Articles

Relationship between Conformational Preferences and Torsional Parameters in Molecular Mechanics (MM3) Calculations

Soo Gyeong Cho* **and Gyoosoon Park**[†]

Agency for Defense Development, P.O. Box 35-1, Yuseong, Taejon 305-600, Korea
[†]*Department of Chemistry, Kookmin University, Seoul 136-702, Korea*
Received July 26, 1996

We have investigated a relationship between conformational preferences of various substituents in monosubstituted cyclohexanes and pertinent torsional parameter values in molecular mechanics calculations. We have manipulated torsional parameters to supply a certain energy difference between gauche and anti conformers, and applied those parameters to monosubstituted cyclohexanes. After investigating 6 different substituents, namely Me, SiH_3, F, Cl, Br, and I, MM3 calculations show that (1) the MM3 calculated A values with the current torsional parameters reproduce the available experimental values well, (2) the conformational energy difference between axial and equatorial conformations (the A value) correlates perfectly with the gauche/anti energy differences of the corresponding butane-like fragment (correlation coefficient=1.000), and (3) the A values are essentially twice as the gauche/anti energy differences (slopes=1.86-2.00). On the basis of our analysis, the A values as well as the gauche/anti energy differences are easily calibrated by an adjustment of the relevant torsional parameter. Thus, our technique for tuning the torsional parameters may be of great use in updating molecular mechanics results about conformational preferences whenever a further refinement is necessary.

Introduction

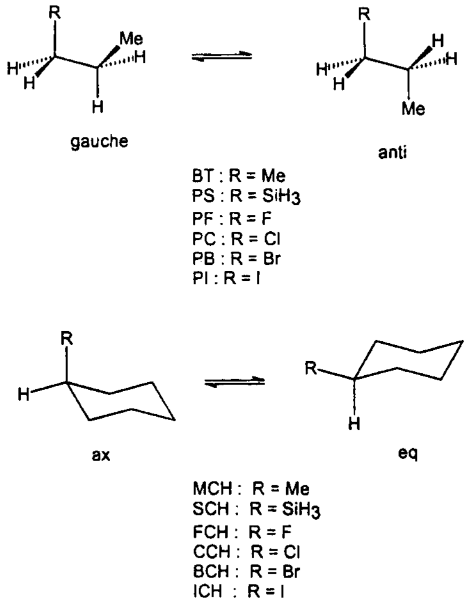
The free energy difference between axial and equatorial conformations in monosubstituted cyclohexane, the A value, provides useful information about the conformational preference of that particular substituent.[1] Two elements may govern the magnitude of the A value, namely steric and electronic. Steric factors will be a determining factor in most substituents without a large excess charge. 1,3-Diaxial interactions are reflected from increased nonbonded interactions due to the substitution of a sterically bulky group in an axial position, while gauche interactions between an axial substituent and C_3 atoms are also displayed by an increase of torsional energies. In case that a substituent has a large excess charge, electrostatic interactions may play a major role to determine the magnitude of the A value.[2]

The conformational energy calculated by molecular mechanics (MM) is consisted of various energy components.[3] Although each energy component illustrates an extremely simplified model for the specific type of an interaction, one may gain useful chemical insight by examining the variation of these energy components according to conformational changes. Electronic reasons may be revealed to charge-charge/dipole-dipole energies. While 1,3-diaxial interactions can be disclosed in van der Waals energies, gauche interactions may be exhibited in torsional energies. However, the analysis of MM calculated energy components is a complicated process due to the transferability of energy components. For instance, if van der Waals energy components are augmented significantly for some reasons, geometric changes usually occur by elongating bonds, bending bond angles, or twisting dihedral angles to be able to relieve unfavorable van der Waals energies. Through this process, portion of increased van der Waals energies is transferred to other energy components, *i.e.* stretching, bending, or torsional energies. Moreover, other energy components, which may not be transferred directly from unfavorable van der Waals energies, are also varied slightly, when the geometry changes. Nevertheless, MM energy decomposition analysis has been successfully applied to understand the origin of conformational preferences,[4] despite (1) the roughness in the analysis of MM calculated energy components and (2) transferability of energy components.

In this study, we have investigated the conformational preference of various groups by using MM calculations. We have examined monosubstituted cyclohexanes and the corresponding butane-like molecules. Especially for butane-like molecules, the potential energy surfaces around the C_2-C_3 bond have been surveyed and analyzed by examining MM energy components. Finally, we have inspected changes of the A values and gauche/anti energy differences due to the modification of torsional parameters.

