

Conformational Analysis of Cyclopropyl Methyl Ketone

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ABSTRACT

The study examines the conformational behavior of cyclopropyl methyl ketone using molecular orbital calculations. We used a program called *Gaussian* which uses *ab initio* quantum mechanical approaches to give results independent of experimental data. We examined issues such as the most stable geometry within the molecule, taking advantage of the improvements in computer technology to extract the necessary information. In our study, we have determined that the most stable conformation for cyclopropyl methyl ketone is the *s-cis* conformation, having a torsion angle of 180° . Our findings agree with previous experimental work done by L.S. Bartell and colleagues.

INTRODUCTION

Conformations are different spatial arrangements of a molecule that are, generated by rotation about single bonds¹. With rotation, different torsion angles are necessarily generated between particular atoms that are three bonds away. In the case of ethane, a torsion angle of 0° describes the eclipsed conformation (fig. 1a) while a torsion angle of 60° represents the staggered conformation (fig. 1b). Intermediate torsion angles with any value between 0° and 60° , represent other unique torsion angles for ethane (fig. 1c).

Stability among the conformations is quantified by differences in their energies. In the case of ethane, the staggered conformation has the lowest potential energy, while the eclipsed form has the highest. Lower energy represents more stability. Energy minima and maxima result from interatomic interaction of electrons. In ethane's eclipsed form, the electrons in the C-H bond of adjacent carbons are aligned, making electron pair repulsion greater. This repulsion causes torsion strain, which makes the molecule slightly less stable by 3 kcal/mole. Such energy differences can be obtained theoretically using no calculations. *Ab initio* quantum chemistry has long promised to be a tool to be used in conjunction with experimental work to study molecular problems of conformational stability and reaction mechanisms. Quantitative applications have now become possible as a result of the tremendous developments in computer hardware and software.

Experimental data to compare our computational work to is available. For example, Dr. Ressano DeSouza-Machado had done experimental work on cyclopropyl methyl ketone in 1986, using a diamond-anvil-pressure cell². In that study, Dr. Machado used Fourier transform spectroscopy to examine the conformational behavior of cyclopropyl methyl ketone. He was unable to draw any conclusions. More useful conformational work was done by Bartell and his colleagues. In Bartell's study, using electron diffraction, cyclopropyl methyl ketone was found as the *s-cis* conformation approximately 80% of the time, in the general region of the *trans* conformation approximately 20% of the

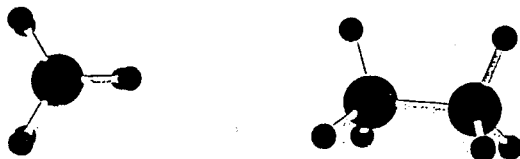


Figure 1a: Different views of ethane's eclipsed confirmation.

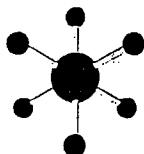


Figure 1b: Ethane's staggered conformation.

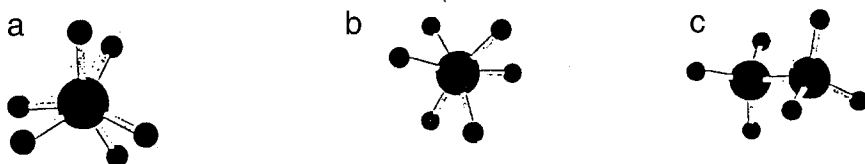


Figure 1c: a is the confirmation with a torsion angle of 30° . b and c are different views of the conformation with a torsion angle of 45° .

time, and very few intermediate isomers were present³. Only today, with the computer advancements, do we have the capability to determine if any interpretations obtained from experimental data were in fact correct.

METHODS

The computer program KEA 340 version 5.00 was used to access the Modeler and *Gaussian 94* programs⁴. The Modeler program allows us to generate 3-dimensional visualization for the molecular species under study. Modeler generates an output file containing the z-matrix. The z-matrix is a matrix containing geometrical information such as bond lengths and angles, and torsion angles⁵. Typical z-matrices for cyclopropyl methyl ketone are shown in figure 2. The z-matrix is input into the *Gaussian 94* program which gives many bits of information for each conformation including, bond orders hybridization and energy of the atoms. In this work however, we are only examining the energy results.

