

# Microwave Spectrum, Intramolecular Hydrogen Bonding and Conformational Equilibrium of *trans*-2-Methylcyclopropanemethanol

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The microwave spectrum of *trans*-2-methylcyclopropanemethanol and one deuterated species has been investigated in the 24.0–39.5 GHz spectral region at  $-15^{\circ}\text{C}$ . Two conformers denoted *I* and *II* were assigned. In rotamer *I* the methyl and the hydroxyl groups are relatively remote from one another, while they are closer to one another in *II*. Both *I* and *II* are stabilized by an intramolecular hydrogen bond formed between the hydroxyl-group hydrogen atom and the pseudo- $\pi$ -electrons present along the outside of the nearest C–C edge of the cyclopropane ring. Rotamer *I* is  $0.9(6)$  kJ mol $^{-1}$  more stable than *II*. The microwave work has been assisted by *ab initio* computations at the 6-31G\*\* level of theory.

Twenty-five years ago infrared spectroscopic studies of solutions<sup>1,2</sup> showed that intramolecular hydrogen (H) bonding is important in  $\alpha$ -hydroxycyclopropane derivatives. In these compounds, the pseudo- $\pi$ -electrons<sup>3</sup> present along the edges of the cyclopropane ring can act as a proton acceptor and the  $\alpha$ -hydroxyl group can act as a proton donor.

The simplest example of this kind of molecule is (hydroxymethyl)cyclopropane. Microwave (MW) studies of this<sup>4</sup> and its congener 1-cyclopropaneethanol<sup>5</sup> have shown that their preferred conformers are indeed stabilized with an internal H bond of this kind.

In the title compound there are two possibilities for such an H bond, as shown in Figs. 1 and 2. In conformer *I*, the H bond is formed with the pseudo- $\pi$ -electrons along the C2–C3 (Fig. 1) edge, while in *II* the pseudo- $\pi$ -electrons on the outside of the C2–C4 bond are involved in internal H bonding. The hydroxyl group is relatively near to the methyl group in *II*, and remote from this group in *I*. There is no steric strain between the two said groups in either rotamer, so this factor is supposed to be of no significance for the conformational preferences of the compound under study. However, the methyl group may contribute to the conformational make-up in another way, because this group may influence the electron density along the edges of the cyclopropyl ring. The methyl group may donate, or withdraw pseudo- $\pi$ -electrons from the edges of the ring. Any significant changes in the electron density might thus influence the H bond strength, resulting in *relatively* in-

creased stability of either *I* or *II*. For example, if the methyl group *withdraws* the pseudo- $\pi$ -electrons of the ring, *I* is presumed to become more stable than *II* because the electron density now has become larger along the C2–C3 bond than along the C2–C4 bond. If the methyl group *donates* electron density to the pseudo- $\pi$ -electrons, conformer *II* should become the more stable because the electron density on the outside of the C2–C4 bond becomes larger than on the outside of the C2–C3 bond. The electron donating or withdrawing properties of the methyl group are not expected to be very great. No great energy difference was therefore expected between conformers *I* and *II* of *trans*-2-methylcyclopropanemethanol, as was indeed found in this work.

## Experimental

The sample used in this work was purchased from Aldrich-Chemie, Steinheim, Germany. The commercial sample contained about 10 % *cis* and 90 % *trans*-2-methylcyclopropanemethanol. The *trans* isomer was separated from the *cis* isomer using preparative gas chromatography. The spectrum was studied employing the Oslo spectrometer, which is described in Ref. 6. The 24.0–39.5 GHz spectral region was investigated with the microwave absorption cell cooled to about  $-15^{\circ}\text{C}$ . Lower temperatures, which would have increased the MW spectral intensities, could not be employed owing to insufficient vapour pressure of the compound. The pressure was about 2–3 Pa, and the accuracy of the spectral measurements is presumed to be better than