Computational Details

MM calculations were carried out using MM3 program.[5] Six substituents, namely Me, SiH_3, F, Cl, Br, and I, have been investigated, since conformational energies are not changed due to the orientation of the substituent. Full geometry optimizations were performed at (1) the axial and equatorial conformations of monosubstituted cyclohexanes, and at (2) the gauche and anti conformations of butane-like fragments. Torsional potential energy functions (TPEFs) of butane-like fragments were obtained by using dihedral driver calculations with a step size of 10°. The compounds inspected in this work are depicted in Scheme 1 along with their conformations. Although some parameters are either in a test stage or have some controversies,[6] standard values have been utilized without any modification since development of new parameters is not our main scope in this study. Rather, we are focusing on how MM3 calculated energies behave according to the values of torsional parameters. Torsional parameters utilized in this study are summarized in Table 1. Analyses of MM3 energy components were carried out by summing several similar energy components, thus resulting 3 energy portions; (1) bonded energies, (2) nonbonded energies, and (3) torsional energies. Bonded energies may represent an energy increase due to deviations from the equilibrium geometry, and are assembled by summing stretching energies, bending energies, stretch-bend energies, and bend-bend energies. Nonbonded energies symbolize an energy build-up due to interactions between two atoms which are more than 1,4-relationship. Torsional energies are the sum of torsional energies and torsion-stretch energies. Electrostatic interactions including dipole-dipole interactions are not considered explicitly in the molecules studied in this work, because (1) excess charge values are not utilized in standard MM3 calculations, and (2) bond dipoles for C-C and C-H bonds are fitted to zero. Thus, these interactions are probably included implicitly in torsional energies, since a Fourier type analysis discloses that torsional energies are composed by dipole/dipole interactions (V_1), conjugation (V_2), and 3-fold steric interactions (V_3).[7] Detailed MM3 force fields can be found elsewhere.[5a]



Scheme 1.

Results and Discussion

Analysis of energy components in the TPEF. Before proceeding our main study, *i.e.* a relationship between MM calculated energies and torsional parameters, it is very important for us to comprehend which energy component contributes primarily to assemble TPEFs in MM calculations. To address the above question, we have carried out dihedral drive calculations for butane-like fragments, and have investigated the changes of total steric energies and energy components. The results are summarized in Table 2.

First, we will discuss the MM results briefly. All 6 butane-like fragments are more stable in the anti conformation than gauche conformations by 0.1-0.8 kcal/mol. Among

Table 1. MM3 torsional parameters[a] utilized in this work

Dihedral angle	V_1	V_2	V_3
C-C-C-C	0.185	0.170	0.520
C-C-C-Si (*)[b]	0.000	0.000	0.500
C-C-C-F (**)[c]	0.000	−0.086	0.930
C-C-C-Cl (**)	0.000	−0.250	0.550
C-C-C-Br (**)	0.000	−0.410	1.060
C-C-C-I (**)	0.000	−0.500	0.267

[a] All standard parameters, which are distributed with the MM3 program, are used. [b] (*) means that the parameter values are not finalized yet. [c] (**) means that the parameter values are in a test stage.

Table 2. Relative conformational energis[a] of BT, PS, PF, PC, PB, and PI conformers calculated by MM3 method

Molecules	Gauche	anti[b]	g-g[c]	g-a[d]
BT	0.809(65.1°)[e]	0.0[f]	4.832	3.316
	[0.242/0.221/0.347][g]	[0.0/0.0/0.0][f]	[1.136/1.104/2.592]	[0.241/0.476/2.599]
PS	0.566(67.2°)	0.0	4.873	3.128
	[0.299/0.173/0.094]	[0.0/0.0/0.0]	[1.452/1.134/2.286]	[0.296/0.533/2.299]
PF	0.098(62.4°)	0.0	4.401	3.694
	[0.056/0.098/−0.056]	[0.0/0.0/0.0]	[0.534/0.893/2.974]	[0.239/0.533/2.921]
PC	0.287(66.9°)	0.0	5.397	3.465
	[0.243/0.177/−0.133]	[0.0/0.0/0.0]	[1.444/1.250/2.703]	[0.337/0.596/2.533]
PB	0.322(67.9°)	0.0	6.422	3.879
	[0.329/0.223/−0.230]	[0.0/0.0/0.0]	[1.854/1.398/3.169]	[0.377/0.622/2.880]
PI	0.213(70.6°)	0.0	5.401	2.740
	[0.317/0.203/−0.306]	[0.0/0.0/0.0]	[1.879/1.372/2.151]	[0.350/0.596/1.793]

[a] Units in kcal/mol. [b] C-C-C-X torsional angle=180.0°. [c] C-C-C-X torsional angle=0.0°. [d] C-C-C-X torsional angle=120.0°. [e] Fully optimized C-C-C-X torsional angle. [f] Reference values. [g] Bonded energies/nonbonded energies/torsional energies. For a detailed description, see the main text.

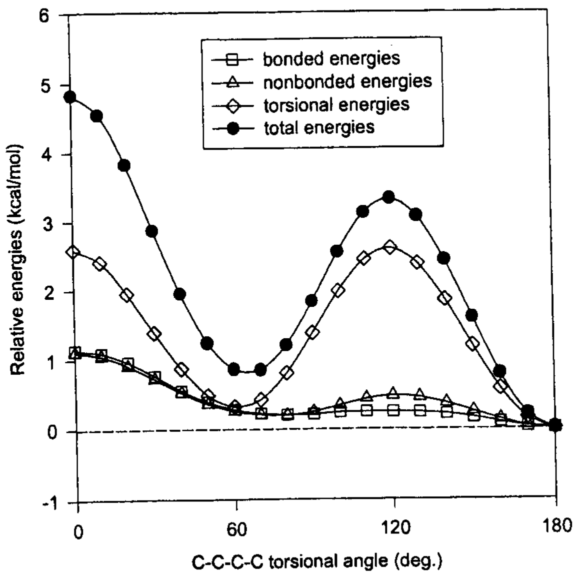


Figure 1. The TPEF of BT calculated by MM3.

