

# High-Level ab Initio Calculations of Torsional Potential of Phenol, Anisole, and *o*-Hydroxyanisole: Effects of Intramolecular Hydrogen Bond

Seiji Tsuzuki,<sup>\*,†,‡</sup> Hirohiko Houjou,<sup>‡</sup> Yoshinobu Nagawa,<sup>‡</sup> and Kazuhisa Hiratani<sup>‡</sup>

National Institute of Materials and Chemical Research, Tsukuba, Ibaraki 305-8565, Japan, and  
National Institute for Advanced Interdisciplinary Research, Tsukuba, Ibaraki 305-8562, Japan

Received: October 11, 1999; In Final Form: December 1, 1999

The internal rotational barrier heights of phenol and anisole were calculated using several basis sets up to cc-pVQZ with MP2-level electron correlation correction to evaluate the basis set effects. The calculations showed that the effects of the further improvement of the basis set beyond the cc-pVTZ were very small. Although the electron correlation substantially increased the barrier heights of the two molecules, the effects of the electron correlation beyond the MP2 method were not large. The barrier heights calculated with the CCSD(T) method were close to those with the MP2 method. The internal rotational potentials of methoxy and hydroxyl groups of *o*-hydroxyanisole were calculated at the MP2/cc-pVTZ/HF/6-311G\*\* level. The calculated potentials were compared with those of phenol and anisole. *o*-Hydroxyanisole preferred planar structure in which the hydroxyl group had an intramolecular hydrogen bond with the oxygen atom of the methoxy group. The calculated torsional potential of the methoxy group had the maximum (7.30 kcal/mol) when the methoxy group rotated 180° from the minimum energy structure, in which the hydroxyl group did not have the hydrogen bond. The barrier height of the methoxy group of *o*-hydroxyanisole was considerably larger than that of anisole (2.99 kcal/mol). The large internal rotational barrier height of *o*-hydroxyanisole showed that the intramolecular hydrogen bond greatly stabilized the energy minimum structure and that the hydrogen bond strictly restricted the conformational flexibility of the methoxy group.

## I. Introduction

The structure and torsional potential of anisole (methoxybenzene) have been the subjects of many experimental<sup>1–14</sup> and theoretical<sup>11,14–25</sup> studies. Anisole, which is the simplest alkyl aryl ether, is a model compound for a lot of chemically and biologically interesting systems. It has been reported that anisole units play important roles in the selective binding of anions by macrocyclic polyethers.<sup>26,27</sup> The number of methoxy substituents and their orientations are important for the pharmacological properties of drugs.<sup>28,29</sup> Detailed information on the torsional potential of anisole is important for the understanding of the three-dimensional structures of these systems and for the design of artificial host molecules.

A few studies were reported the effects of ortho substituents on the conformation of the methoxy group of anisole.<sup>1,9,12,15</sup> These studies showed that halogen atoms and alkyl groups in the ortho position gave substantial effects on the torsional potential of the methoxy group, indicating that the conformation of the methoxy group can be controlled by the choice of the ortho substituent. It is expected that the hydroxyl group in the ortho position will greatly affect the torsional potential of the methoxy group, because the hydroxyl group will have an intramolecular hydrogen bond with the oxygen atom of the methoxy group. Electron diffraction studies of *o*-nitrophenol showed that the intramolecular hydrogen bond considerably changed the torsional potential of the nitro group.<sup>30,31</sup> Although the effects of the ortho hydroxyl group on the torsional potential of the methoxy group is important for the design of artificial

host molecules, the torsional potential of *o*-hydroxyanisole is still not certain. In this paper, we have studied the torsional potentials of methoxy and hydroxyl groups of *o*-hydroxyanisole by high-level ab initio calculations. It is well-known that the calculated torsional potential depends greatly on the choice of the basis set and electron correlation correction procedure.<sup>32–37</sup> Fortunately, however, the calculated torsional potentials of ethers agree well with the experimental ones, if a reasonably large basis set is used and electron correlation is properly corrected.<sup>35–38</sup> In this study, we have also evaluated in detail the effects of basis set and electron correlation on the calculated torsional potentials to judge the accuracy of the calculated torsional potentials.

