Refinement of Molecular Mechanics Parameters for Ethers Based on the Conformational Energies of Me–O–X (X = Me, Et, Pr^i and Bu^t) Obtained by *ab initio* Molecular Orbital Calculations

Seiji Tsuzuki* and Kazutoshi Tanabe
National Chemical Laboratory for Industry, Tsukuba, Ibaraki 305, Japan

The conformational energies of 13 conformers, including saddle points of internal rotation, of the title compounds were calculated by various levels of the *ab initio* molecular orbital method. The calculated conformational energies at MP4(SDQ)/6-31G*//HF/6-31G* were close to the experimental values, the only exception being the eclipsed barrier height of ethyl methyl ether. The conformational energies obtained by the Hartree–Fock method did not agree well with the experimental values. Molecular mechanics parameters for the ether molecules were refined to reproduce the calculated conformational energies at the MP4(SDQ)/6-31G*//HF/6-31G* level. The refinement of bending parameters was important to reproduce the calculated conformational energies, as well as the refinement of torsional parameters.

The study of torsional interactions of ether molecules is important for the understanding of the structural properties of crown ethers and polyethers. Detailed information on the torsional potential of ether molecules is also necessary for molecular mechanics and molecular dynamics simulation of molecules containing the ether group. The *gauche–trans* energy difference of ethyl methyl ether, a key molecule to understanding this torsional interaction, has been studied by various methods,[1,2] but relatively little has been done to estimate the internal rotational barrier heights of this molecule[2] and the torsional potentials of other small ethers, such as isopropyl methyl ether[3] and t-butyl methyl ether.[4] Recently we have reported the energy calculation of the four stationary points of the internal rotation of ethyl methyl ether by an *ab initio* method at various levels.[5] The calculated *trans–gauche* energy difference using polarized basis sets with electron correlation is close to the experimental values. In this paper we describe the calculation of the energies of the conformers of dimethyl ether, ethyl methyl ether, isopropyl methyl ether and t-butyl methyl ether (shown in Figs. 1–4) at several theoretical levels. The calculated conformational energies are compared with the experimental values and those obtained by MM2.[6] Molecular mechanics parameters for ethers are refined to reproduce the conformational energies at the MP4(SDQ)/6-31G*//HF/6-31G* level.