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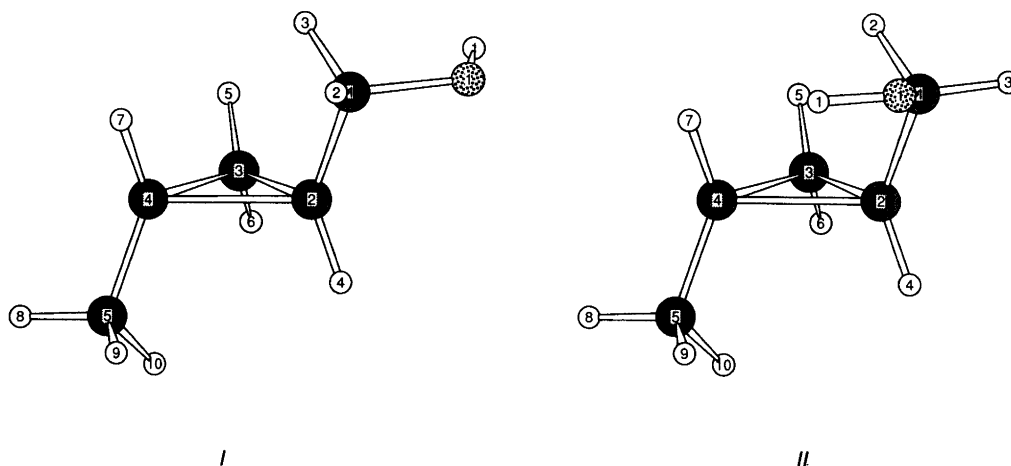


Fig. 1. The two H-bonded conformers (with atom numbering) that are possible for *trans*-2-methylcyclopropanemethanol. Conformer *I* was found to be 0.9(6) kJ mol<sup>-1</sup> more stable than *II*.

±0.10 MHz. The deuteration of the hydroxyl group was achieved by conditioning the MW cell with heavy water and then introducing the normal species.

## Results

**Ab initio calculations.** A large number of conformers is possible for *trans*-2-methylcyclopropanemethanol. A full mapping of the potential surface of this molecule using high-level basis functions is beyond our present possibilities. The calculations were therefore restricted to rotamers *I* and *II* because these two forms are expected to be the low-energy rotamers of the molecule, as previous findings indicate.<sup>1-5</sup> The computations were made using the Gaussian 90 program package<sup>7</sup> running on the Cray-X-MP/216 computer in Trondheim. The 6-31G\*\* basis set was chosen, and the geometries of conformers *I* and *II* were completely optimized by the gradient method<sup>8</sup> included in the standard calculation package.<sup>7</sup> The fully optimized structures of *I* and *II* are given in Table 1. Further parameters of interest are listed in Table 2; some results are also given in the text below. It is seen in Table 2 that *I* was calculated to be 0.3 kJ mol<sup>-1</sup> more stable than rotamer *II*. Bond distances, angles and dihedral angles not connected with the conformational problem are calculated to be rather similar in *I* and *II* (Table 1), as one would expect.

**MW spectrum and assignment of conformer I.** According to the theoretical predictions (Table 2) conformer *I* was predicted to have a rather large *a*-axis dipole moment component. The strongest transitions expected for this conformer were thus the *a*-type *R*-branch lines. These transitions were readily assigned, and some of them\* are found in Table 3.

\* The complete spectra of the parent and deuterated species are available from the authors upon request, or from The National Institute of Standards and Technology, Microwave Data Center, Molecular Physics Division, Bldg. 221, Rm. B265, Gaithersburg, MD 20899, USA, where they have been deposited.

These lines are quite weak. For example, the low- $K_{-1} J = 8 \leftarrow 7$  transitions have peak absorption coefficients of roughly  $7 \times 10^{-8}$  cm<sup>-1</sup>.

Searches for *b*-type transitions were made next, and the strongest of the <sup>*b*</sup>*Q*-lines were identified, as shown in the same table. These transitions were even weaker (roughly 1/3) than the <sup>*a*</sup>*R*-type lines referred to above. The hypothetical frequencies of the strongest ones of the <sup>*c*</sup>*Q*-transitions could now be predicted accurately, and some of them were measured. These transitions were about 50% as intense as the *b*-type *Q*-branch lines. The spectroscopic constants (*A*-reduction *F*-representation)<sup>11</sup> are collected in Table 4.

