Recently the crystal structure of partially Ag^+-exchanged zeolite A, $Ag_{3.2}Na_{8.8}$-A, vacuum dehydrated at 360 °C and then exposed to 0.1 torr of cesium vapor for 12 hours at 250 °C has been studied.[28] In this crystal only Na^+ ions were also reduced by Cs vapor and replaced by Cs^+ ions. It appears that Ag^+ ions are more stable than Na^+ ions and Ca^{2+} ion in Cs vapor at 250 °C. But when fully dehydrated, fully Ag^+ exchanged zeolite A were exposed to 0.1 torr Cs vapor at 250 °C, the resulting crystal showed no single crystal diffraction pattern, indicating that Ag^+ ions are reduced by Cs vapor and migrated out of zeolite frameworks.[8] This exchange reaction using metal vapor may be viewed as a way of achieving ion exchange without the use of a solvent. This method of ion exchange allows problems of hydrolysis and overexchange to be circumvented. These problems are often encounter when ion exchange from aqueous solution is attempted.

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The Molecular Structure and Conformational Stability of Cyclobutylmethyl Ketone by MM2

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The molecular structure of cyclobutylmethyl ketone (c-$C_4H_7COCH_3$) has been investigated by molecular mechanics II (MM2). For the monosubstituted cyclobutane there are two possible ring conformations, the equatorial and axial form, but for the cyclobutylmethyl ketone the equatorial form is predominant conformation. For the $COCH_3$ moiety there are two stable orientations which are the equatorial-gauche and the equatorial-trans form. The equatorial-gauche form where the C = O bond is nearly eclipsing (torsional angle ∠C4-C3-C2-O10 = 14.5°) one of the αC-C bonds of the four-membered ring was preferred conformer with steric energy of 13.37 kcal/mol. The equatorial-trans form where the C = O bond is nearly eclipsing (∠C4-C3-C2-O10 = 145.0°) the αC-H bond of the four-membered ring was less stable conformer with steric energy of 15.40 kcal/mol.

Introduction

Previous works by several groups have shown that halocyclobutanes similar with cyclobutylmethyl ketone exist only as a equatorial conformer.[1-7]

For cyclobutylmethly ketone two conformers, equatorial-gauche and equatorial-trans, have been studied with IR and Raman spectra. Durig *et al.* reported[8] that the molecular existed predominantly the equatorial-gauche conformation (the $COCH_3$ group is in the equatorial position relative to the four-membered ring with the C=O nearly eclipsing one of the C-C bonds of ring) in the gaseous and liquid states and exclusively in this conformation in the solid state based on the band contours in the IR spectrum. By Raman spectra of the fluid phases, they also reported that a second conformer is present at ambient temperature and this conformer is believed to be equatorial-trans where the C=O is eclipsing the α CH bond of the four-membered ring.

But detailed molecular structure has not yet been reported. In this paper we have calculated the molecular structure and conformational stability of cyclobutylmethyl ketone by the molecular mechanics computer program, MM2.[9]

Theory

The molecular mechanics method is now being used to an ever increasing extent by chemist to calculate geometric, spectroscopic, and thermodynamic properties of organic molecules. Since the predicted values by molecular mechanics method often approach experimental accuracy and can be obtained much faster and more easily than experimental measurements.[10-14]

In molecular mechanics, a molecule is considered to be a collection of atoms held together by elastic and harmonic forces. These forces can be described by potential energy functions of structural features like bond lengths, bond angles, nonbonded interaction, and so on. The combination of these potential energy function is the force field.[15,16]

Steric energy is the difference in energy between the real molecule and a hypothetical molecule where all the structual values are exactly at their ideal or natural values.[16]

The steric energy of molecule, then relative to an arbitrary natural point is so far given by equation (1).

$$E=E_s+E_\theta+E_{vdw}+E_w \qquad (1)$$

In equation (1), E_s is the stretching energy, E_θ is the bending energy, E_{vdw} is the van der Waals interaction[17] and E_w is the torsional energy

The basis for the energy minimization scheme is as follows.[12,16,18] The structure of the molecule will correspond to that geometry where the energy is at a minimum. It is assumed that the energy surface in the vicinity of an energy minimum can be approximated by the equation (2), where x,y and z represent the cartesian coordinates of the atom in equation, and A-J have numerical values that one wants to determine.

$$E=Ax^2+By^2+Cz^2+Dxy+Eyz+Fxz+Gx+Hy+Iz+J \qquad (2)$$

A necessary condition for an energy minimum is that the partial derivatives of the energy with respect to each coordinate equal to zero. If we take our initial structure, and work on one atom at a time, what we need to do is to differentiate the above equation with respect to x,y and z and set each of the resulting equations equal to zero, and iterate over all atoms. We can therefore apply this procedure in turn to the individual atoms, and then keep on applying it and approach the energy minimum more and more closely.