A.
 %mem=2000000
 #N HF/6-31G* POP=NBORead
 *** ** * ** * ** * ** * ** * CH3CH2HC::OCH3
 0 1
 H

C	1	1.0900				
C	2	1.5400	1	109.4712		
C	3	1.5400	2	60.0000	1	120.0098
H	2	1.0900	3	109.4713	4	240.0043
H	3	1.0900	2	109.4713	1	240.0055
H	3	1.0900	2	109.4713	1	0.0000
H	4	1.0900	2	109.4712	1	10.0000
C	4	1.5400	2	109.4712	1	170.0000
C	9	1.5200	4	120.0000	2	212.6420
H	10	1.0900	9	109.4712	4	180.0000
O	9	1.2200	4	120.0000	2	32.6420
H	10	1.0900	9	109.4712	4	300.0000
H	10	1.0900	9	109.4712	4	60.0000

B.
 %mem=2000000
 #N HF/6-31G*
 POP=NBORead
 *** ** * ** * ** * ** * ** * CH3CH2HC::OCH3
 0 1
 H

C	1	1.0900				
C	2	1.5400	1	109.4712		
C	3	1.5400	2	60.0000	1	120.0098
H	2	1.0900	3	109.4713	4	240.0043
H	3	1.0900	2	109.4713	1	240.0055
H	3	1.0900	2	109.4713	1	0.0000
H	4	1.0900	2	109.4712	1	10.0000
C	4	1.5400	2	109.4712	1	170.0000
C	9	1.5200	4	120.0000	2	27.8780
H	10	1.0900	9	109.4712	4	180.0000
O	9	1.2200	4	120.0000	2	-152.1220
H	10	1.0900	9	109.4712	4	300.0000
H	10	1.0900	9	109.4712	4	60.0000

Figure 2: z-matrices for cyclopropyl methyl ketone. A is the z-matrix for the s-cis conformation. B is the z-matrix for the trans conformation.

The energy values for each conformation were calculated then tabulated to create an energy diagram to determine which conformer was the most stable.

RESULTS

Computations on the conformations of cyclopropyl methyl ketone were performed having torsion angles of 0°, 90°, 180°, and many intermediate angles. The torsion angle is the one created between the carbonyl group and the α hydrogen on the cyclopropyl ring. The conformation with a torsion angle of 0° represents the trans conformation (fig. 3a),

while the conformation having a torsion angle of 180° represents the s-cis conformation (fig. 3b). Each data point represents about an hour of computational time, not including the time taken to prepare a *Gaussim* input file. The energy values yielded for each conformation were put together into an energy diagram by plotting these values versus their corresponding torsion angle (fig. 4). The energy values are summarized in Table 1. Based on the energy values, the most stable conformation has a torsion angle of 180° , while the least stable appears to have a torsion angle of about 50° .

Table 1: Torsion angles and their Corresponding Energy Values

Torsion angle ($^\circ$)	Energy Value (RHF)
0	-268.772568157
45	-268.769826638
90	-268.776528060
135	-268.785169724
180	-268.785169724

When comparing these results to the information obtained in Bartell's study, we get agreement. The most stable conformation in their experimental study is the s-cis conformation.

We then rotated the methyl group on the s-cis conformation in order to see the effect. The energy change is small, as seen in figure 5. Additional work will be done later in order to geometry optimize the molecule.

DISCUSSION

Conformational analysis allows us to study the conformations for a specific molecule, determine their relative stability, and investigate the role they play in defining the properties of the molecule¹. Cyclopropyl methyl ketone's most and least stable conformations have been determined based on steric effects or van der Waal's strain. This concept

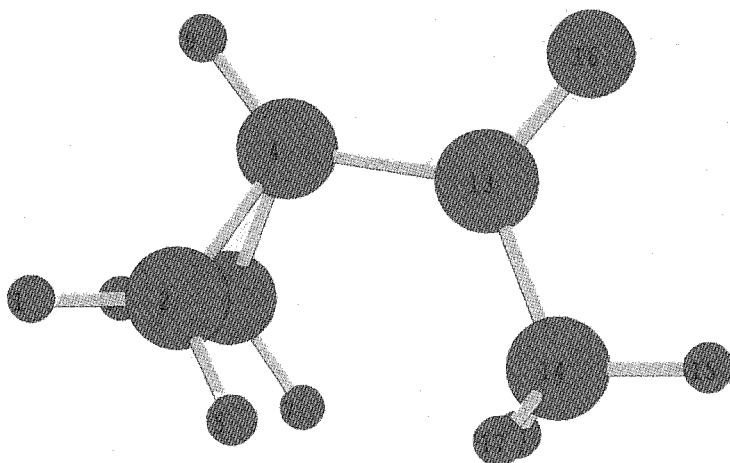


Figure 3a: The trans conformation for cyclopropyl methyl ketone.

states that the least stable conformation is produced when two atoms or groups approach each other too closely¹. In the case of cyclopropyl methyl ketone, the cyclopropyl group and the carbonyl group come too close, resulting in the van der Waal's strain. Because of the repulsion between the carbonyl and cyclopropyl groups, an increase in the torsion strain causes the conformation to become less stable.