The ground-state transitions were accompanied by satellite lines presumably originating from vibrationally excited states of this conformer. Only one such excited state was measured owing to the weakness of the spectrum. The spectroscopic constants of this excited state, which is presumed to be the first excited state of the C1-C2 torsional vibration, are shown in Table 5. Relative intensity measurements<sup>12</sup> yielded 109(20) cm<sup>-1</sup> for this fundamental mode, as compared to 112 cm<sup>-1</sup> calculated above by *ab initio* methods, but not reported in Table 1 or 2.

The hydroxyl-group deuterated species was studied in order to locate exactly the position of the H atom of the said group using Kraitchman's equations.<sup>10</sup> The assignments were again made in a straightforward manner for the <sup>*a*</sup>*R*-transitions; the <sup>*b*</sup>*Q*- and <sup>*c*</sup>*Q*-lines were too weak to be assigned with certainty. The spectroscopic constants are

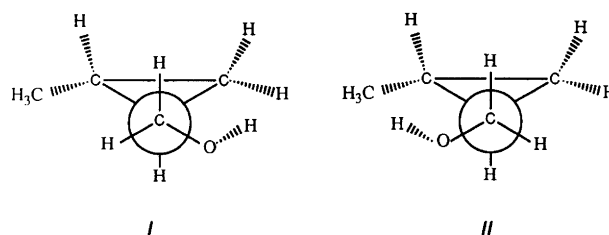


Fig. 2. The two H-bonded conformers of *trans*-2-methylcyclopropanemethanol viewed along the C1-C2 bond.

Table 1. Structure of conformer *I* and *II* of trans-2-cyclopropanemethanol as calculated by *ab initio* methods using the 6-31G\*\* basis set.

Distances/pm			Angles/°			Dihedral angles <sup>a/°</sup>		
	<i>I</i>	<i>II</i>		<i>I</i>	<i>II</i>		<i>I</i>	<i>II</i>
O1–H1	94.4	94.3	H1–O1–C1	109.0	109.1	H1–O1–C1–H2	175.9	66.5
C1–O1	140.2	140.2	O1–C1–H2	106.0	110.8	H1–O1–C1–H3	–68.0	182.5
C1–H2	108.4	108.4	O1–C1–H3	110.8	106.0	H1–O1–C1–C2	55.3	–56.8
C1–H3	109.0	109.0	O1–C1–C2	112.5	112.6	O1–C1–C2–C3	–84.6	156.3
C1–C2	150.8	150.8	C1–C2–C3	120.0	120.1	O1–C1–C2–C4	–155.3	85.6
C2–C3	150.5	149.9	C1–C2–C4	120.7	120.6	O1–C1–C2–H4	59.1	–59.0
C2–C4	149.5	150.1	C1–C2–H4	113.7	113.7	C1–C2–C3–H5	–2.6	–1.9
C3–C4	149.9	149.8	C2–C3–H5	118.3	118.2	C1–C2–C4–H6	141.8	141.8
C2–H4	107.9	107.9	C2–C3–H6	118.2	118.0	C1–C2–C3–H7	3.5	3.9
C3–H5	107.8	107.7	C2–C4–H7	115.5	115.6	C1–C2–C4–C5	–140.6	–140.8
C3–H6	107.7	107.7	C2–C4–C5	120.8	120.9	C2–C4–C5–H8	–155.7	–154.8
C4–H7	107.9	108.0	C4–C5–H8	111.0	111.1	C2–C4–C5–H9	84.4	85.0
C4–C5	151.2	151.2	C4–C5–H9	111.1	111.3	C2–C4–C5–H10	–35.8	–34.9
C5–H8	108.6	108.6	C4–C5–H10	111.1	110.0			
C5–H9	108.6	108.7						
C5–H10	108.6	108.6						