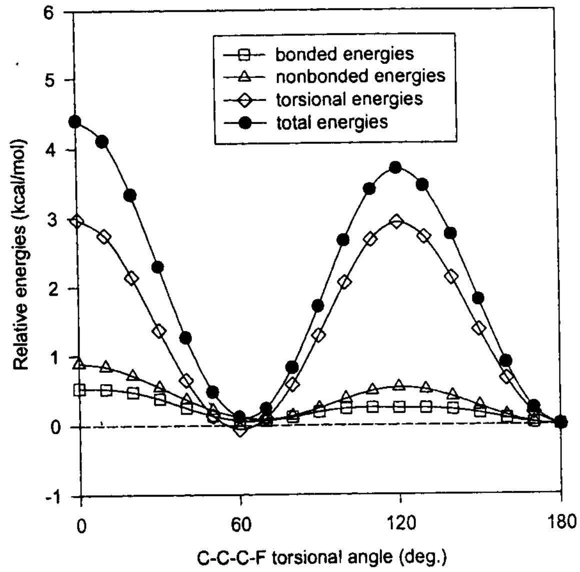


Figure 2. The TPEF of PF calculated by MM3.

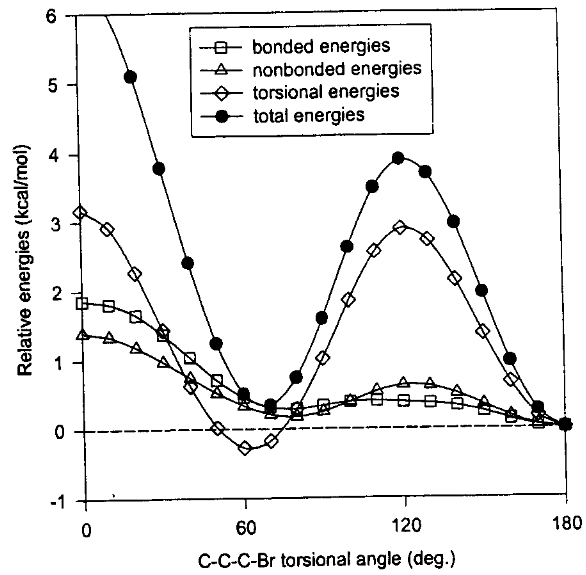


Figure 3. The TPEF of PB calculated by MM3.

these, BT reveals the largest gauche interaction of 0.81 kcal/mol in MM3. The gauche interaction of PS is slightly lower than that of BT by 0.24 kcal/mol, which probably arises from a longer C-Si bond compared to a C-C bond. All butane-like fragments containing halogen atoms exhibit diminished gauche interactions of 0.1-0.3 kcal/mol. The smaller gauche interaction of halogen containing butane-like fragments is probably attributed to electrostatically attractive 1,4-interactions ($CH_3^{\delta+}\cdots X^{\delta-}$). The steric hindrance in gauche conformations may not be substantial even for PB and PI, probably owing to the large C-Br and C-I bond lengths. PF displays a diminutive gauche interaction of 0.1 kcal/mol, and PI has a 0.2 kcal/mol gauche interaction. The heights of rotational barriers appear not to correlate with the gauche/anti energy differences. Rotational barriers seem to be augmented with the atomic size, except the case of I. The largest rotational barrier is 6.4 kcal/mol for the gauche-gauche barrier of PB. Except the barrier heights and gauche/anti energy differences, the shape of TPEFs is generally the same for all compounds inspected in this work.

In order to comprehend MM3 results better, we have probed changes of total steric energies and energy components for all 6 butane-like fragments according to the change of C-C-C-X dihedral angles (X=C, Si, F, Cl, Br, or I). Figure 1 to 3 depict those of BT, PF, and PB. Changes of energy components also are summarized in Table 2. This result clearly demonstrates that torsional energy term is the major component in assembling rotational barriers in MM3. It seems likely that the torsional energy component constitutes about 50-80% of conformational energy changes during rotation. The portion of the torsional energy term which constructs total conformational energy changes during the rotation varies notably depending on conformations as well as compounds. In PF, where rotational barriers are small and gauche/anti energy difference is quite shallow, the torsional energy term appears to be the major contribution. Bonded and nonbonded energy components are less than 1 kcal/mol. In PB, which has large rotational barriers, bonded and nonbonded energy components also construct large portions of the rotational barrier, and become quite larger at the eclipsed conformation. As far as the gauche/anti energy difference is concerned, it is difficult to judge which energy component contributes more.

