	Lowest. tors.	Second low. tors.	Lowest bend.
No. of transitions	64	55	44
R.m.s./MHz	0.076	0.120	0.139
<i>A</i> ₀ /MHz	6175.957(11)	6163.775(17)	6208.321(21)
<i>B</i> ₀ /MHz	2191.2708(42)	2196.0478(70)	2179.4882(88)
<i>C</i> ₀ /MHz	1752.4774(42)	1752.9521(70)	1741.8965(87)
$\Delta_{J'}$ /kHz	0.755(27)	0.807(47)	0.830(57)
$\Delta_{JK'}$ /kHz	-1.185(31)	-2.580(44)	-1.794(84)
$\Delta_{K'}$ /kHz	13.93(36)	8.31(53)	8.86(94)
$\delta_{J'}$ /kHz	0.2072(14)	0.2162(22)	0.2185(26)
$\delta_{K'}$ /kHz	1.070(44)	2.103(65)	1.530(87)

^{a-c}Comments as for Table 2. ^dSee text for discussion of the assignments of these excited states.

Table 4. Plausible molecular structure^a (bond length/pm; angles/°) of CH₃OCH₂CH₂CH₂OH.

Structural parameters kept fixed ^b			
C1-O	142.0	\angle H-O-C1	98.0
C3-O	141.5	\angle O-C1-C2	112.0
C4-O	141.5	\angle C1-C2-C3	112.5
C-C	153.0	\angle C3-O-C4	111.8
O-H	98.0	\angle H-O-C1	106.0
C-H	109.3	\angle O-C4-H	109.47
		\angle C-C-H	109.47
Fitted ^{a,c}			
\angle O-C1-C2-C3	75(4) from <i>syn</i>	\angle C1-C2-C3-O	60(4) from <i>syn</i>
\angle H-O-C1-C2	50(5) from <i>syn</i>		
Hydrogen bond parameters			
O...O	281	H...O	201
\angle O-H...O	138	\angle O-H...O-C4 ^d	16
\angle O-H...O-C3 ^d	119		
Sum of van der Waals radii ^e			
O...O	280	H...O	260
Kraitchman's coordinates for hydroxyl group hydrogen atom			
Calculated from rotational constants			
a	b	c	
26.90(12)	137.841(25)	20.01(17)	
Calculated from plausible structure			
a	b	c	
62.5	137.7	15.9	
Rotational constants/MHz			
Parent species			
Observed:	<i>A</i> ₀ = 6181.59	<i>B</i> ₀ = 2190.94	<i>C</i> ₀ = 1750.05
Calculated:	<i>A</i> ₀ = 6227.78	<i>B</i> ₀ = 2204.78	<i>C</i> ₀ = 1763.97
Deuterated species			
Observed:	<i>A</i> ₀ = 6039.05	<i>B</i> ₀ = 2189.88	<i>C</i> ₀ = 1738.22
Calculated:	<i>A</i> ₀ = 6084.85	<i>B</i> ₀ = 2200.76	<i>C</i> ₀ = 1750.07

^a See text. Atom numbering: HOC1H₂C2H₂C3H₂OC4H₃. ^b The atoms attached to the carbon atoms were assumed to be arranged tetrahedrally around these atoms. The C2-C3-O-C4 dihedral angle was assumed to be exactly 180°. ^c Heavy-atom dihedral angles were obtained by fitting them to the rotational constants, while the H-O-C1-C2 dihedral angle was obtained by fitting the *b*-axis coordinate of the hydroxyl group hydrogen atom to the value found by Kraitchman's equation. See text. ^d Angle between the O-H and C-O bonds. ^e Taken from Ref. 19.

coordinates¹⁷ can be calculated for the hydrogen atom using the rotational constants shown in Table 2. The result of this computation is shown in Table 4. It is known that the substitution coordinates are not always accurate in cases where hydrogen is involved and large amplitude motions are important.¹⁸ This is the case for the title compound. It was therefore decided to try to reproduce the largest, in this case the *b*-axis substitution coordinate (Table 4). This was found with the H-O-C1-C2 dihedral angle 50(5)° from *syn*. The calculated rotational constants obtained using the fitted values for the dihedral angles are listed in Table 4.

Discussion

The conformational preference of 3-methoxypropanol is very similar to that of 3-aminopropanol⁷ and butane-1,3-diol.⁶ In these three cases, the internal H bonds cause the molecules to fold themselves into compact six-membered rings. The H bonds are so strong that no further forms could be detected. This situation is different from that for 3-fluoropropanol, where three conformations were found.³ This indicates that the methoxy group, hydroxyl group and amino group are all stronger proton acceptors than the fluorine atom.