Fig. 1 Calculated conformers of dimethyl ether

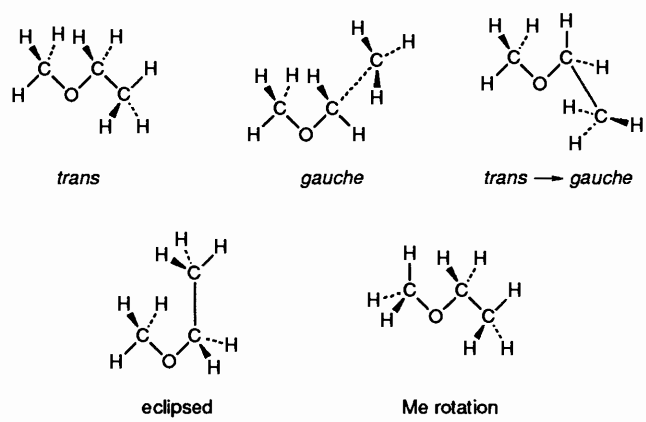

Fig. 2 Calculated conformers of ethyl methyl ether

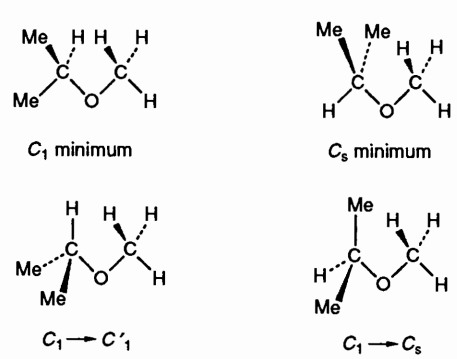

Fig. 3 Calculated conformers of isopropyl methyl ether

Computational Technique.—The GAUSSIAN82[7] and GAUSSIAN86[8] programs were used for the molecular orbital calculations. The geometries were fully optimized using the gradient optimization routine in these programs. Default convergence criteria were used for SCF and geometry optimization. The basis sets implemented in these programs were used for the calculation. The basis set 3-21G[9] is of a double-zeta type; 6-31G*[10] is also a double-zeta type basis set and has d functions on carbon and oxygen atoms. The electron correlation energy was corrected by the Møller–Plesset perturbation method[11] by the single point computation on the geometries obtained by the HF/6-31G* level geometry optimization. The MM2 program[6] was used for the molecular mechanics calculations.

Results and Discussion

Geometrical Features.—The calculated geometries of ethers obtained by *ab initio* calculations are compared with the experimental values in Table 1, from which it can be seen that the HF/6-31G* level optimized geometries are close to the experimental data. However, the calculated geometrical parameters deviate slightly from the experimental values. The C–O bond distances calculated at the HF/3-21G level are 0.01–0.02 Å longer than the experimental values, whereas the calculated C–O bond distances at the HF/6-31G* level are 0.02 Å shorter than the experimental values. (The same tendency has been

Table 1 Calculated geometries of ethers[a]

	HF/3-21G	HF/6-31G*	MM2[b]	MM[b] (this work)	Experimental
Dimethyl ether[c]					
C–O	1.4324	1.3913	1.422	1.420	1.415(1)[e]
C–O–C	113.99	113.80	111.7	111.5	111.8(2)[e]
Ethyl methyl ether, *trans*[d]					
C1–O	1.4321	1.3911	1.422	1.420	1.413(9)[f]
O–C3	1.4366	1.3964	1.423	1.422	1.422(7)[f]
C3–C4	1.5250	1.5160	1.534	1.534	1.520(4)[f]
C1–O–C3	114.69	114.22	111.9	111.6	111.9(5)[f]
O–C3–C4	106.76	108.59	108.8	109.0	109.4(3)[f]
C1–O–C3–C4	180.0	180.0	180.0	180.0	180.0[f]
Ethyl methyl ether, *gauche*					
C1–O	1.4335	1.3927	1.421	1.421	
O–C3	1.4379	1.3993	1.424	1.424	
C3–C4	1.5326	1.5235	1.535	1.537	
C1–O–C3	115.59	115.79	113.2	113.2	
O–C3–C4	112.41	113.42	112.3	111.4	
C1–O–C3–C4	75.16	76.95	70.0	76.5	84(6)[f]
Isopropyl methyl ether, C_1					
C1–O	1.4328	1.3923	1.421	1.421	1.416[g]
O–C3	1.4434	1.4058	1.426	1.427	1.422[g]
C3–C4	1.5324	1.5270	1.538	1.541	1.519[g]
C3–C5	1.5271	1.5209	1.539	1.540	1.528[g]
C1–O–C3	116.35	116.42	113.6	113.4	112.5[g]
O–C3–C4	111.07	111.80	111.9	111.0	113.7[g]
O–C3–C5	105.11	106.32	107.4	108.1	107.7[g]
C1–O–C3–C4	74.87	74.38	67.3	76.3	71.9[g]
C1–O–C3–C5	−164.21	−163.31	−171.7	−163.0	−162.6[g]
Isopropyl methyl ether, C_s[d]					
C1–O	1.4345	1.3943	1.421	1.421	
O–C3	1.4436	1.4086	1.427	1.428	
C3–C4	1.5342	1.5275	1.537	1.539	
C1–O–C3	118.02	118.59	115.0	115.7	
O–C3–C4	112.11	112.54	112.5	112.0	
C1–O–C3–C4	63.31	64.07	64.1	63.2	
t-Butyl methyl ether, C_s[d]					
C1–O	1.4335	1.3938	1.421	1.421	1.412(7)[h]
O–C3	1.4493	1.4167	1.430	1.433	1.429(7)[h]
C3–C4	1.5308	1.5272	1.545	1.547	1.533(3)[h]
C3–C5	1.5350	1.5320	1.541	1.545	1.533(3)[h]
C1–O–C3	119.06	119.60	115.8	116.2	115.8(13)[h]
O–C3–C4	102.88	103.66	105.5	106.4	102.9(7)[h]
O–C3–C5	111.11	111.16	111.6	111.2	110.7(6)[h]
C1–O–C3–C4	180.0	180.0	180.0	180.0	180.0[h]
C1–O–C3–C5	61.99	61.97	62.3	61.8	

