

Microwave spectrum of 2,6-dimethylcyclohexanone



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ABSTRACT

The rotational spectrum of 2,6-dimethylcyclohexanone (DMCHO) was measured in the frequency region from 6 to 12 GHz. Among three possible conformational isomers, two conformers were identified where two methyl groups are aligned in the equatorial/equatorial (**ee**) and the equatorial/axial (**ea**) positions. Both *b*-type and *c*-type transitions for (e,e)-2,6-DMCHO, and *a*-type, *b*-type, and *c*-type transitions for (e,a)-2,6-DMCHO were assigned to determine the rotational constants and quartic centrifugal distortion constants based on the Watson-A reduction Hamiltonian: (**ee**) $A = 2150.95789(48)$ MHz, $B = 1578.76212(40)$ MHz, $C = 990.19141(45)$ MHz, $\Delta_J = 0.086(11)$ kHz, $\Delta_{JK} = -0.134(20)$ kHz, $\Delta_K = 0.298(15)$ kHz, $\delta_J = 23.4(24)$ Hz, and $\delta_K = 101.4(77)$ Hz; and (**ea**) $A = 2082.62538(83)$ MHz, $B = 1566.59564(59)$ MHz, $C = 1113.90153(75)$ MHz, $\Delta_J = 0.066(23)$ kHz. In addition, dipole moment components of the two isomers were determined by Stark effect measurements: (**ee**) $\mu_b = 2.6673(12)$ D, $\mu_c = 1.0379(11)$ D, $\mu_{total} = 2.8621(12)$ D; and (**ea**) $\mu_a = 1.385(253)$ D, $\mu_b = 2.358(104)$ D, $\mu_c = 1.172(21)$ D, $\mu_{total} = 2.975(144)$ D. *Ab initio* calculations for all three isomers were compared with each other and with experimental results.

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1. Introduction

Cyclohexane and its derivatives are well-known carbocyclic ring systems in stereochemistry and conformational analysis, and constitute a large part of modern organic chemistry [1]. Analogous to those of cyclohexane, cyclohexanone conformations have been of interest and investigated by various methods including microwave [2], electron diffraction [3], NMR [4], and computational [5,6] analyses. The stable conformer of both cyclohexane and cyclohexanone is the chair form. Thus, we supposed that all the conformers of 2,6-dimethylcyclohexanones are in the chair form.

Conformational analysis of alkyl substituted cyclohexanones [7,8] based on microwave spectroscopy initially was performed by comparing the experimentally determined rotational constants to calculated ones for all possible conformers to determine the most stable conformer. The microwave spectra of 2-, 3-, and 4-methylcyclohexanone [9–12] were further studied along with structural analysis through *ab initio* calculations, and dipole moment components were derived from observing frequency shifts due to the Stark effect.

2,6-Dimethylcyclohexanone (DMCHO) is a volatile organic compound (VOC) [13] and a good reagent in stereoselective total synthesis [14]. Its stereochemistry has been investigated by

analyzing the proportion of alcohol products after NaBH_4 reduction using GC–MS and NMR [15–17]. This is a well-developed green chemistry method [18], but the ratio of alcohol products can vary depending on the kind of solvent. This suggests that there is a need to study the conformations of 2,6-DMCHO in an environment without solvents. Its *cis* and *trans* isomers have shown different performances in chemical reactions such as asymmetric deprotonation [19].

To the authors' knowledge, this is the first microwave study on 2,6-dimethylcyclohexanone. We have observed the rotational spectra of two conformers, (e,e)-2,6-dimethylcyclohexanone and (e,a)-2,6-dimethylcyclohexanone, among the three possible conformers shown in Fig. 1. Rotational constants and centrifugal distortion constants were determined by fitting rotational transition frequencies to the Watson A-reduction Hamiltonian in I' representation and by comparing with *ab initio* values. In addition, Stark effect measurements for both conformers were performed to determine each dipole moment.

2. Methods

The rotational spectra of gaseous 2,6-dimethylcyclohexanone were measured using a Fourier Transform Microwave Spectrometer (FTMS) with a pulsed gas nozzle, as described previously [20–22]. The sample was purchased from Aldrich Chemical Company. About 1–2 atm of Ar gas was bubbled through a liquid sample of

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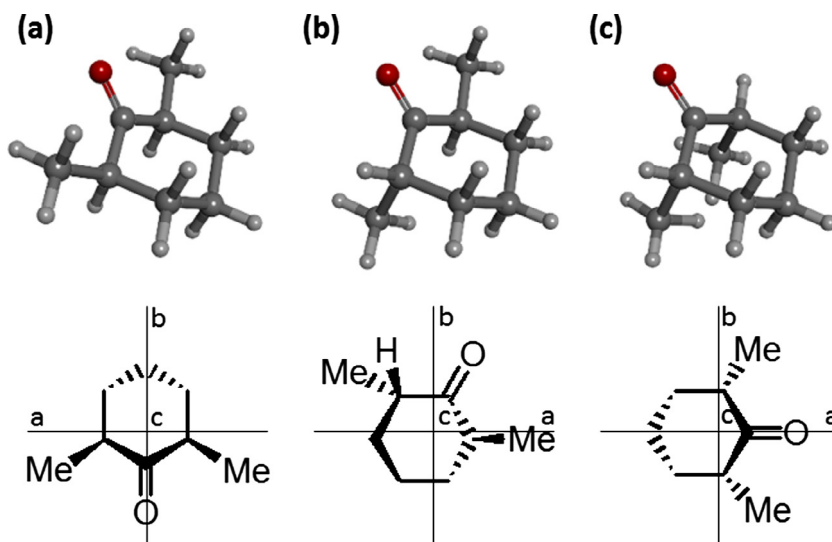


Fig. 1. Three possible conformers of 2,6-dimethylcyclohexanone (DMCHO) with principal axes of *ab initio* results: (a) (e,e)-2,6-DMCHO, (b) (e,a)-2,6-DMCHO, and (c) (a,a)-2,6-DMCHO.