The structure of the H-bonded conformer reveals several interesting features. The O...H distance is about 60 pm shorter than the sum of the van der Waals radii of hydrogen and oxygen (Table 4). The O-H...O angle is 138°, while approximately 180° would produce an ideal H-bond interaction. The O-H and O-C4 bonds are approximately 16° from being parallel, and this is very favourable for a bond dipole stabilization.

It is worth noting that the O-C1-C2-C3 dihedral angle of 3-methoxypropanol is distorted by 15° from the normal 60° to 75°. A repulsive contribution to the H bond is likely to show up somewhere in the structure because the O...H non-bonded distance is about 60 pm shorter (Table 4) than the sum of the van der Waals radii of oxygen and hydrogen. Similar effects have been seen in its counterparts 3-aminopropanol⁷ (76.6°), butane-1,3-diol⁶ (77.0°), and in the H-bonded conformation of 3-fluoropropanol³ (77(2)°). It is suggested that the increase to 75–77° of the O-C1-C2-C3 dihedral angle seen in these four molecules is caused by repulsive effects.

The fact that the H-O-C1-C2 dihedral angle is reduced by approximately 10° from the staggered position (dihedral

angle 60°) brings the hydrogen atom of the hydroxyl group into closer proximity with the ether oxygen atom, thereby strengthening the intramolecular H bond. This finding parallels the results obtained in the cases of the three other molecules.^{3,6,7}

References

1. (a) Bastiansen, O., Brunvoll, J. and Hargittai, I. *Kem. Közle-men.* 37 (1972) 379; (b) Bastiansen, O., Brunvoll, J. and Hargittai, I. In: Cyvin, S. J., Ed., *Molecular Structures and Vibrations*, Elsevier, Amsterdam 1972, p. 330.
2. Fuller, M. J., Wilson, E. B. and Caminati, W. *J. Mol. Spectrosc.* 96 (1982) 131.
3. Caminati, W. *J. Mol. Spectrosc.* 92 (1982) 101.
4. (a) Trættestad, M., Bakken, P., Seip, R., Lüttke, W. and Knieriem, B. *Acta Chem. Scand., Ser. A* 42 (1988) 578; (b) Trættestad, M., Bakken, P., Seip, R., Lüttke, W. and Knieriem, B. *J. Mol. Struct.* 128 (1985) 191.
5. (a) Walder, E., Bauder, A. and Günthard, H. H. *Chem. Phys.* 51 (1980) 223; (b) Caminati, W. and Corbelli, G. *J. Mol. Spectrosc.* 90 (1981) 572; (c) Kristiansen, P.-E., Marstokk, K.-M. and Møllendal, H. *Acta Chem. Scand., Ser. A* 41 (1987) 403.
6. Caminati, W. and Corbelli, G. *J. Mol. Struct.* 78 (1982) 197.
7. McMahan, M. A., Sharma, S. D. and Curl, R. F., Jr. *J. Mol. Spectrosc.* 75 (1979) 220.
8. Kuhn, L. P. and Wires, R. A. *J. Am. Chem. Soc.* 86 (1964) 2161.
9. Prabhuram, L. S. *Trans. Faraday Soc.* 74 (1978) 1567.
10. Marstokk, K.-M. and Møllendal, H. *J. Mol. Struct.* 5 (1970) 205.
11. Wordarczyk, F. J. and Wilson, E. B. *J. Mol. Spectrosc.* 37 (1971) 445.
12. Marstokk, K.-M. and Møllendal, H. *Acta Chem. Scand., Ser. A* 42 (1988) 374.
13. Smyth, C. P. *Dielectric Behavior and Structure*, McGraw-Hill, New York 1955, p. 244.
14. Gordy, W. and Cook, R. L. *Microwave Molecular Spectra*, Wiley, New York 1984, p. 329.
15. Esbitt, A. S. and Wilson, E. B. *Rev. Sci. Instrum.* 34 (1963) 901.
16. (a) Buckley, P. and Brochu, M. *Can. J. Chem.* 50 (1970); (b) Brochu, M. and Buckley, P. *Can. J. Spectrosc.* 18 (1973) 165; (c) Caminati, W. and Wilson, E. B. *J. Mol. Spectrosc.* 81 (1980) 356; (d) Caminati, W., Cervellati, R. and Smith, Z. *J. Mol. Struct.* 97 (1983) 87.
17. Kraitchman, J. *Am. J. Phys.* 21 (1953) 17.
18. van Eijck, B. P. *J. Mol. Spectrosc.* 91 (1982) 348.
19. Pauling, L. *The Nature of the Chemical Bond*, 3rd ed., Cornell University Press, New York 1960, p. 260.

Received October 5, 1988.