Effect of torsional parameters to conformational preferences. The MM3 calculated TPEFs exhibit that torsional energy component plays a major role in constructing rotational isomerisms. However, torsional energy component may not be ascribed exclusively to assemble the TPEFs, unless the variation of other energy components are transferred from torsional energies. Accodingly, the gauche/anti energy differences and the A values may not be interpreted by a torsional energy term solely. On the other hand, several previous occasions[8] indicated that the choice of torsional terms is quite important to quantify these values.

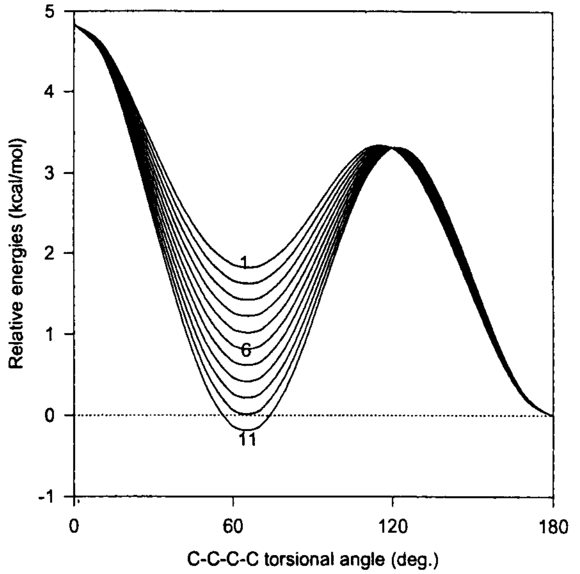


Figure 4. The TPEFs of BT calculated by MM3 with different C-C-C-C torsional parameter values (From the top to the bottom, the parameter number for the C-C-C-C torsional parameter is 1 to 11. 6, the middle one, is the standard one used in the MM3 program The numbers are the parameter numbers given in Table 3).

Thus, we have decided to alter the values of torsional parameters to see whether a certain amount of the change in the torsional energy component is reflected directly to the A value as well as gauche/anti energy difference.

We have performed a least square fitting of V_1, V_2, and V_3 values to yield desired relative energies at minima and maxima in the TPEF.[9] We have decided to modify the energy difference between gauche and anti conformations up to ±1 kcal/mol by a step of 0.2 kcal/mol. Our least square analyses inform that an increase of 0.2 kcal/mol gauche/anti energy difference can be achieved by raising the V_1 and V_2 values by 0.133 and lowering the V_3 value by 0.133, without altering relative energies of other conformations. On the other hand, a decrease of 0.2 kcal/mol gauche/anti energy difference can be obtained by lowering the V_1 and V_2 values by 0.133 and raising the V_3 value by 0.133. An example of modified TPEFs with different values of the C-C-C-C torsional parameter is shown in Figure 4. This result clearly demonstrates that changes of the torsional energy component are exclusively delivered to the gauche/anti energy differences. By investigating MM energy compoments carefully, we have found that other energy components are nearly invariant to the changes of torsional energy component. Although this phenomenon is probably arised from the coarseness of MM force field, it appears to provide a simple, but useful tactics in refining MM calculated energetics. Our approach enables MM users to obtain accurate MM results in energetics by simply modifying the pertinent torsional parameters without altering other MM results seriously.

We have further applied these parameters to cyclohexane systems to calculate the A values. We also have examined the relationship between the A value of Me and gauche/anti energy differences of BT. The results are depicted in Figure 5. The A value of Me correlates perfectly with the gauche/anti energy differences of BT. Furthermore, the magnitude of the A value of Me is almost twice as the gauche/anti energy difference of BT. Since MM force field is based on extremely simplified forms of interactions, the above perfect correlation may come from an artifact in MM calculations, rather than from a meaningful chemical reason. We have extended same type of calculations to other molecules, which are summarized in Table 3. All the results from other molecules essentially display the same trend as that of Me. Thus, our maneuver for fitting the torsional parameter can be applied to a broad range of substituents. In addition, it can also utilize the experimental data derived from the A values as well as gauche/anti energy differences.

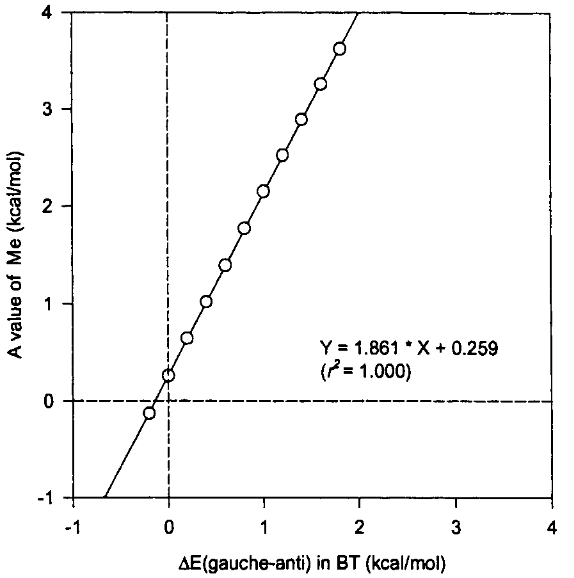


Figure 5. Relationship between the A value of Me and the gauch/anti energy difference of BT (For details, see Table 3).