[a] Distances in Å, angles in degrees. Results of the *ab initio* calculations of ethyl methyl ether are taken from ref. 5. [b] Details of the molecular mechanics parameters are shown in the text and in Table 4. [c] C_{2v} symmetry is assumed in the geometry optimization. [d] C_s symmetry is assumed in the geometry optimization. [e] From K. Tamagawa, M. Takemura, S. Konaka and M. Kimura, *J. Mol. Struct.*, 1984, **125**, 131. [f] Ref. 1(*d*). [g] Ref. 13. [h] Ref. 14(*b*).

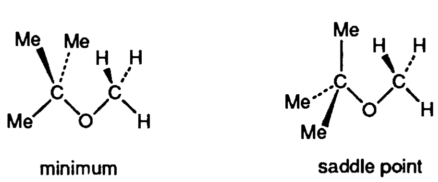

Fig. 4 Calculated conformers of t-butyl methyl ether

observed for the calculation of methanol.[12]) The calculated C–C bond distances are close to the experimental values at both levels. The calculated C–O–C angles are 2–4° larger than the experimental values. The calculated O–C–C angles are close to the experimental values.

The calculated C–O–C–C dihedral angles of *gauche* ethyl methyl ether are slightly smaller than the value obtained by electron diffraction.[1d] The calculated torsional angles of the C_1 conformer of isopropyl methyl ether are close to the values from microwave spectroscopy.[13] The molecular structure of t-butyl methyl ether has been studied by electron diffraction:[14] Suwa *et al.* reported that the C–O–C–C dihedral angle was twisted 13 ± 4° from C_s geometry,[14a] whereas Liedle *et al.* reported that this molecule had C_s symmetry.[14b] Here we optimized the geometry at the HF/6-31G* level from the 13° twisted geometry, whereas the structure was converged to a C_s minimum.

Conformational Energy Calculation by ab initio *Molecular Orbital Method*.—The calculated conformational energies of ethers at several theoretical levels are compared with experimental values in Table 2. The calculated conformational energies at the MP4(SDQ)/6-31G*//HF/6-31G* level are close

Table 2 Relative energies obtained by various levels of *ab initio* calculations

Structure	Relative energy[a] HF/ 3-21G[b]	HF/ 6-31G*[c]	MP2/ 6-31G*[c]	MP3/ 6-31G*[c]	MP4(SDQ)/ 6-31G*[c]	Experimental
Dimethyl ether						
staggered[d,e]	0.0	0.0	0.0	0.0	0.0	0.0
eclipsed[f]	2.621	2.577	2.884	2.721	2.777	2.72[k]
Ethyl methyl ether						
trans[f,g]	0.0	0.0	0.0	0.0	0.0	0.0
gauche	0.998	1.669	1.404	1.384	1.360	1.11,[l] 1.5[m]
trans $\longrightarrow$ *gauche*	2.331	2.556	2.669	2.568	2.582	2.93[l]
eclipsed[f]	5.565	6.838	7.002	6.784	6.827	4.07[l]
Me rotation[f,h]	2.458	2.476	2.743	2.587	2.643	2.70[n]
Isopropyl methyl ether						
C_1 minimum[i]	0.0	0.0	0.0	0.0	0.0	0.0
C_s minimum[f]	1.598	2.307	2.172	2.095	2.114	2.2[o]
$C_1 \longrightarrow C'_1$	1.179	0.851	1.209	1.129	1.159	1.2[o]
$C_1 \longrightarrow C_a$	4.348	5.112	5.406	5.256	5.281	5.8[o]
t-Butyl methyl ether						
minimum[f,j]	0.0	0.0	0.0	0.0	0.0	0.0
saddle point[f]	2.622	2.767	3.253	3.151	3.161	3.57[p]