## II. Computational Method

The *Gaussian 94* program<sup>39</sup> was used for the ab initio molecular orbital calculations. The basis sets implemented in the program were used.<sup>40–42</sup> The geometries were optimized at the HF/6-311G\*\* level, if not otherwise noted. In the geometry optimization of phenol and anisole, the phenyl ring was assumed to be planar. Single point calculations with the electron correlation correction by the second-order Møller–Plesset perturbation method (MP2)<sup>43,44</sup> were carried out for the optimized geometries. The electron correlation was also corrected by the higher order Møller–Plesset methods and by the coupled cluster method using single and double substitutions with noniterative triple excitations (CCSD(T)).<sup>45</sup>

## III. Results and Discussion

**A. Geometry Optimization.** We calculated the internal rotational barrier heights of phenol and anisole using both the

\* E-mail: tsuzuki@nimc.go.jp.

<sup>†</sup> National Institute of Materials and Chemical Research.

<sup>‡</sup> National Institute for Advanced Interdisciplinary Research.

**TABLE 1: Optimized Geometries of Planar and Perpendicular Phenol and Anisole<sup>a</sup>**

	planar		perpendicular	
	HF <sup>b</sup>	MP2 <sup>c</sup>	HF <sup>b</sup>	MP2 <sup>c</sup>
Phenol				
C <sub>1</sub> –C <sub>2</sub>	1.385	1.400	1.384	1.398
C <sub>2</sub> –C <sub>3</sub>	1.387	1.399	1.385	1.398
C <sub>3</sub> –C <sub>4</sub>	1.382	1.397	1.385	1.399
C <sub>4</sub> –C <sub>5</sub>	1.388	1.400	1.385	1.399
C <sub>5</sub> –C <sub>6</sub>	1.380	1.396	1.385	1.398
C <sub>1</sub> –C <sub>6</sub>	1.388	1.400	1.384	1.398
C <sub>1</sub> –O <sub>7</sub>	1.350	1.367	1.369	1.389
O <sub>7</sub> –H <sub>8</sub>	0.940	0.962	0.941	0.960
C <sub>1</sub> –C <sub>2</sub> –C <sub>3</sub>	119.7	119.9	119.7	119.8
C <sub>2</sub> –C <sub>3</sub> –C <sub>4</sub>	120.7	120.4	120.4	120.2
C <sub>3</sub> –C <sub>4</sub> –C <sub>5</sub>	119.1	119.4	119.5	119.8
C <sub>4</sub> –C <sub>5</sub> –C <sub>6</sub>	120.9	120.6	120.4	120.2
C <sub>2</sub> –C <sub>1</sub> –O <sub>7</sub>	122.5	122.9	119.9	119.9
C <sub>1</sub> –O <sub>7</sub> –H <sub>8</sub>	110.7	107.7	109.7	106.6
C <sub>2</sub> –C <sub>1</sub> –O <sub>7</sub> –H <sub>8</sub>	0.0	0.0	90.0	90.0
Anisole				
C <sub>1</sub> –C <sub>2</sub>	1.385	1.402	1.385	1.399
C <sub>2</sub> –C <sub>3</sub>	1.391	1.402	1.384	1.398
C <sub>3</sub> –C <sub>4</sub>	1.378	1.395	1.385	1.399
C <sub>4</sub> –C <sub>5</sub>	1.391	1.402	1.385	1.399
C <sub>5</sub> –C <sub>6</sub>	1.377	1.393	1.384	1.398
C <sub>1</sub> –C <sub>6</sub>	1.393	1.404	1.385	1.399
C <sub>1</sub> –O <sub>7</sub>	1.347	1.364	1.361	1.380
O <sub>7</sub> –H <sub>8</sub>	1.398	1.418	1.405	1.424
C <sub>1</sub> –C <sub>2</sub> –C <sub>3</sub>	119.5	119.4	119.7	119.7
C <sub>2</sub> –C <sub>3</sub> –C <sub>4</sub>	121.1	121.0	120.4	120.2
C <sub>3</sub> –C <sub>4</sub> –C <sub>5</sub>	118.9	119.2	119.6	119.8
C <sub>4</sub> –C <sub>5</sub> –C <sub>6</sub>	120.7	120.4	120.4	120.2
C <sub>2</sub> –C <sub>1</sub> –O <sub>7</sub>	124.6	124.9	119.9	119.8
C <sub>1</sub> –O <sub>7</sub> –C <sub>8</sub>	119.9	116.4	115.6	111.4
C <sub>2</sub> –C <sub>1</sub> –O <sub>7</sub> –C <sub>8</sub>	0.0	0.0	90.0	90.0