2,6-dimethylcyclohexanone placed just upstream of a pulsed gas valve, and the nozzle was positioned perpendicular to the microwave cavity axis. The center frequencies were reproducible to ± 2 kHz and typical linewidths of about 20 kHz (FTMW) from Doppler broadening were observed. For the Stark electric field, two parallel plates supplied DC voltages of up to 8 kV. The calibration of the electric field was performed based on the frequency shift of the $\Delta M_j = 0$ component of the OCS $J = 0-1$ transition [23] with the dipole moment of OCS being 0.71519(3) D [24,25]. All spectroscopic fits were carried out using the Pickett's SPCAT/SPFIT packages [26], in accordance with Watson A-reduction Hamiltonian in the I' representation [27]. For comparison, *ab initio* optimization and single point energy calculations were performed for each conformer at the MP2/6-31 + G(d,p) or MP2/6-311++G(2d,2p) level using Gaussian 03 [28].

3. Results and discussion

It is known that 1,3-dimethylcyclohexane (DMC) has two stereoisomers: *cis*-1,3-DMC and *trans*-1,3-DMC. The *cis*-1,3-DMC has both methyl (Me) groups in either the equatorial positions or in the axial positions, while *trans*-1,3-DMC has one equatorial Me group and one axial Me group. In *cis* isomers, the di-equatorial (**ee**) conformer is more stable than the di-axial (**aa**) conformer because the **aa** conformer costs more energy with one Me/Me 1,3-diaxial interaction (3.7 kcal/mol) and two Me/H 1,3-diaxial interactions (1.8 kcal/mol) [29].

Likewise, it is expected that 2,6-dimethylcyclohexanone (DMCHO) has three possible conformers in the chair conformation: **ee**, **ea**, and **aa** conformers (Fig. 1). *cis*-2,6-DMCHO includes the **ee** conformer, which has both Me groups in equatorial positions, and the **aa** conformer, which has both Me groups in axial positions. *trans*-2,6-DMCHO has one equatorial Me group and one axial Me group, referred to as the **ea** (or **ae**) conformer. The **ee** conformer of *cis*-2,6-DMCHO is also expected to be more stable than the **aa** conformer, because the **aa** conformer can have interactions like the 1,3-diaxial interactions in *cis*-1,3-DMC.

Relative energies of the equilibrium structures for all three conformers were calculated using Gaussian 03 [28] with second-order Møller-Plesset (MP2) perturbation theory (Table 1) and the 6-31 + G(d,p) and 6-311++G(2d,2p) basis sets. Both results show that the **ee** conformer is most stable, and the **ea** conformer is less stable

Table 1
Spectroscopic constants for 2,6-dimethylcyclohexanone.

	(e,e)-2,6-DMCHO	(e,a)-2,6-DMCHO	(a,a)-2,6-DMCHO
<i>MP2/6-31+G(d,p)</i>			
A (calc, MHz) ^a	2157.	2085.	1786.
B (calc, MHz) ^a	1581.	1569.	1773.
C (calc, MHz) ^a	995.	1119.	1258.
κ (Kappa) ^b	0.009	-0.069	0.950
E(kcal/mol) ^a	-243050.25162	-243048.58466	-243046.09994
ΔE (kcal/mol) ^a	0.00	1.67	4.15
<i>MP2/6-311++G(2d,2p)</i>			
A (calc, MHz) ^a	2171.	2101.	1799.
B (calc, MHz) ^a	1587.	1571.	1776.
C (calc, MHz) ^a	1001.	1130.	1274.
κ (Kappa) ^b	0.002	-0.092	0.910
E(kcal/mol) ^a	-243192.68753	-243191.03097	-243188.47857
ΔE (kcal/mol) ^a	0.00	1.66	4.21
A (MHz)	2150.95789(48)	2082.62538(83)	
B (MHz)	1578.76212(40)	1566.59564(59)	
C (MHz)	990.19141(45)	1113.90153(75)	
Δ_j (kHz) ^a	0.086(11)	0.066(23)	
Δ_{jk} (kHz) ^a	-0.134(20)		
Δ_k (kHz) ^a	0.298(15)		
δ_j (Hz) ^a	23.4(24)		
δ_k (Hz) ^a	101.4(77)		
N	33	17	
Δv_{rms} (kHz)	1.8	3.2	
κ (Kappa) ^b	0.014	-0.065	

^a *Ab initio* optimization and single point energy calculations were performed using Gaussian 03.

^b Ray's asymmetry parameter $\kappa = (2B - A - C)/(A - C)$: $\kappa = -1$, the prolate symmetric top; $\kappa = +1$, the oblate symmetric top.

than the **ee** conformer by ~ 1.66 kcal/mol, while the **aa** conformer is less stable by ~ 4.21 kcal/mol. Thus, the *cis* isomer is thermodynamically more stable than the *trans* isomer by ~ 1.66 kcal/mol. Compared to 1,3-DMC, the steric energy from Me/Me and Me/H 1,3-diaxial interactions is almost the same: 1.8 kcal/mol and 1.66 kcal/mol in the **ea** conformer, whereas it is reduced from 5.5 kcal/mol to 4.21 kcal/mol in the **aa** conformer.

There are two kinds of views to explain the decrease: one is the less stable **ee** conformer and the other is the more stable **aa** conformer, compared to energy differences in 1,3-DMC conformers. The former case is consistent with the "2-alkyl ketone effect"

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