Comparison of MM3 calculated A values with previous results. The MM3 calculated A values are summarized in Table 4 along with previous experimental and theoretical results. The A values of all the substituents inspected in this study have been examined extensively by experimental means.[1c] Nevertheless, until quite recent years, reliable ab initio calculations have not been applied probably due to the large molecular size of these compounds. Furthermore, to the best of our knowledge, we have not observed any ab initio results for BCH and ICH yet.

Wiberg and Murcko[11] have utilized the MP3/6-31G*//HF/6-31G* level of theory to MCH, and have found that the A value of Me is 2.01 kcal/mol. Further correction for ZPVE by utilizing HF/3-21G* frequency calculations pushes the A value of Me to be 2.17 kcal/mol, which is approximately 0.5 kcal/mol higher than the experimental values. More recently, one of authors (S. G. Cho) has carried out MP4(SDTQ)/6-31G*//MP2/6-31G* calculations on MCH and SCH.[10] Since the A values obtained theoretically are the $\Delta E^\ddagger$ (0 K) value, several steps of thermodynamic corrections should be done to compare with experimental data, which are usually reported as the $\Delta G^\ddagger$ (298 K) value. Full corrections of theoretical results to access the $\Delta G^\ddagger$ (298 K) values require ZPVE, TVE, and entropy corrections.[13] By following this scheme

Table 3. MM3 calculated A values and gauche/anti energy differences[a] by using different torsional parameter values

No.	Torsional parameters			X	Y
	V_1	V_2	V_3	E_{gauche}-E_{anti}	A value
X=BT; Y=MCH					
1	0.850	0.835	-0.145	1.817	3.621
2	0.717	0.702	-0.012	1.615	3.258
3	0.584	0.569	0.121	1.414	2.892
4	0.451	0.436	0.254	1.212	2.522
5	0.318	0.303	0.387	1.011	2.149
6[b]	**0.185**	**0.170**	**0.520**	**0.809**	**1.774**
7	0.052	0.037	0.653	0.608	1.398
8	-0.081	-0.096	0.786	0.406	1.019
9	-0.214	-0.229	0.919	0.204	0.639
10	-0.347	-0.362	1.052	0.003	0.257
11	-0.480	-0.495	1.185	-0.199	-0.126
statistics : A value=1.861* (E_{gauche}-E_{anti})+0.259 (correlation coefficient=1.000)					
X=PS; Y=SCH					
1	0.665	0.665	-0.165	1.567	3.066
2	0.532	0.532	-0.032	1.367	2.687
3	0.399	0.399	0.101	1.167	2.307
4	0.266	0.266	0.234	0.967	1.925
5	0.133	0.133	0.367	0.766	1.543
6[b]	**0.000**	**0.000**	**0.500**	**0.566**	**1.159**
7	-0.133	-0.133	0.633	0.365	0.775
8	-0.266	-0.266	0.766	0.164	0.390
9	-0.399	-0.399	0.899	-0.037	0.004
10	-0.532	-0.532	1.032	-0.237	-0.383
11	-0.665	-0.665.	1.165	-0.438	-0.770
statistics : A value=1.913* (E_{gauche}-E_{anti})+0.073 (correlation coefficient=1.000)					
X=PF; Y=FCH					
1	0.665	0.579	0.265	1.103	2.240
2	0.532	0.446	0.398	0.902	1.837
3	0.399	0.313	0.531	0.701	1.434
4	0.266	0.180	0.664	0.500	1.031
5	0.133	0.047	0.797	0.299	0.627
6[b]	**0.000**	**-0.086**	**0.930**	**0.098**	**0.225**
7	-0.133	-0.219	1.063	-0.104	-0.178
8	-0.266	-0.352	1.196	-0.305	-0.582
9	-0.399	-0.485	1.329	-0.506	-0.985
10	-0.532	-0.618	1.462	-0.708	-1.388
11	-0.665	-0.751	1.595	-0.909	-1.792
statistics : A value=2.004* (E_{gauche}-E_{anti})+0.029 (correlation coefficient=1.000)					
X=PC; Y=CCH					
1	0.665	0.415	-0.115	1.290	2.542
2	0.532	0.282	0.018	1.090	2.150
3	0.399	0.149	0.151	0.889	1.757
4	0.266	0.016	0.284	0.689	1.364
5	0.133	-0.117	0.417	0.488	0.971
6[b]	**0.000**	**-0.250**	**0.550**	**0.287**	**0.577**
7	-0.133	-0.383	0.683	0.086	0.182
8	-0.266	-0.516	0.816	-0.114	-0.213
9	-0.399	-0.649	0.949	-0.315	-0.608
10	-0.532	-0.782	1.082	-0.516	-1.003
11	-0.665	-0.915	1.215	-0.717	-1.399
statistics : A value=1.964* (E_{gauche}-E_{anti})+0.019 (correlation coefficient=1.000)					
X=PB; Y=BCH					
1	0.665	0.255	0.395	1.321	2.596
2	0.532	0.122	0.528	1.121	2.208
3	0.399	-0.011	0.661	0.922	1.819
4	0.266	-0.144	0.794	0.722	1.430
5	0.133	-0.277	0.927	0.522	1.040
6[b]	**0.000**	**-0.410**	**1.060**	**0.322**	**0.650**
7	-0.133	-0.543	1.193	0.122	0.259
8	-0.266	-0.676	1.326	-0.078	-0.133
9	-0.399	-0.809	1.459	-0.279	-0.525
10	-0.532	-0.942	1.592	-0.479	-0.917
11	-0.665	-1.075	1.725	-0.680	-1.310
statistics : A value=1.952* (E_{gauche}-E_{anti})+0.019 (correlation coefficient=1.000)					
X=PI; Y=ICH					
1	0.665	0.165	-0.398	1.190	2.256
2	0.532	0.032	-0.265	0.996	1.882
3	0.399	-0.101	-0.132	0.801	1.506
4	0.266	-0.234	0.001	0.606	1.129
5	0.133	-0.367	0.134	0.410	0.750
6[b]	**0.000**	**-0.500**	**0.267**	**0.213**	**0.371**
7	-0.133	-0.633	0.400	0.016	-0.010
8	-0.266	-0.766	0.533	-0.181	-0.391
9	-0.399	-0.899	0.666	-0.379	-0.774
10	-0.532	-1.032	0.799	-0.578	-1.157
11	-0.665	-1.165	0.932	-0.776	-1.541
statistics : A value=1.931* (E_{gauche}-E_{anti})-0.041 (correlation coefficient=1.000)					