<sup>a</sup> Bond distance is in angstroms; bond and torsional angles are in degrees. <sup>b</sup> Optimized geometries at HF/6-311G\*\* level. <sup>c</sup> Optimized geometries at MP2/6-311G\*\* level.

HF/6-311G\*\* and MP2/6-311G\*\* level-optimized geometries to evaluate the effects of the electron correlation in the geometry optimization. The HF- and MP2-level-optimized geometries are shown in Table 1. The MP2/6-311G\*\* level calculations were carried out for the optimized geometries to obtain the internal rotational barrier heights. The calculated barrier heights of phenol and anisole using the HF/6-311G\*\* geometries were 3.39 and 2.23 kcal/mol, respectively. These values are very close to those obtained using the MP2/6-311G\*\* geometries (3.42 and 2.34 kcal/mol, respectively), indicating that the electron correlation in the geometry optimization has a negligible effect on the calculated barrier heights. The calculations of the torsional potential of ethyl methyl ether also show that the effects of electron correlation in the geometry optimization are negligible.<sup>35</sup> Due to the good performance of the HF/6-311G\*\* level-optimized geometries, we used the HF/6-311G\*\* geometries for the further calculations of conformational energies.

**B. Effects of Electron Correlation.** The internal rotational barrier heights of phenol and anisole were calculated with electron correlation correction by the MP2, MP3, MP4(SDQ), CCSD, and CCSD(T) methods. The calculated barrier heights of phenol using the 6-31G\* basis set were 3.58, 3.14, 3.34, 3.23, and 3.38 kcal/mol, respectively, as summarized in Table 2. Those of anisole were 2.23, 1.89, 2.20, 2.05, and 2.17 kcal/mol, respectively. The calculated barrier heights of phenol and anisole by the HF method were 2.69 and 1.42 kcal/mol, respectively. The electron correlation substantially increases the calculated barrier heights. The effects of electron correlation beyond the MP2 method are not large. The barrier heights

**TABLE 2: Calculated Internal Rotational Barrier Heights of Phenol and Anisole Using Several Basis Sets<sup>a</sup>**

basis set	BF <sup>b</sup>	HF	MP2	MP3	MP4(SDQ)	CCSD	CCSD(T)
Phenol							
6-31G*	117	2.69	3.58	3.14	3.34	3.23	3.38
6-311G*	144	2.93	4.04	3.55	3.76	3.66	3.88
6-311G**	162	2.61	3.39	2.97	3.17	3.08	3.26
6-311++G**	196	2.49	3.08				
6-311G(2d,2p)	215	2.54	3.41				
6-311G(3d,3p)	268	2.52	3.20				
cc-pVDZ	128	2.81	3.74	3.29	3.51	3.42	3.58
cc-pVTZ	294	2.77	3.56				
cc-pVQZ	565	2.79	3.52				
basis set limit <sup>c</sup>			(3.51)				
exp.							3.47 <sup>d</sup>
Anisole							
6-31G*	136	1.42	2.23	1.89	2.20	2.05	2.17
6-311G*	168	1.49	2.23	1.88	2.17	2.04	2.19
6-311G**	192	1.49	2.36	1.99	2.26	2.13	2.30
6-311++G**	232	1.46	2.10				
6-311G(2d,2p)	256	1.40	2.83				
6-311G(3d,3p)	320	1.55	2.68				
cc-pVDZ	152	1.49	2.55	2.15	2.44	2.31	2.48
cc-pVTZ	352	1.72	2.99				
cc-pVQZ	680	1.77	2.99				
basis set limit <sup>c</sup>			(2.99)				
exp.							<3.1 <sup>e</sup>