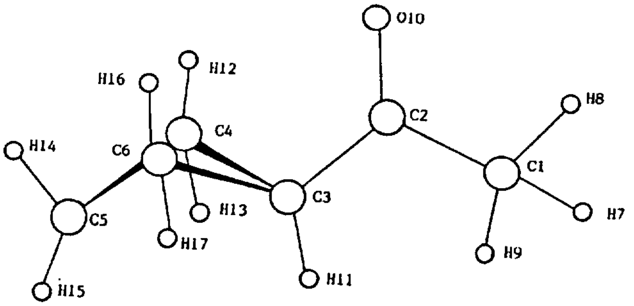

Figure 1. Molecular model and atom numbering for the equatorial conformer of c-$C_4H_7COCH_3$.

Table 1. Energy Optimized Structure for the Equatorial-gauche Conformer of c-$C_4H_7COCH_3$

Bond length (Å)	C1-C2	1.520	C1-H7	1.113
	C2-C3	1.499	C2-O10	1.199
	C3-C4	1.551	C3-H11	1.117
	C4-C5	1.548		
Bond angle (degree)	C1-C2-C3	119.0	C2-C3-H11	110.6
	C3-C4-C5	88.4	C4-C3-H11	111.4
	C2-C1-H7	110.0	H7-C1-H8	108.2
	C3-C2-O10	120.6	H12-C4-H13	113.5
Dihedral angle (degree)	C1-C2-C3-C4	-166.7	C6-C3-C2-O10	116.1
	C2-C3-C4-C5	139.2	C5-C4-C3-H11	-91.2
	C3-C4-C5-C6	-21.2	O10-C2-C3-H11	156.0
	C4-C3-C2-O10	14.5		

Table 2. Energy Optimized Structure for the Equatorial-trans Conformer of c-$C_4H_7COCH_3$

Bond length (Å)	C1-C2	1.503	C1-H7	1.113
	C2-C3	1.498	C2-O10	1.201
	C3-C4	1.551	C3-H11	1.117
	C4-C5	1.548		
Bond angle (degree)	C1-C2-C3	122.7	C2-C3-H11	110.6
	C3-C4-C5	88.4	C4-C3-H11	111.4
	C2-C1-H7	110.1	H7-C1-H8	107.6
	C3-C2-O10	118.6	H12-C4-H13	112.5
Dihedral angle (degree)	C1-C2-C3-C4	-35.1	C6-C3-C2-O10	-113.4
	C2-C3-C4-C5	139.2	C5-C4-C3-H11	-91.2
	C3-C4-C5-C6	-21.2	O10-C2-C3-H11	15.0
	C4-C3-C2-O10	145.0		

Results and Discussion

As an example, the molecular model and atom numbering for the equatorial conformer of cyclobutylmethyl ketone are shown in Figure 1.

The energy optimized structure calculated by the energy minimization scheme for the equatorial-gauche and equatorial-trans conformers are given in Table 1 and 2. Table 1

Table 3. Nonbonded Distence and van der Waals Energy

Atom pair	Distance (Å)	Energy	(Kcal/mol)
C1, C3	2.585		
C1, C4	3.980	-0.05	*
C1, C5	4.526	-0.03	
C2, C4	2.615		
C2, C5	3.484	-0.03	*
C3, C5	2.160		
C4, C6	2.144		
C1, O10	2.350		
C4, O10	2.874	0.31	*
C1, H11	2.907	0.03	*
C2, H11	2.162		
H7, H8	1.804		

* 1.4 Interaction.

Table 4. Steric Energy (Kcal/mol) of c-$C_4H_7COCH_3$ as a Function of the Torsional Angle (C4-C3-C2-O10)

Torsional angle	Steric energy	Torsional angle	Steric energy
14.5	13.37	180	15.95
0	13.59	190	15.80
10	13.38	200	15.45
20	13.42	210	14.95
30	13.71	220	14.43
40	14.23	230	13.63
50	14.88	240	13.62
60	15.54	250	13.63
70	16.08	260	13.90
80	16.33	270	14.28
90	16.24	280	14.73
100	15.92	290	15.13
110	15.61	300	15.41
120	15.48	310	15.50
130	15.54	320	15.38
140	15.42	330	15.08
150	15.44	340	14.63
160	15.64	350	14.13
170	15.88		

gives the several of bond length, bond angle and dihedral angle data among the results of these calculation for the equatorial-gauche conformer.

The calculated dihedral angle data show the detailed molecular structure. The most stable structure was the equatorial-gauche conformer with the dihedral angle (∠C4-C3-C2-O10) of 14.5°. In Table 2, the calculated dihedral angle (∠C4-C3-C2-O10) of the equatorial-trans conformer was 145.0°.

The several of van der Waals energy data among the nonbonded interactions are shown in Table 3.

The steric energies of the calculated results with changing the torsional angle of every 10 degree against the rotating axis C2-C3 are shown in Table 4.