Hydrogen-bond parameters<sup>b</sup>

Conformer <i>I</i>				Conformer <i>II</i>			
Distances/pm		Angles/°		Distances/pm		Angles/°	
H1...C2	255.9	O1–H1...C2	70.9	H1...C2	257.3	O1–H1...C2	70.2
H1...C3	300.4	O1–H1...C3	99.8	H1...C2	303.6	O1–H1...C4	98.8
O1...C3	329.8	O1–H1,C2–C3 <sup>c</sup>	26.1	O1...C3	331.4	O1–H1, C2–C3 <sup>d</sup>	27.0

Sum of van der Waals radii<sup>e</sup>

H...C <sub>ring</sub> <sup>f</sup>	290
C <sub>ring</sub> <sup>f</sup> ...O	310

Substitution coordinates<sup>g</sup> of hydroxyl group hydrogen atom/pm

	Conformer <i>I</i>			Conformer <i>II</i>		
	a	b	c	a	b	c
Calc. from rotational constants	234.72(3) <sup>h</sup>	94.26(8) <sup>h</sup>	30.5(3) <sup>h</sup>	164.05(5) <sup>i</sup>	142.62(6) <sup>i</sup>	42.7(2) <sup>i</sup>
From <i>ab initio</i> <sup>a</sup>	248.8	89.6	27.2	172.1	148.7	42.5

<sup>a</sup>Measured from *syn*. <sup>b</sup>Calculated from the structure above. <sup>c</sup>Angle between the O1–H1 and C2–C3 bonds. <sup>d</sup>Angle between the O1–H1 and C2–C4 bonds. <sup>e</sup>Ref. 9. <sup>f</sup>The van der Waals radius of carbon has been assumed to be 170 pm, as for the half-thickness in aromatic molecules. <sup>g</sup>Employing Kraitchman's equations. <sup>h</sup>Reported in Table 4 below. <sup>i</sup>Reported in Table 7 below.

collected in Table 4, whereas Kraitchman's substitution coordinates<sup>10</sup> are reported in Table 1. These coordinates are very different from those of the two other conformations that have a staggered hydroxyl group, and show beyond doubt that the hydroxyl-group H atom is directed towards the pseudo- $\pi$ -electrons of the C2–C3 bond. A similar finding was made for *II* below.

The dipole moment could not be determined for either *I* or *II* because the transitions are too weak.

**Assignment of conformer *II*.** This conformer was predicted (Table 2) to possess a rather large dipole moment component along the *a*-principal inertial axis. The <sup>a</sup>*R*-branch tran-

sitions were readily assigned, and are presented in Table 6. These lines were as weak as the *a*-type *R*-branch lines belonging to *I*. No *b*- or *c*-type transitions were assigned, presumably because they are very weak. This is probably a result of relatively small dipole moment components along the corresponding principal inertial axis, as the computations (Table 2) also indicate. The rotational constants derived from the transitions in Table 6 are listed in Table 7.

One vibrationally excited state, presumably the C1–C2 torsional vibration, was assigned. Its rotational constants are shown in Table 8. The torsional frequency was found to be 106(20) cm<sup>–1</sup>, which is similar to that of *I*, as expected. The *ab initio* value was 118 cm<sup>–1</sup>. The assignment of the

Table 2. Selected parameters obtained in the *ab initio* calculations with the 6-31G\*\* basis set.

Energy difference <sup>a</sup> : $E_{II} - E_I = 0.3 \text{ kJ mol}^{-1}$		
	Conformer I	Conformer II
Rotational constants/MHz		
A	9471.7	6519.0
B	1864.9	2234.6
C	1727.4	1827.5
Dipole moments <sup>b</sup> /10 <sup>-30</sup> C m		
$\mu_a$	5.41	5.86
$\mu_b$	2.93	0.76
$\mu_c$	1.93	2.59

<sup>a</sup>The total energy of conformer I was calculated to be  $-543\,454.64 \text{ kJ mol}^{-1}$ . <sup>b</sup>Components of the total dipole moment along the principal inertial axes. 1 debye =  $3.335\,64 \times 10^{-30} \text{ C m}$ .

deuterated species was straightforward; its rotational constants are given in Table 7.