[a] Energies in kcal mol^{-1}. Results of the *ab initio* calculations of the conformational energies of C–O–C–C bond rotation of ethyl methyl ether are taken from Ref. 5. [b] HF/3-21G geometries used for the calculation. [c] HF/6-31G* geometries used for the calculation. [d] C_{2v} symmetry is assumed in the geometry optimization. [e] The calculated energies of the staggered conformer at HF/3-21G, HF/6-31G*, MP2/6-31G*, MP3/6-31G* and MP4(SDQ)/6-31G* levels are −153.213 21, −154.064 75, −154.502 07, −154.526 83 and −154.535 34 hartree, respectively. [f] C_s symmetry is assumed in the geometry optimization. [g] The calculated energies of the *trans* conformer at HF/3-21G, HF/6-31G*, MP2/6-31G*, MP3/6-31G* and MP4(SDQ)/6-31G* levels are −192.037 55, −193.104 87, −193.673 04, −193.707 27 and −193.717 73 hartree, respectively. [h] The barrier of the internal rotation of O–Me bond for the *trans* conformer. [i] The calculated energies of the C_1 minimum conformer at HF/3-21G, HF/6-31G*, MP2/6-31G*, MP3/6-31G* and MP4(SDQ)/6-31G* levels are −230.860 92, −232.141 58, −232.843 29, −232.886 47 and −232.898 92 hartree, respectively. [j] The calculated energies of the minimum conformer at HF/3-21G, HF/6-31G*, MP2/6-31G*, MP3/6-31G* and MP4(SDQ)/6-31G* levels are −269.683 38, −271.175 63, −272.013 16, −272.064 63 and −272.079 05 hartree, respectively. [k] Ref. 15. [l] Ref. 2(*a*). [m] Ref. 1(*a*). [n] Ref. 17. [o] Ref. 3(*b*). [p] Ref. 4.

to the experimental values, the only exception being the eclipsed barrier height of ethyl methyl ether. The calculated conformational energies at the MP3 level are very close to those calculated at the MP4(SDQ) level (the maximum deviation is 0.06 kcal mol^{-1}). The calculated conformational energies at the MP2 level are 0.04–0.18 kcal mol^{-1} larger than those obtained at the MP4(SDQ) level. The agreement between the experimental conformational energies and those obtained at HF levels is worse.

Dimethyl ether. The internal rotational barrier height of dimethyl ether (see Fig. 1) has been reported to be 2.72 kcal mol^{-1},† from microwave spectroscopy.[15] The calculated barrier height of 2.78 kcal mol^{-1} at the MP4(SDQ)/6-31G*//HF/6-31G* level is close to the experimental value.

Ethyl methyl ether. Recently we have reported *ab initio* calculations of the relative energies of the four stationary points of the internal rotation of the C–O–C–C skeleton of ethyl methyl ether at several theoretical levels.[5] In addition to the calculations for these conformers, the barrier height of the internal rotation of C–O–C–H bond was calculated (Me rotation in Fig. 2). The results are summarized in Table 2. The energy difference between *trans* and *gauche* conformers in the gas phase has been reported to be 1.1–1.5 kcal mol^{-1} from several experimental measurements.[1a,1d,2a] The calculated energy difference of 1.36 kcal mol^{-1} at the MP4(SDQ)/6-31G*//HF/6-31G* level is close to these experimental values. The internal rotational barrier height of C–O–C–H bonds has been reported to be 2.61 and 2.5 ± 0.1 kcal mol^{-1} from the measurement of infrared spectra[2a,16] and 2.70 ± 0.01 kcal mol^{-1} from microwave spectroscopy.[17] The calculated barrier height of 2.64 kcal mol^{-1} at the MP4(SDQ)/6-31G*//HF/6-31G* level is close to these values.

