

The heavy atom microwave structure of 2-methyltetrahydrofuran



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ABSTRACT

The rotational spectra of 2-methyltetrahydrofuran have been observed using a pulsed molecular beam Fourier transform microwave spectrometer operating in the frequency range 2–26.5 GHz. Conformational analysis using quantum chemical calculations yields two stable conformers; both of them possess an *envelope* structure. The conformational transformation can occur via two different transition states. The Cremer-Pople notation for five-membered rings is chosen for describing the conformations. Only one conformer with *equatorial* position of the methyl group is assigned in the experimental spectrum. The fits of its parent species, ¹³C- and ¹⁸O-isotopologues result in highly accurate molecular parameters, and enable the determination of a heavy atom *r_s* structure using Kraitchman's equations. This experimentally determined structure is in excellent agreement with the structure calculated by anharmonic frequency calculations.

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1. Introduction

Rotational spectroscopy in the gas phase has increasingly been applied to determine the structure of medium-sized molecules, which often exhibit complex conformational landscapes [1–3]. Since the traditional method by isotopic substitutions is not always possible, the support of quantum chemistry becomes a helpful tool, whereby *ab initio* structures can be taken as references for a comparison of the experimental and calculated molecular parameters. On the other hand, quantum chemical calculations at different levels of theory often differ in a wide range, whereas atomic positions determined by rotational spectroscopy are highly precise [4], in particular when using the molecular beam Fourier transform microwave (MB-FTMW) technique. With high sensitivity and excellent experimental accuracy, it is possible to observe singly substituted isotopologues such as ¹³C, ³⁴S, ¹⁵N, and ¹⁸O in natural abundances. Comparisons of experimentally and computationally derived molecular parameters can therefore validate the quality of various theoretical methods in characterizing the studied system.

In this paper, we will report on the heavy atom *r_s* structure of 2-methyltetrahydrofuran (MTHF) studied by MB-FTMW spectroscopy, and compare it with results from quantum chemistry. MTHF

is a promising environmentally friendly solvent and biofuel component, which is derived from renewable resources. Following the principles of Green Chemistry, MTHF has been evaluated as an eco-friendly substance in various fields like organometallics [5], metathesis [6], and biosynthesis [7].

The methyl group in MTHF exhibits internal rotation with a rather high barrier of 13.12 kJ mol⁻¹ (i.e. 1097 cm⁻¹) calculated at the CCSD(T)/6-311++G(d,p) level of theory. In the experimental spectrum, narrow torsional splittings only occur in a few transitions with high *J* values.

2. Quantum chemical calculations

2.1. Geometry optimizations

Several starting geometries of MTHF were created based on the structures of two conformers of cyclopentane used as a prototype [8]. Geometry optimizations were performed at the MP2/6-311++G(d,p) level of theory using the GAUSSIAN package [9]. This level was chosen, since it yielded rotational constants which were close to the experimental values for other heterocyclic molecules [10,11]. We only considered the (*S*)-configuration, because enantiomers cannot be distinguished using our technique. The geometry optimizations signified two *envelope* conformers, called the *equatorial* and the *axial* conformer. Harmonic frequency calculations at the same level of theory were also carried out to decide, whether

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the optimized geometries are true minima or saddle points. Anharmonic frequency calculations resulted in the quartic centrifugal distortion constants (shown in Table 1) and the rotational constants B_0 of the vibrational ground state. The equatorial conformer is illustrated in Fig. 1; the Cartesian coordinates of both conformers are also available in Table S-1 in the Electronic Supporting Information (ESI).

The envelope conformations can be described by the ring plane determined by the O, C₃, C₄, C₅ atoms, and the envelope flap determined either by C₂, O, C₃, C₄ or C₂, C₃, O, C₅, as depicted in Fig. 2. The dihedral angle $\phi = \angle(\text{O}, \text{C}_5, \text{C}_4, \text{C}_3)$ of the ring plane is zero and both angles $\gamma = \angle(\text{C}_2, \text{O}, \text{C}_3, \text{C}_4)$ and $\gamma' = \angle(\text{C}_2, \text{C}_3, \text{O}, \text{C}_5)$ of the envelope flap are equal, if the ring structure is not distorted.

Similar to the case of methylcyclopentane, the equatorial orientation of the methyl group is lower in energy than the axial orientation due to steric effects, where the hydrogen atoms in the methyl group are closer to the hydrogen atoms of the ring. The equatorial conformer was afterwards re-optimized at different levels of theory using the HF, DFT, MP2, and CCSD methods and various basis sets. The calculated rotational constants are listed in Table S-2 in the ESI. If not otherwise stated, all values given from now on will refer to the MP2/6-311++G(d,p) level of theory.

2.2. Transition states

Using the Berny algorithm [12], two transition states (called 2T_3 and E_1) were found. We notice that in both 2T_3 and E_1 , the ring structure is slightly distorted. The transition state energies were obtained from single-point calculations at the CCSD(T)/6-311++G(d,p) level of theory using the geometries optimized at the MP2/6-311++G(d,p) level. The envelope transition state E_1 is 2.00 kJ mol⁻¹ higher in energy than the twist configuration 2T_3 . Their Cartesian coordinates are also available in Table S-1. Fig. 3 indicates the intramolecular conversion between the stable conformers via 2T_3 and E_1 . Since 2T_3 is only 0.10 kJ mol⁻¹ higher in energy than the axial conformer, the barrier to convert the axial conformer in the equatorial conformer via 2T_3 is very low.