**Internal energy difference.** The internal energy difference between conformers I and II was determined by relative intensity measurements, observing the precautions of Ref. 12. The strongest ones of the *a*-type *R*-branch transitions of both rotamers were used for this purpose. The  $\mu_a$  dipole moments components of Table 2 were used, since no experimental values are available. In this manner an internal energy difference of  $0.9(6) \text{ kJ mol}^{-1}$  was determined with I as the most stable conformer. The uncertainty, which represents one standard deviation, was estimated to be  $\pm 0.6 \text{ kJ mol}^{-1}$ . It is not easy to estimate this uncertainty, because many factors contribute to it. The *ratio* of the *a*-axis dipole moment components is used in the derivation of the energy difference, and it is presumed that the theoretical ratio taken from Table 2 is accurate to within 15%. Uncertainties associated with the base line contribute another 10–20% to the peak absorption intensities. The line breadths are uncertain by 20%. There are also other sources of uncertainty. In the estimate of the standard deviation of  $\pm 0.6 \text{ kJ mol}^{-1}$  efforts have been made to treat all these sources of error in a realistic manner.

**Structure.** The experimental rotational constants shown in Tables 4 and 7 are close to the calculated ones shown in Table 2. The substitution coordinates for the hydroxyl group H atom shown in Table 1 are also fairly close to the experimental ones listed in the same table. Moreover, the calculated structural parameters of Table 2 are close to experimental counterparts found in closely related molecules.<sup>13</sup> It is therefore presumed that the theoretical structure is a good approximation to the real structure.

The theoretical structures of I and II (Table 1) reveal quite ordinary bond angles, distances and dihedral angles, which may reflect that no important or unusual strain is

involved in either conformer. It is noted, however, that the H1–O1–C1–C2 dihedral angle in both rotamers is calculated to be about 5° smaller than the ordinary *gauche* ( $\pm 60^\circ$ ) angle. This decrease will bring the hydroxyl-group H atom into closer proximity with the pseudo- $\pi$ -electrons, thereby strengthening the H bond.

Table 3. MW spectrum of the ground vibrational state of conformer I of *trans*-2-methylcyclopropanemethanol.