[a] Units in kcal/mol. [b] Regular parameters.

Table 4. Comparison of MM3 Calculated A Values[a] with Previous Experimental and Theoretical Values

Substituent	MM3[b]	Experimental Work[c]	*Ab Initio*
CH_3	1.77	1.6,[d] 1.74[e]	2.14,[f] 2.17[g]
SiH_3	1.16	1.45,[h] 1.52[i]	1.90[f]
F	0.23	0.35,[j] 0.25[k]	-0.69[l]
Cl	0.58	0.53,[m] 0.64[i]	1.01[n]
Br	0.65	0.53,[o] 0.50[i]	
I	0.37	0.49[o]	

[a] Units in kcal/mol. [b] This work. [c] Except when noted, experimental data are taken from ref. 1(c). [d] In neat liquid at 163 K. [e] In $CFCl_3/CDCl_3$ at 300 K. [f] At the MP4(SDTQ)/6-31G*//MP 2/6-31G* level (including zero point vibrational energy (ZPVE), thermal vibrational energy, and entropy corrections), ref. 10. [g] At the MP3/6-31G*//HF/6-31G*+ZPVE. ZPVE is from HF/3-21G* calculations, ref. 11. [h] In $CDCl_2$ at 188 K. [i] In the gas phase at 300 K. [j] In CS2 at 183 K. [k] In the gas phase at 243 K. [l] At the MP4(SDTQ)/6-31G*//MP2/6-31G* level, ref. 12. [m] In CS_2 at 191 K. [n] At the HF/6-31G* level, ref. 12. [o] In CS_2 at 189 K.

to acquire the $\Delta G^{\ddagger}$ (298 K) value from MP4(SDTQ)/6-31G*//MP2/6-31G* calculations, our best estimates for the A values of Me and SiH_3 are 2.14, and 1.90 kcal/mol, respectively.[10] Both improving basis sets and incorporating higher order electron correlation terms hardly alter the A values. Although these values are within the limit of accuracy which can be obtained from the state-of-art ab initio calculations, the ab initio calculated A values of Me and SiH_3 appear to be approximately 0.5 kcal/mol higher than experimental values.

Salzner and Schleyer have examined the A values of F and Cl by using *ab initio* calculations.[12] Surprisingly, and in contrast to previous experimental results, FCH is calculated to be more stable (0.6 kcal/mol) in an axial position than in an equatorial one at MP4/6-31G*//MP2/6-31G*+ZPVE.[12] On the other hand, the SCF calculation with the 6-31+G* basis set yields the A value of F to be 0.3 kcal/mol, which is in excellent agreement with the experimental value.[1c] Thus, it is very hard for one to judge which level of ab initio theory is good enough to be utilized for the reference of MM force fields. Much higher levels of ab initio theories with the larger basis sets such as QCISD/6-311++G** may address these quantities properly, but these levels of theories are hardly accessible with our computational resources due to the large size of molecules.

When one bears the performance of high level initio theories in mind, the MM3 calculated A values are, in fact, in an excellent agreement with experimental results. Errors from experimental values are less than 0.5 kcal/mol.