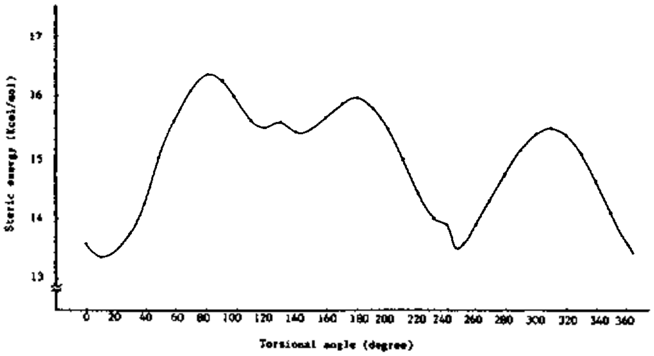

Figure 2. Steric energy (Kcal/mol) as a function of the torsional angle.

Table 5. Steric Energy (Kcal/mol) of c-$C_4H_7COCH_3$ as a Function of the Torsional Angle (C4-C3-C2-O10)

Torsional angle	Steric energy	Torsional angle	Steric energy
240	13.62	251	13.65
241	13.61	252	13.67
242	13.60	253	13.69
243	13.59	254	13.71
244	13.59	255	13.74
245	13.59	256	13.77
246	13.59	257	13.80
247	13.60	258	13.83
248	13.61	259	13.86
249	13.62	260	13.90
250	13.63		

Figure 2 is a plot of the calculated steric energy as a function of the torsional angle (∠C4-C3-C2-O10). When the torsional angle was 14.5° the steric energy had minimum value. Therefore, the equatorial-gauche conformer which had the torsional angle of 14.5° was the most stable structure. Another less stable conformer was the equatorial-trans conformer when the torsional angle was 120° or 150°. In Figure 2, cyclobutylmethyl ketone has three minimum energy values with the torsional angle of 14.5°, 145° and 245°. However the torsional angle of 14.5° 245° have nearly equivalent value of the steric energy so that the two conformer is the same structure. Theoretically the conformer with the torsional angle of about 255.5° is the same structure with the torsional angle of 14.5° by symmetrical coordinations since the torsional angles of C4-C3-C2-O10 and C6-C3-C2-O10 are symmetrically equivalent angle positions. But the calculated results shows the conformer with the torsional angle of 245° has minimum energy. The energy difference between the torsional angle (245° and 255°) is 0.16 Kcal/mol. Therefore this conformer can exist between the torsional angle of 240° and 255°. The calculated steric energies with changing the torsional angle of every 1 degree are given in Table 5.

To identify detailed structure of the equatorial-trans conformer we calculated steric energies with changing the torsional angle every 5 degree in the double minimum region (from 110° to 150°) of Figure 2. The results of this calculation are given in Table 6. In Table 6, when the torsional

Table 6. Steric Energy (Kcal/mol) of c-$C_4H_7COCH_3$ as a Function of the Torsional Angle (C4-C3-C2-O10)

Torsional angle	Steric energy
110	15.61
115	15.52
120	15.48
125	15.50
130	15.54
135	15.49
140	15.45
145	15.40
150	15.44

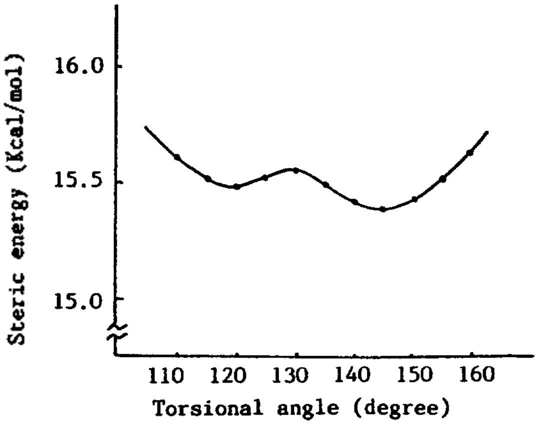

Figure 3. Steric energy (Kcal/mol) as a function of the torsional angle.

angle was 145° the steric energy was the smallest. A plot of the calculated steric energy as a function of the torsional angle is shown in Figure 3. The steric energy difference between the torsional angle of 120° and 145° is 0.08 Kcal/mol. The energy barrier between the torsional angle of 130° and 145° is only 0.14 Kcal/mol. Consequently the equatorial-trans conformer can exist between 120° and 145° of the torsional angle.

Conclusion

Each conformation of cyclobutylmethyl ketone was characterized by the calculated torsional angle.

The steric energy of the most stable equatorial-gauche conformer with the torsional angle of 14.5° was 13.37 Kcal/mal. The second stable equatorial-trans conformer with the torsional angle of 145.0° was 15.40 Kcal/mol.

The steric energy differences of the two conformer was 2.03 Kcal/mol and was consistent with the IR and Raman experimental data.[8]

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