2.3. Cremer-Pople puckering parameters

The Cremer-Pople puckering parameters [13] for both conformers and the transition states are calculated using the program

Table 1

Experimentally deduced molecular parameters of the equatorial conformer of MTHF compared to the r_0 vibrational ground state values calculated by anharmonic frequency calculation at the MP2/6-311++G(d,p) level of theory.

Par. ^a	Unit	Fit 1 ($J \leq 15$)	MP2
A	GHz	6.59156823 (22)	6.5798
B	GHz	3.170370175 (84)	3.1425
C	GHz	2.367116054 (88)	2.3457
Δ_J	kHz	0.3312 (13)	0.257
Δ_{JK}	kHz	0.0641 (35)	0.761
Δ_K	kHz	2.855 (20)	0.849
δ_J	kHz	0.05881 (44)	0.057
δ_K	kHz	0.5322 (69)	0.561
H_{JK}	Hz	-0.788 (96)	$-0.163 \cdot 10^{-3}$
H_{KJ}	Hz	2.83 (35)	$0.111 \cdot 10^{-3}$
h_{JK}	Hz	0.331 (46)	$0.059 \cdot 10^{-3}$
h_K	Hz	-2.84 (55)	$2.367 \cdot 10^{-3}$
σ^b	kHz	2.2	
N^c		111	

^a All parameters refer to the principal axis system. Watson's A reduction in I^r representation was used.

^b Standard deviation of the fit.

^c Number of lines.

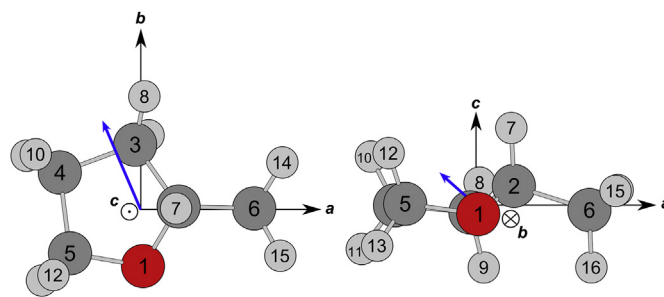


Fig. 1. The optimized geometry in the principal axes of inertia of the most stable conformer of MTHF calculated at the MP2/6-311++G(d,p) level of theory. Left-hand side: view along the c -axis; right-hand side: view along the b -axis. The circled dot and cross indicate that the axis direction points out of and into the paper plane, respectively. The blue arrow presents the dipole moment vector.

RING [14] to characterize the ring geometries in more detail. The conformational space for a five-membered ring has two dimensions defined by the puckering amplitude q_2 and the phase angle φ_2 [13]. The orientation of the methyl group as a ring substituent is described by the angle α between the mean plane of the puckered ring and the bond of the methyl group [15]. Fig. 4 illustrates possible conformations based on the model of Altona and Sundaralingam [16]. The calculated as well as the experimental geometry of the equatorial conformer has an envelope structure E_2 with significant contribution of the twist structure 1T_2 , and the methyl substituent in equatorial orientation with $q_2 = 0.39$, $\varphi_2 = 32.4^\circ$, and $\alpha = 67.7^\circ$ as well as $q_2 = 0.40$, $\varphi_2 = 27.48^\circ$, and $\alpha = 68.5^\circ$, respectively. The axial conformer is a 1:1 mixture of the envelope structure 2E and the twist structure 2T_3 and has the methyl substituent in axial orientation with $q_2 = 0.38$, $\varphi_2 = 226.6^\circ$, and $\alpha = 10.1^\circ$. The axial orientation is higher in energy than the equatorial orientation due to steric effects. The lower energy transition state 2T_3 has a more pronounced twist structure with $q_2 = 0.38$, $\varphi_2 = 242.4^\circ$, and $\alpha = 13.1^\circ$, whereas the transition state E_1 has an envelope structure with $q_2 = 0.36$, $\varphi_2 = 179.5^\circ$, and $\alpha = 17.1^\circ$. In both of them, the methyl group is in axial orientation.

3. Microwave spectroscopy

3.1. Measurements

MTHF was purchased from Alfa Aesar GmbH & Co. KG, Karlsruhe, Germany with a stated purity of 99% and stabilized with approximately 150–400 ppm BHT (butylated hydroxytoluene). Additional purification was not necessary, since the vapor pressure of BHT is too low for an observation in the gas phase under the

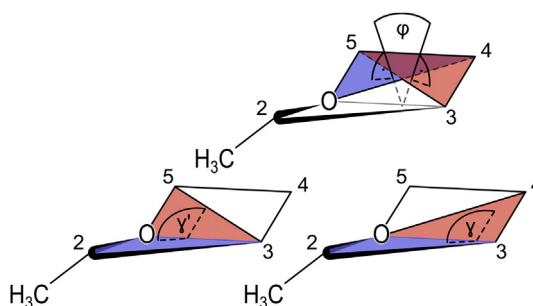


Fig. 2. The envelope conformation is described by the dihedral angles angle $\phi = \angle(\text{O}, \text{C}_5, \text{C}_4, \text{C}_3)$ of the ring plane and two angles $\gamma = \angle(\text{C}_2, \text{O}, \text{C}_3, \text{C}_4)$ and $\gamma' = \angle(\text{C}_2, \text{C}_3, \text{O}, \text{C}_5)$, which describe the envelope flap. If the ring structure is not distorted, $\phi = 0$ and $\gamma = \gamma'$.

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