Comments on the magnitude of the A value. The magnitude of the A values reflects the conformational preference of that particular substituent. The main reason to adapt the equatorial position preferentially over the axial position is known to be a steric reason, which is attributed to the size of a substituent. By following the same reason, we can interpret the preference of the anti conformation over the gauche conformation. The size of a substituent alone, however, do not fully accounts for the magnitude of the A value. For instance, the A value of SiH_3, 1.16 kcal/mol, is significantly smaller than the one of Me, 1.77 kcal/mol (see Table 4). If the magnitude of the A value is explained in terms of the size of a substituent, it is surprising that the A value of SiH_3 is smaller than that of Me, since the volume of SiH_3 is presumably much larger than that of Me. A conceivable explanation for this is the longer Si-C bond (1.894 Å) compared to the C-C bond (1.539 Å).[10] Therefore, the SiH_3 group attached to cyclohexane resides further from other atoms in the ring. An erratic variation of the A values in a series of halogen substituents also seems to be a compromise between the C-X bond length and the size of X atom.

Conclusions

We have investigated the relationship between the conformational preference of various groups and the values of relevant torsional parameters. We are able to obtain desired gauche/anti energy differences by manipulating the values of torsional parameters. These values of torsional parameters have further been applied to the substituents of cyclic 6-membered ring systems. Our MM3 calculations with the current torsional parameters furnish excellent values, which are in an good agreement with the experimental ones. Furthermore, in MM3, the A values correlate perfectly with the gauche/anti energy differences. Thus, both the A values and gauche/anti energy differences can be acquired by simply modifying the relevant torsional parameter, although the analysis of MM calculated energy components indicates that the torsional energy components are not exclusively attributed to the TPEFs. Our study demonstrates that (1) MM3 calculated A values are dictated by torsional parameters, and may not be physically meaningful ones, and (2) the user can modify the A values in MM3 by simply updating the values of a torsional parameter if accurate experimental results of the A value are available. On the basis on our MM and previous results, the magnitude of the A value seems to be a compromise between the bond lengths and the size of subtituents.

References

1. (a) Eliel, E. L.; Wilen, S. H. *Stereochemistry of Organic Compounds*; John Wiley & Sons, Inc.: New York, 1994; Chapter 11. (b) Juaristi, E. *Introduction to Stereochemistry and Conformational Analysis*; John Wiley & Sons, Inc.: New York, 1991; Chapter 14. (c) Bushweller, C. H. Steredynamics of Cyclohexane and Substituted Cyclohexanes. Substituent A-Values. In *Conformational Behavior of Six-Membered Rings: Analysis, Dynamics, and Stereochemical Effect*; Juaristi, E., Ed.; VCH Publishers: New York, 1995; Chapter 2.
2. Cho, S. G. *Bull. Korean Chem. Soc.* **1995**, *16*, 905.
3. (a) Burkert, U.; Allinger, N. L. *Molecular Mechanics*; American Chemical Society: Washington, DC, 1982. (b) Bowen, J. P.; Allinger, N. L. In *Reviews in Computational Chemistry*; Lipkowitz, K. B.; Boyd, D. B., Eds.; VCH: New York, NY, 1991; Vol. 2, Chapter 3.
4. (a) Profeta, S. Jr.; Unwalla, R. J.; Nguyen, B. T.; Cartledge, F. K. *J. Comput. Chem.* **1986**, *7*, 528. (b) Chung-Phillips, A. *J. Comput. Chem.* **1989**, *10*, 733. (c) Cho, S. G.; Cartledge, F. K.; Unwalla, R. J.; Profeta, S. Jr. *J. Mol. Struct. (THEOCHEM)* **1989**, *204*, 79. (d) Bond, D.; Schleyer, P. v. R. *J. Org. Chem.* **1990**, *55*, 1003. (e) Dinur, U.; Hagler, A. T. *J. Comput. Chem.* **1990**, *11*, 1234. (f) Chung-Phillips, A. *J. Comput. Chem.* **1992**, *13*, 874. (g) Goodman, L.; Kundu, T.; Leszczynski, J. *J. Phys. Chem.* **1996**, *100*, 2770.
5. (a) Allinger, N. L.; Yuh, Y. H.; Lii, J.-H. *J. Am. Chem. Soc.* **1989**, *111*, 8551. (b) Lii, J.-H.; Allinger, N. L. *J. Am. Chem. Soc.* **1989**, *111*, 8566. (c) Lii, J.-H.; Allinger, N. L. *J. Am. Chem. Soc.* **1989**, *111*, 8576.
6. For the controversy of the C-C-C-Si torsional parameter values, see Unwalla, R. J.; Profeta, S. Jr.; Cartledge, F. K. *J. Org. Chem.* **1988**, *53*, 5658.
7. (a) Radom, L.; Hehre, W. J.; Pople, J. A. *J. Am. Chem. Soc.* **1972**, *94*, 2371. (b) Allinger, N. L.; Sprague, J. T. *J. Am. Chem. Soc.* **1973**, *95*, 3893. (c) Allinger, N. L. *J. Am. Chem. Soc.* **1977**, *99*, 8127. (d) Goodman, L.; Leszczynski, J.; Kundu, T. *J. Chem. Phys.* **1994**, *100*, 1274.
8. (a) Houk, K. N.; Eksterowicz, J. E.; Wu, Y.-D.; Fuglesang, C. D.; Mitchell, D. B. *J. Am. Chem. Soc.*