Transition	Observed frequency <sup>a</sup> /MHz	Obs.–calc. freq./MHz
7 <sub>0,7</sub> ← 6 <sub>0,6</sub>	24 996.64	0.01
7 <sub>1,6</sub> ← 6 <sub>1,5</sub>	25 544.92	0.09
7 <sub>1,7</sub> ← 6 <sub>1,6</sub>	24 599.86	0.08
7 <sub>2,5</sub> ← 6 <sub>2,4</sub>	25 180.99	-0.03
7 <sub>2,6</sub> ← 6 <sub>2,5</sub>	25 081.81	-0.03
7 <sub>3,5</sub> ← 6 <sub>3,4</sub>	25 109.75	0.12
7 <sub>6,1</sub> ← 6 <sub>6,0</sub>	25 100.16	-0.05
7 <sub>6,2</sub> ← 6 <sub>6,1</sub>	25 100.16	-0.05
8 <sub>0,8</sub> ← 7 <sub>0,7</sub>	28 533.11	0.01
8 <sub>1,7</sub> ← 7 <sub>1,6</sub>	29 184.24	0.00
8 <sub>2,6</sub> ← 7 <sub>2,5</sub>	28 806.62	0.00
8 <sub>3,5</sub> ← 7 <sub>3,4</sub>	28 703.95	-0.08
8 <sub>4,4</sub> ← 7 <sub>4,3</sub>	28 693.08	-0.04
8 <sub>4,5</sub> ← 7 <sub>4,4</sub>	28 693.08	0.00
8 <sub>5,3</sub> ← 7 <sub>5,2</sub>	28 689.10	0.00
8 <sub>5,4</sub> ← 7 <sub>5,3</sub>	28 689.10	0.00
8 <sub>7,1</sub> ← 7 <sub>7,0</sub>	28 685.42	-0.02
8 <sub>7,2</sub> ← 7 <sub>7,1</sub>	28 685.42	-0.02
9 <sub>0,9</sub> ← 8 <sub>0,8</sub>	32 056.87	-0.01
9 <sub>1,8</sub> ← 8 <sub>1,7</sub>	31 608.82	0.05
9 <sub>2,8</sub> ← 8 <sub>2,7</sub>	32 233.52	-0.06
9 <sub>3,6</sub> ← 8 <sub>3,5</sub>	32 298.89	-0.08
9 <sub>4,5</sub> ← 8 <sub>4,4</sub>	32 282.61	-0.10
9 <sub>4,6</sub> ← 8 <sub>4,5</sub>	32 282.61	-0.02
9 <sub>6,3</sub> ← 8 <sub>6,2</sub>	32 273.93	0.00
9 <sub>6,4</sub> ← 8 <sub>6,3</sub>	32 273.93	0.00
9 <sub>8,1</sub> ← 8 <sub>8,0</sub>	32 271.97	0.01
9 <sub>8,2</sub> ← 8 <sub>8,1</sub>	32 271.97	0.01
10 <sub>0,10</sub> ← 9 <sub>0,9</sub>	35 567.40	0.03
10 <sub>2,9</sub> ← 9 <sub>2,8</sub>	35 805.57	0.04
10 <sub>7,3</sub> ← 9 <sub>7,2</sub>	35 858.74	-0.03
10 <sub>7,4</sub> ← 9 <sub>7,3</sub>	35 858.74	-0.03
11 <sub>0,11</sub> ← 10 <sub>0,10</sub>	34 448.16	0.04
11 <sub>2,10</sub> ← 10 <sub>2,9</sub>	39 374.47	-0.03
16 <sub>3,13</sub> ← 16 <sub>2,14</sub>	35 325.01	0.04
17 <sub>3,15</sub> ← 17 <sub>2,15</sub>	34 165.59	-0.03
19 <sub>3,17</sub> ← 19 <sub>2,17</sub>	32 363.44	-0.03
21 <sub>3,18</sub> ← 21 <sub>2,19</sub>	32 061.19	-0.02
23 <sub>3,20</sub> ← 23 <sub>2,21</sub>	30 832.50	0.03
26 <sub>3,23</sub> ← 26 <sub>2,24</sub>	29 534.61	0.00
29 <sub>2,27</sub> ← 29 <sub>1,28</sub>	33 219.31	0.02
31 <sub>2,29</sub> ← 31 <sub>1,30</sub>	37 601.28	-0.01
34 <sub>3,31</sub> ← 34 <sub>2,32</sub>	32 139.90	0.02
36 <sub>3,33</sub> ← 36 <sub>2,34</sub>	34 569.62	0.02
38 <sub>3,35</sub> ← 38 <sub>2,36</sub>	37 750.42	-0.02
40 <sub>4,36</sub> ← 40 <sub>3,37</sub>	38 638.49	0.00
42 <sub>4,38</sub> ← 42 <sub>3,39</sub>	38 780.49	0.01
51 <sub>5,47</sub> ← 51 <sub>4,47</sub>	34 881.73	-0.11
53 <sub>5,49</sub> ← 53 <sub>4,49</sub>	30 343.26	0.01

<sup>a</sup> $\pm 0.10 \text{ MHz}$ .

Table 4. Ground-state spectroscopic constants<sup>a,b</sup> of conformer *I* of *trans*-2-methylcyclopropanemethanol.

Species:	Parent	Deuterated <sup>c</sup>
No. of transitions:	109	54
R.m.s. deviation <sup>d</sup> /MHz:	0.041	0.031
$A_0$ /MHz	9461.9172(69)	9296.20(52)
$B_0$ /MHz	1860.2182(12)	1822.7120(19)
$C_0$ /MHz	1724.9368(12)	1688.2361(19)
$\Delta_J$ /kHz	0.1927(68)	0.1916(69)
$\Delta_{JK}$ /kHz	1.2306(87)	1.128(12)
$\Delta_K$ /kHz	15.15(72)	15.15 <sup>e</sup>
$\delta_J$ /kHz	0.013416(58)	0.013416 <sup>e</sup>
$\delta_K$ /kHz	0.623(11)	0.623 <sup>e</sup>

<sup>a</sup>A-reduction, *J*-representation.<sup>10</sup> <sup>b</sup>Uncertainties represent one standard deviation. <sup>c</sup>Deuteration has taken place in the hydroxyl group. <sup>d</sup>Root-mean-square deviation. <sup>e</sup>Fixed at this value in the least-squares fit.