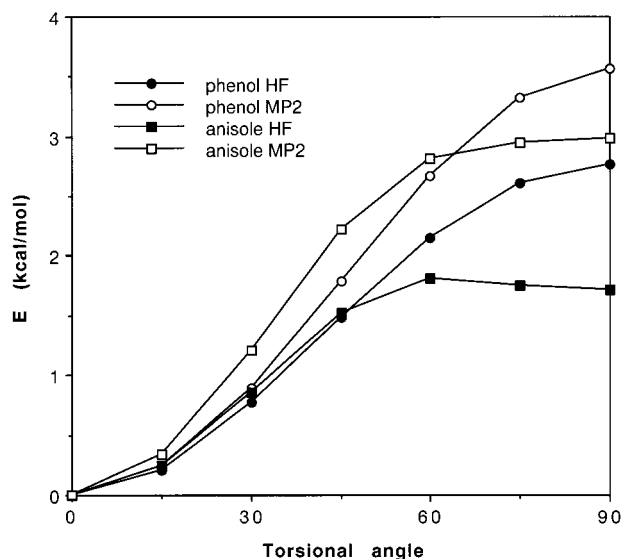
<sup>a</sup> Energies are in kilocalories/mole. HF/6-311G\*\* geometries were used. <sup>b</sup> Number of basis functions. <sup>c</sup> Estimated values at the basis set limit. See text. <sup>d</sup> From Berden et al.<sup>48</sup> <sup>e</sup> From Spellmeyer et al.<sup>23</sup>

obtained by the MP2 calculations (3.58 and 2.23 kcal/mol) are close to those obtained by the CCSD(T) calculations (3.38 and 2.17 kcal/mol). The calculations using larger 6-311G\*, 6-311G\*\*, and cc-pVDZ basis sets also show that the effects of electron correlation correction beyond the MP2 are not large, as summarized in Table 2. It has been reported that conformational energies of *n*-alkanes and biphenyl calculated with the MP2 method are close to those with the CCSD(T) method.<sup>38,46</sup>

**C. Effects of Basis Set.** The internal rotational barrier heights of phenol and anisole were calculated using several basis sets up to cc-pVQZ (565 and 680 basis functions, respectively) to evaluate the basis set effects. The basis set effects are very small, if the basis sets larger than cc-pVTZ are used, as shown in Table 2. The calculated barrier heights of phenol and anisole at the MP2 level with this basis set were 3.56 and 2.99 kcal/mol, respectively. These values are close to those calculated with the larger cc-pVQZ basis set (3.52 and 2.99 kcal/mol, respectively) and the estimated values at the basis set limit (3.51 and 2.99 kcal/mol, respectively). The barrier heights at the basis set limit were estimated by the method proposed by Feller.<sup>46,47</sup> The calculated barrier height of phenol agrees well with the recently reported experimental value of 3.47 kcal/mol.<sup>48</sup> The experimental measurements show that the barrier height of anisole is less than 3.1 kcal/mol,<sup>23</sup> which also agrees well with the calculated barrier heights. These results indicate that the calculations with cc-pVTZ are very accurate.