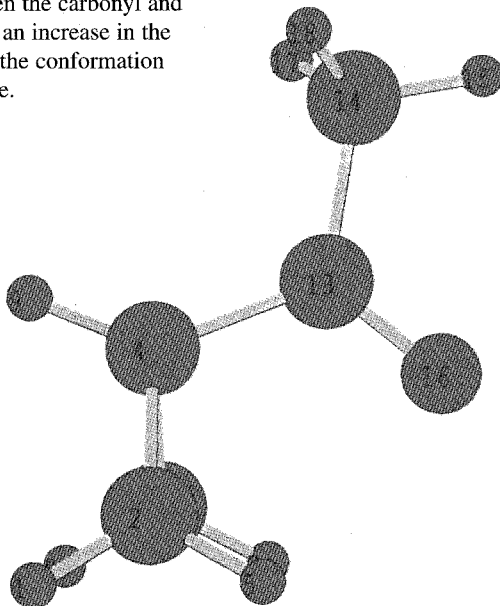


Figure 3b: The s-cis conformation for cyclopropyl methyl ketone.

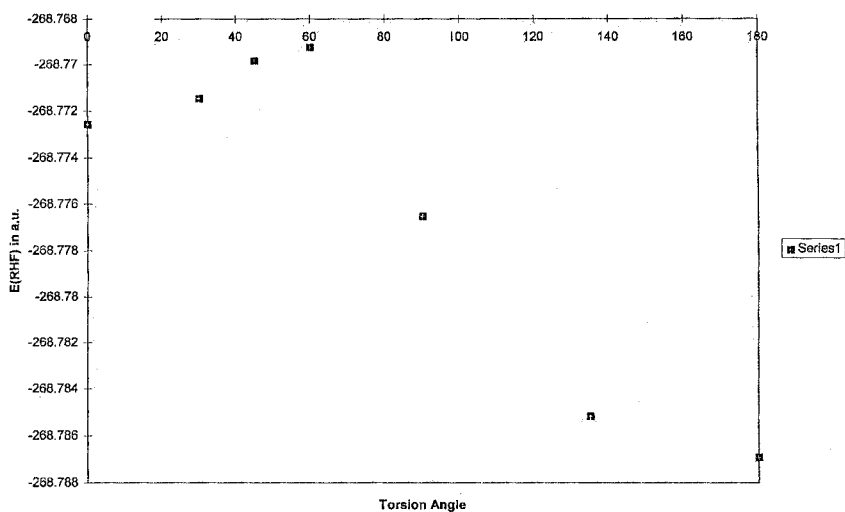


Figure 4: Potential energy diagram for cyclopropyl methyl ketone.

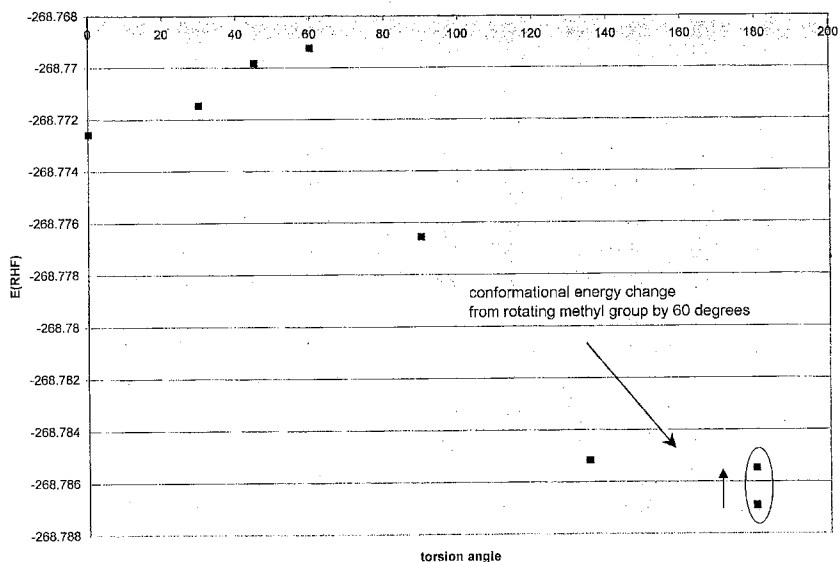


Figure 5: Potential energy diagram for cyclopropyl methyl ketone, comparing different energy values for the conformation having a torsion angle of 180° .

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