Table 5. Spectroscopic constants<sup>a,b</sup> of the parent species of conformer *I* of *trans*-methylcyclopropanemethanol in the first excited state of the lowest torsional vibration.

No. of transitions:	61
R.m.s. deviation <sup>c</sup> /MHz:	0.033
$A_v$ /MHz	9358.6151(84)
$B_v$ /MHz	1860.7298(19)
$C_v$ /MHz	1725.3267(19)
$\Delta_J$ /kHz	0.178(11)
$\Delta_{JK}$ /kHz	1.036(22)
$\Delta_K$ /kHz	7.0(14)
$\delta_J$ /kHz	0.01365(12)
$\delta_K$ /kHz	0.388(23)

<sup>a,b</sup>Comments as for Table 4. <sup>c</sup>Comments as for <sup>d</sup>in Table 4.

## Discussion

*trans*-2-Methylcyclopropanemethanol takes the two expected H-bonded conformations *I* and *II* (Figs. 1 and 2) as its most stable rotamers. The energy difference is small, as expected. *I* tends to be slightly more stable than *II*, although this cannot be claimed with certainty because the energy difference of 0.9 kJ mol<sup>-1</sup> is only slightly larger than one standard deviation ( $\pm 0.6$  kJ mol<sup>-1</sup>). The methyl group thus appears to have little influence on the pseudo- $\pi$ -electrons of the ring in the present case. The tendency that *I* is more stable than *II* perhaps indicates that the methyl group slightly withdraws pseudo- $\pi$ -electrons from the ring. This is the opposite of what one would expect. Interestingly, the *ab initio* method also predicts *I* to be more stable than *II* by about 0.3 kJ mol<sup>-1</sup>.

Table 6. MW spectrum of the ground vibrational state of conformer *II* of *trans*-2-methylcyclopropanemethanol.