† 1 cal = 4.184 J.

The internal rotational potential of the C–O–C–C bonds of ethyl methyl ether has been studied by the analysis of infrared spectra of the torsional mode.[2a] The *trans* $\longrightarrow$ *gauche* and eclipsed barriers have been estimated to be 2.93 and 4.07 kcal mol^{-1}, respectively. These barriers are calculated to be 2.58 and 6.83 kcal mol^{-1}, respectively, at the MP4(SDQ)/6- 31G*//HF/6-31G* level. The calculated eclipsed barrier height is considerably higher than the experimental value, although it decreases slightly when a basis set which has double d functions on heavy atoms is used.[5] However, the calculated eclipsed barrier height of 6.41 kcal mol^{-1} at the MP2/6-31G(2d,2p)//HF/6-31G* level[5] is still larger than the experimental value.

Other experimental conformational energies of ethyl methyl ether are reproduced well by MP4(SDQ)/6-31G*//HF/6-31G* level calculations. One possible reason of the disagreement of the eclipsed barrier height is the insufficient accuracy of the calculation at these levels. The experimental internal rotational potential is deduced from the analysis of infrared spectra of the torsional mode based on some assumptions,[2a] and another possibility is the inappropriateness of the assumptions used.

Isopropyl methyl ether. Isopropyl methyl ether has two stable conformers (Fig. 3). It has been deduced from several experimental observations that the C_1 conformer is more stable than the C_s conformer.[3,18] The energy difference between these two conformers has been reported to be 2.2 ± 0.2 kcal mol^{-1} (from ^{13}C NMR spectra in [$^2H_{12}$] cyclohexane)[3b] and 2.4 ± 0.6 kcal mol^{-1} (from Raman spectra in an Ar matrix).[3a] The calculated energy difference of 2.11 kcal mol^{-1} at the MP4(SDQ)/6-31G*//HF/6-31G* level is close to these experimental values. The $C_1 \longrightarrow C'_1$ and the $C_1 \longrightarrow C_s$ barriers have been estimated to be 1.2 and 5.8 kcal mol^{-1}, respectively, from the joint analysis of the measured NMR coupling constant and simple force-field calculations.[3b] The calculated barrier

Table 3 Relative energies calculated by molecular mechanics

Structure	Relative energy [a] MM2 [b]	MM [b] (this work)	*ab initio* [c]	Experimental
Dimethyl ether				
staggered	0.0	0.0	0.0	0.0
eclipsed	2.519	2.679	2.777	2.72 [g]
Ethyl methyl ether				
trans	0.0	0.0	0.0	0.0
gauche	1.732	1.650	1.360	1.11,[h] 1.5 [i]
trans $\longrightarrow$ *gauche*	2.865 [d]	2.714 [d]	2.582	2.93 [h]
eclipsed	5.863 [e]	6.821 [e]	6.827	4.07 [h]
O–Me rotation	2.523 [f]	2.684 [f]	2.643	2.70 [j]
Isopropyl methyl ether				
C_1 minimum	0.0	0.0	0.0	0.0
C_s minimum	1.719	1.984	2.114	2.2 [k]
$C_1 \longrightarrow C_1'$	1.378 [d]	1.011 [d]	1.159	1.2 [k]
$C_1 \longrightarrow C_s$	4.401 [e]	5.152 [e]	5.281	5.8 [k]
t-Butyl methyl ether				
minimum	0.0	0.0	0.0	0.0
saddle point	2.895 [e]	3.043 [e]	3.161	3.57 [l]
RMSD [m]	0.503	0.142		