1993, *115*, 4170. (b) De Mare, G. R.; Panchenko, Y. N.; Abramenkov, A. V.; Bock, C. W. *Can. J. Chem.* **1993**, *71*, 656. (c) Carballeira, L.; Perez-Juste, I. *J. Mol. Struct. (THEOCHEM)* **1994**, *309*, 267.
9. Cho, S. G. to be submitted.
10. Cho, S. G.; Rim, O. K.; Kim, Y.-S. *J. Mol. Struct. (THEOCHEM)* **1996**, *306*, 59.
11. Wiberg, K. B.; Murcko, M. A. *J. Am. Chem. Soc.* **1989**, *110*, 8029.
12. Salzner, U.; Schleyer, P. v. R. *J. Org. Chem.* **1994**, *59*, 2138.
13. Hehre, W. J.; Radom, L.; Schleyer, P. v. R.; Pople, J. A. *Ab Initio Molecular Orbital Theory*; John Wiley & Sons: New York, 1986; p 228.

Barrier Height from V-I Characteristics of Semiconductor Contact: Reaction of Adsorbed Oxygen with Carbon Monoxide on ZnO (1010)

Hye Jung Kim and Chong Soo Han*

Department of Chemistry, Chonnam National University, Kwangju 500-757, Korea

Receive September 12, 1996

Barrier height on the surface was monitored at 77 K by observing the inflection of V-I characteristics of ZnO (10$\bar{1}$0)-ZnO(10$\bar{1}$0) contact in the surface reaction of oxygen species with carbon monoxide. The contact showed inflections at 10-20 mV and 10-50 mV for the sample adsorbed oxygen at 298 K and 573 K, respectively. When the sample adsorbed oxygen at 573 K was exposed to carbon monoxide at 298 K and 573 K, inflections were observed at 10-40 mV and 10-30 mV, respectively. The results indicated that the adsorption of oxygen on ZnO increased the surface barrier height, and the reaction of carbon monoxide with the oxygen-preadsorbed (at 573 K) ZnO decreased the surface barrier height.

Introduction

Catalytic reactions on semiconductor surface are often controlled by the surface barrier of the semiconductor which was developed by reactants. A measurement of the barrier height during the reaction process is important to understand the detailed mechanism of the reactions. We found a method to estimate the variation of the surface barrier height using *V-I* characteristics of semiconductor-semiconductor contact.

When acceptor type molecules are adsorbed on the surface of an n-type semiconductor crystal with n_b or N_D-N_A bulk electrons, the electrons in the semiconductor move to the molecules leaving a depletion layer with a depth, x_0. The mathematical description of surface barrier height V_s^0 of the layer is obtained from Poisson relation.[1]

$$V_s^0 = \frac{q_e(N_D - N_A)x_0^2}{2\kappa_s\varepsilon_0} \tag{1}$$

where κ_s, ε_0 and q_e are the static dielectric constant of semiconductor (≈ 8 for ZnO), the permittivity of the vacuum (8.854$\times 10^{-12}$ C^{2}m^{-1}J^{-1}) and the unit charge (1.602$\times 10^{-19}$ C), respectively. If faces of two semiconductors with the same layer are contacted and a bias voltage is applied to them, the new surface barrier height of the negatively biased semiconductor, V_S^- becomes[2]

$$V_s^- = V_s^0\left(1 - \frac{V}{4V_s^0}\right)^2 \tag{2}$$

and the surface barrier height of the positively biased semiconductor, V_S^+ becomes

$$V_s^+ = V_s^0\left(1 + \frac{V}{4V_s^0}\right)^2 \tag{3}$$

Since the electron moves from the negatively biased semiconductor to the positively biased semiconductor through the contact zone, the electron current can be given by

$$\begin{aligned} I &\approx C\cdot T\cdot n_e\cdot\mu_e\cdot q_e\cdot\frac{A}{2t}\cdot e^{-\frac{q_eV^-}{k_BT}}\cdot V \quad (V < 4V_s^0) \\ &\approx C\cdot T\cdot n_e\cdot\mu_e\cdot q_e\cdot\frac{A}{2t}\cdot V \qquad (V \geq 4V_s^0) \end{aligned} \tag{4}$$

where *c*, *T*, n_e and μ_e are the fraction of contact of the crystals, the tunneling factor through the contact, the number of free electron per unit volume and the mobility of the electron, respectively. Eq. (4) implies that *V-I* characteristics shows inflection at the bias voltage, $4V_S^0$ for the depletion layer. In the most cases, *V-I* characteristics shows a simple straight line and it is difficult to decide the bias voltage showing the inflection. We represented *V-I* characteristics as *I-kV vs. V* plot to visualize the inflection where *k* is the mean conductance of the sample. In fact, the contact of two single crystals is a sum of many microscopic contacts having different heights of the surface barrier and there can be many inflections. In this paper, we reported observations on the variation of surface barrier height in the surface reaction of carbon monoxide with adsorbed oxygen on ZnO surface.

Experimental

Polished single crystal ZnO(10$\bar{1}$0) was obtained from A-