**D. Torsional Potential of Phenol and Anisole.** Torsional potentials of phenol and anisole were calculated at the HF/cc-pVTZ and MP2/cc-pVTZ levels using the HF/6-311G\*\* geometries as shown in Figure 1. Phenol and anisole prefer planar structure. The barrier heights calculated with the MP2 method were 3.56 and 2.99 kcal/mol, respectively.

The calculated torsional potential of anisole is flat where the torsional angle is 60–90°, indicating that the potential has a large *V*<sub>4</sub> component,<sup>49</sup> as suggested by previous calculations.<sup>12–14,22</sup> The possibility of the existence of the second stable conformer of anisole was a controversial issue.<sup>23</sup> HF calculations



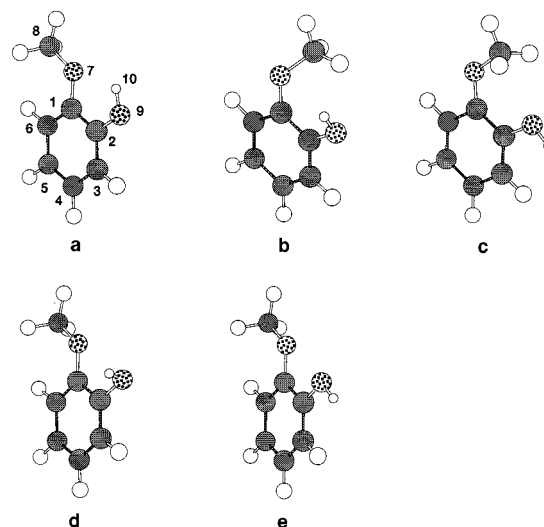
**Figure 1.** Calculated HF and MP2 torsional potentials of phenol and anisole using the cc-pVTZ basis set. The HF/6-311G\*\* level-optimized geometries were used. 0° corresponds to planar structures.

showed that the perpendicular structure is the second stable conformer.<sup>11,14,17,18,20,22–25</sup> Spellmeyer et al. reported the geometry optimization of the transition-state structure between the planar and perpendicular structures at the HF/6-31G\* level. The torsional angle of the transition state structure was 59.7°. <sup>23</sup> However, their MP2/6-31G\* level calculations for the HF level-optimized geometries showed that the perpendicular structure was 0.1 kcal/mol less stable than the twisted structure. They concluded that the perpendicular structure was the maximum of the torsional potential. Our MP2/cc-pVTZ//HF/6-311G\*\* level potential had a maximum when the torsional angle was 90°. The potential was very flat near the maximum. The calculated energy difference between the two structures ( $\theta = 60^\circ$  and  $90^\circ$ ) was only 0.17 kcal/mol.

The calculated torsional potential of methyl group is a 3-fold potential. The calculated internal rotational barrier height at the MP2/6-311G\*\*//HF/6-311G\*\* level is 4.05 kcal/mol. This barrier height is substantially larger than that of dimethyl ether. The calculated internal rotational barrier height of dimethyl ether at the MP4(SDTQ)//HF/6-31G\* level is 2.78 kcal/mol.<sup>50</sup> The experimental barrier height is 2.72 kcal/mol.<sup>51</sup> Steric repulsion between the methyl group and the *o*-hydrogen atom would be the cause of the larger barrier height of anisole.

**E. Torsional Potential of the Methoxy Group of *o*-Hydroxyanisole.** The torsional potential of the methoxy group of *o*-hydroxyanisole was calculated. The C<sub>2</sub>–C<sub>1</sub>–O<sub>7</sub>–C<sub>8</sub> torsional angle ( $\alpha$ ) was fixed at 0°, 30°, 60°, 90°, 120°, 150°, and 180°, respectively, and other geometrical parameters were optimized. The optimized geometries for  $\alpha = 180^\circ$ , 60°, and 0° are shown in Figure 2 (conformers a, b, and c). The relative energies of the optimized geometries were calculated at the MP2/cc-pVTZ level, as summarized in Table 3.