[a] Energies in kcal mol^{-1}. [b] Parameters listed in Table 4. [c] MP4(SDQ)/6-31G*//HF/6-31G* level calculation. See details in Table 2. [d] The C1–O–C3–H angle is kept as 0° in the geometry optimization. [e] The C1–O–C3–C4 angle is kept as 0° in the geometry optimization. [f] The barrier of the internal rotation of the O–Me bond for the *trans* conformer. The C3–O–C1–H angle is kept as 0° in the geometry optimization. [g] Ref. 15. [h] Ref. 2*a*. [i] Ref. 1*a*. [j] Ref. 17. [k] Ref. 3*b*. [l] Ref. 4. [m] Root mean square deviation between the *ab initio* conformational energies and those from molecular mechanics calculations.

heights of 1.16 and 5.28 kcal mol^{-1} at the MP4(SDQ)/6-31G*//HF/6-31G* level are close to these values.

t-Butyl methyl ether. The internal rotational barrier height of the C–O–C–C bonds of t-butyl methyl ether has been estimated to be 3.57 kcal mol^{-1} from the analysis of far-infrared spectra in the gas phase (Fig. 4).[4] The calculated barrier height of 3.16 kcal mol^{-1} at MP4(SDQ)/6-31G*//HF/6-31G* level is slightly lower than the experimental value.

Conformational Energy Calculation by Molecular Mechanics.—The conformational energies of these ethers were also calculated by the commonly used empirical force field MM2.[6] The calculated conformational energies are compared with the experimental values and those obtained by the *ab initio* method in Table 3. The energy difference between the *trans* and *gauche* conformers of ethyl methyl ether and the energy difference between the C_1 and the C_s conformers of isopropyl methyl ether are reproduced well by the MP4(SDQ)/6-31G*//HF/6-31G* level *ab initio* calculation, whereas MM2 overestimates the former energy difference and underestimates the latter. The calculated barrier heights at the MP4(SDQ)/6-31G*//HF/6-31G* level agree with the experimental barrier heights better than those obtained by MM2 if the two barrier heights of ethyl methyl ether are excluded.

Refinement of Molecular Mechanics Parameters.—Usually molecular mechanics parameters are optimized to reproduce a large number of experimental data.[6] This strategy worked well for the optimization of parameters for hydrocarbons,[19] but is often not practicable for the optimization of parameters for molecules containing a heteroatom. The experimental information on these molecules is often limited and is not sufficient to determine parameters accurately.[20,2b] Another difficulty arising from the use of experimental data is that the accuracy and the reliability of these data are not constant.[20d] Experimental data are collected by several methods, and each method has a different accuracy and reliability.[6] These difficulties can be overcome by the use of the data obtained by theoretical calculation.[20d] As mentioned before, the overall performance of the calculations at the MP4(SDQ)/6-31G*//HF/6-31G* level is satisfactory to reproduce the experimental data. Thus the molecular mechanics parameters for ethers were refined based on the conformational energies at this level.

Some parameters used in the MM2 force field were refined to reproduce the MP4(SDQ)/6-31G*//HF/6-31G* level conformational energies. Jaime and Osawa have claimed that the MM2 parameters for carbon and hydrogen atoms are not appropriate, and that this force field underestimates the internal rotational barrier heights of some congested hydrocarbons.[21] They have refined some MM2 parameters to eliminate this defect and called the new force field MM2′. Some of the ether molecules to be calculated here have a congested hydrocarbon group. Therefore, the MM2′ parameters for the carbon and hydrogen atoms in such groups are used. Other parameters are taken from the MM2 force field.

First the 1–1–6–1 and 5–1–6–1 torsional parameters were optimized to reproduce the MP4(SDQ)/6-31G*//HF/6-31G* level conformational energies. Other parameters were not changed. Atom types are shown in the footnote to Table 4. The root mean square deviation (RMSD) between the conformational energies obtained by the *ab initio* method and those obtained by MM2 is 0.503 kcal mol^{-1}. The use of the refined parameters decreases the RMSD to 0.267 kcal mol^{-1}. The overall agreement is improved, whereas the agreement of the calculated internal rotational barrier height of dimethyl ether and the *trans–gauche* energy difference of ethyl methyl ether with the experimental values becomes worse. This shows the defect of our strategy to refine only torsional parameters to reproduce the calculated conformational energies: the refinement of other parameters would be necessary to get better agreement.