Transition	Observed frequency <sup>a</sup> /MHz	Obs. - calc. freq./MHz
6 <sub>0,6</sub> ← 5 <sub>0,5</sub>	23 567.36	-0.13
6 <sub>1,5</sub> ← 5 <sub>1,4</sub>	25 430.55	0.10
6 <sub>1,6</sub> ← 5 <sub>1,5</sub>	23 019.30	-0.07
6 <sub>2,4</sub> ← 5 <sub>2,3</sub>	25 220.59	0.11
6 <sub>2,5</sub> ← 5 <sub>2,4</sub>	24 329.46	-0.02
6 <sub>3,3</sub> ← 5 <sub>3,2</sub>	24 658.24	0.01
6 <sub>3,4</sub> ← 5 <sub>3,3</sub>	24 587.56	0.06
7 <sub>0,7</sub> ← 6 <sub>0,6</sub>	27 232.07	-0.07
7 <sub>1,6</sub> ← 6 <sub>1,5</sub>	29 519.02	0.03
7 <sub>1,7</sub> ← 6 <sub>1,6</sub>	26 779.22	-0.13
7 <sub>2,5</sub> ← 6 <sub>2,4</sub>	29 610.57	0.06
7 <sub>2,6</sub> ← 6 <sub>2,5</sub>	28 311.73	0.04
7 <sub>3,4</sub> ← 6 <sub>3,3</sub>	28 861.67	0.01
7 <sub>4,4</sub> ← 6 <sub>4,3</sub>	28 680.91	0.02
7 <sub>5,2</sub> ← 6 <sub>5,1</sub>	28 642.17	-0.05
7 <sub>5,3</sub> ← 6 <sub>5,2</sub>	28 642.17	0.04
7 <sub>6,1</sub> ← 6 <sub>6,0</sub>	28 621.03	0.05
7 <sub>6,2</sub> ← 6 <sub>6,1</sub>	28 621.03	0.06
8 <sub>0,8</sub> ← 7 <sub>0,7</sub>	30 862.61	-0.03
8 <sub>1,7</sub> ← 7 <sub>1,6</sub>	33 524.35	-0.04
8 <sub>1,8</sub> ← 7 <sub>1,7</sub>	30 516.57	-0.02
8 <sub>2,6</sub> ← 7 <sub>2,5</sub>	33 996.88	-0.07
8 <sub>2,7</sub> ← 7 <sub>2,6</sub>	32 262.07	0.02
8 <sub>3,5</sub> ← 7 <sub>3,4</sub>	33 122.19	0.00
8 <sub>3,6</sub> ← 7 <sub>3,5</sub>	32 821.20	-0.03
8 <sub>4,4</sub> ← 7 <sub>4,3</sub>	32 828.28	-0.02
8 <sub>4,5</sub> ← 7 <sub>4,4</sub>	32 812.99	-0.01
8 <sub>6,2</sub> ← 7 <sub>6,1</sub>	32 726.04	0.00
8 <sub>6,3</sub> ← 7 <sub>6,2</sub>	32 726.04	0.01
8 <sub>7,1</sub> ← 7 <sub>7,0</sub>	32 707.69	-0.01
8 <sub>7,2</sub> ← 7 <sub>7,1</sub>	32 707.69	-0.01
9 <sub>0,9</sub> ← 8 <sub>0,8</sub>	34 483.00	0.11
9 <sub>1,9</sub> ← 8 <sub>1,8</sub>	34 234.35	0.17
9 <sub>2,8</sub> ← 8 <sub>2,7</sub>	36 177.96	0.05
9 <sub>3,6</sub> ← 8 <sub>3,5</sub>	37 450.52	-0.05
9 <sub>3,7</sub> ← 8 <sub>3,6</sub>	36 926.63	-0.07
9 <sub>4,5</sub> ← 8 <sub>4,4</sub>	36 992.01	-0.06
9 <sub>4,6</sub> ← 8 <sub>4,5</sub>	36 955.83	-0.02
9 <sub>6,3</sub> ← 8 <sub>6,2</sub>	36 837.66	-0.01
9 <sub>6,4</sub> ← 8 <sub>6,3</sub>	36 837.66	0.01
9 <sub>7,2</sub> ← 8 <sub>7,1</sub>	36 811.21	-0.01
9 <sub>7,3</sub> ← 8 <sub>7,2</sub>	36 811.21	-0.01
9 <sub>8,1</sub> ← 8 <sub>8,0</sub>	36 794.88	0.00
9 <sub>8,2</sub> ← 8 <sub>8,1</sub>	36 794.88	0.00

<sup>a</sup> $\pm 0.10$  MHz.

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Table 7. Ground-state spectroscopic constants<sup>a,b</sup> of conformer II of *trans*-2-methylcyclopropanemethanol.

Species:	Parent	Deuterated <sup>c</sup>
No. of transitions:	44	28
R.m.s. deviation <sup>d</sup> /MHz:	0.062	0.031
$A_0$ /MHz	6425.51(17)	6253.36(17)
$B_0$ /MHz	2245.2264(36)	2216.7807(46)
$C_0$ /MHz	1831.5883(41)	1800.8555(59)
$\Delta_J$ /kHz	0.816(21)	0.788(31)
$\Delta_{JK}$ <sup>e</sup> /kHz	-4.856(34)	-4.692(61)

<sup>a-d</sup>Comments as for Table 4. <sup>e</sup>Further quartic constants preset at zero.

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Table 8. Spectroscopic constants<sup>a,b</sup> of the parent species of conformer II of *trans*-methylcyclopropanemethanol in the first excited state of the lowest torsional vibration.

No. of transitions:	36
R.m.s. deviation <sup>c</sup> /MHz:	0.070
$A_v$ /MHz	6440.28(17)
$B_v$ /MHz	2241.1868(44)
$C_v$ /MHz	1831.0015(50)
$\Delta_J$ /kHz	0.670(27)
$\Delta_{JK}$ <sup>d</sup> /kHz	-4.496(39)

<sup>a,b</sup>Comments as for Table 7. <sup>c,d</sup>Comments as for <sup>d,e</sup>in Table 7.

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