The next step was to refine the bending parameters. The *ab initio* calculations show that the valence angles of ethers change by the internal rotation. The importance of this type of deformation for the estimation of internal rotational barrier heights by *ab initio* calculation has been reported.[12] Thus the use of an accurate bending potential would be necessary in order to obtain accurate conformational energies by molecular mechanics calculation.

Table 4 Molecular mechanics parameters used in this work

Parameter type[a]	MM2	This work[b]
Bending force constants, k_θ/mdyn Å rad^{-2}		
1 1 1	0.45	0.800
1 1 5	0.36	0.610
5 1 5	0.32	0.626
5 1 6	0.54	0.840
1 6 1	0.77	0.770
1 1 6	0.70	0.980
Torsional parameter, V_1/kcal mol^{-1}		
1 1 6 1	0.40	0.628
5 1 6 1	0.0	0.0
Twofold torsional parameter, V_2/kcal mol^{-1}		
1 1 6 1	0.52	0.017
5 1 6 1	0.0	0.0
Threefold torsional parameter, V_3 kcal mol^{-1}		
1 1 6 1	0.47	0.393
5 1 6 1	0.53	0.591

[a] Atom type 1 is for carbon, 5 is for hydrogen and 6 is for oxygen. [b] Other parameters for carbon and hydrogen atoms are taken from the MM2′ force field and those for oxygen from the MM2 force field.

The bending parameters were refined as follows. The energies of the equilibrium structure of the ethers were calculated. The valence angle was then changed from the value in the equilibrium conformer. The energy increment due to this deformation was defined as the deformation energy (DE).[20e] The bending potential was obtained from the calculated DEs for several angle values at the MP4(SDQ)/6-31G*//HF/6-31G* level. Then the bending parameters were optimized to reproduce this bending potential. The 6–1–5 bending parameters were refined based on the O–C–H bending potential of dimethyl ether. The 1–6–1 bending parameters were refined based on the C–O–C bending potential of dimethyl ether. The 1–1–6 bending parameters were refined based on the C–C–O bending potential of ethyl methyl ether. The 1–1–1, 1–1–5 and 5–1–5 bending parameters are also necessary for the molecular mechanics calculation of ethers. These angle bending parameters were refined based on the MP4(SDQ)/6-31G*//HF/6-31G* level bending potentials of methane, ethane and propane.[22] The changes of the bending parameters affect the calculated conformational energies. Thus the torsional parameters were refined again to reproduce the *ab initio* conformational energies using the new bending parameters. The refined parameters are shown in Table 4.

The calculated conformational energies of ethers using the new parameters are shown in the third column of Table 3. The agreement with the *ab initio* conformational energies is improved, the RMSD decreasing to 0.142 kcal mol^{-1}. The calculated internal rotational barrier height of dimethyl ether and the energy difference between the *trans* and *gauche* isomers of ethyl methyl ether agree well with the experimental values. These calculations show that the refinement of bending parameters is important as well as the refinement of torsional parameters to reproduce the conformational energies.

The calculated geometries of the ethers using the new parameters are shown in Table 1. The calculated geometrical parameters agree well with the experimental values, as do those obtained by MM2 force field calculations.

Conclusions

The conformational energies of four ethers were calculated by several levels of *ab initio* method. The calculated conformational energies at the MP4(SDQ)/6-31G*//HF/6-31G* level were close to the experimental values if the eclipsed barrier of ethyl methyl ether was excluded. The agreement between the calculated conformational energies at the HF level and the experimental values were not good. The incorporation of electron correlation energy corrections was important in the conformational energy calculation. Some MM2 parameters were refined to reproduce the conformational energies at the MP4(SDQ)/6-31G*//HF/6-31G* level. The refinement of bending parameters was necessary to reproduce the *ab initio* conformational energies as well as the refinement of torsional parameters.

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