*o*-Hydroxyanisole prefers planar structure (conformer a) in which the hydroxyl group has an intramolecular hydrogen bond with the oxygen atom of the methoxy group. The torsional potential has the maximum when the methoxy group rotates 180° (conformer c) from the minimum. In this conformer, the hydroxyl group does not have the hydrogen bond, due to the steric repulsion with the methyl group. The C<sub>8</sub>...O<sub>9</sub> distance in the optimized geometry is only 2.74 Å. The rotation of the methoxy group changes the torsional angle of the hydroxyl group, as summarized in Table 3. The C<sub>1</sub>–C<sub>2</sub>–O<sub>9</sub>–H<sub>10</sub> torsional



**Figure 2.** Optimized geometries of *o*-hydroxyanisole at the HF/6-311G\*\* level. The C<sub>2</sub>–C<sub>1</sub>–O<sub>7</sub>–C<sub>8</sub> torsional angle ( $\alpha$ ) was fixed at 180°, 60°, and 0°, respectively, in the conformers a, b, and c. The C<sub>1</sub>–C<sub>2</sub>–O<sub>9</sub>–H<sub>10</sub> torsional angle ( $\beta$ ) was fixed at 90° and 180°, respectively, in the conformers d and e.

**TABLE 3: Calculated Torsional Potential of *o*-Hydroxyanisole<sup>a</sup>**

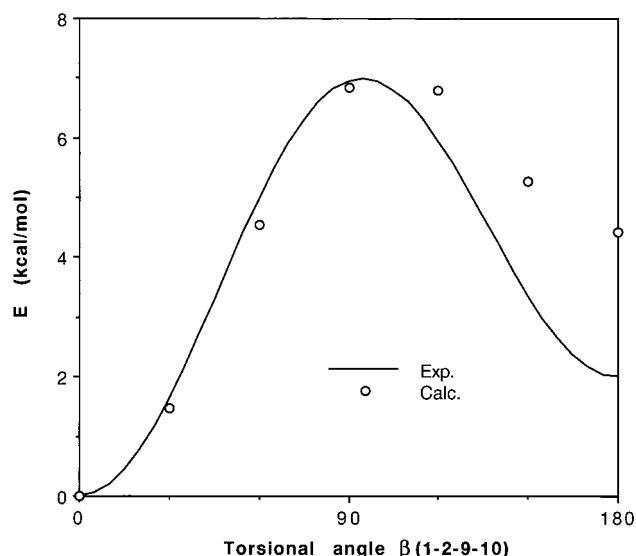
$\alpha^b$	$\beta^c$	HF	MP2	$\alpha^b$	$\beta^c$	HF	MP2
Rotation of Methoxy Group <sup>d</sup>				Rotation of Hydroxyl Group <sup>e</sup>			
0.0	180.0	6.96	7.30	180.0	0.0	0.00	0.00
30.0	178.7	6.03	6.55	179.5	30.0	1.17	1.47
60.0	33.0	4.42	5.30	177.3	60.0	3.57	4.54
90.0	15.4	1.31	2.41	176.1	90.0	5.42	6.83
120.0	5.9	0.97	1.97	176.9	120.0	5.80	6.79
150.0	0.7	0.53	0.87	178.4	150.0	4.95	5.28
180.0	0.0	0.00	0.00	180.0	180.0	4.33	4.43

<sup>a</sup> Energies are in kilocalories/mole. HF/6-311G\*\* geometries were used. Energies were calculated at the MP2/cc-pVTZ level. <sup>b</sup> The C<sub>2</sub>–C<sub>1</sub>–O<sub>7</sub>–C<sub>8</sub> torsional angle. <sup>c</sup> The C<sub>1</sub>–C<sub>2</sub>–O<sub>9</sub>–H<sub>10</sub> torsional angle. <sup>d</sup>  $\alpha$  was fixed in the geometry optimization. <sup>e</sup>  $\beta$  was fixed in the geometry optimization.

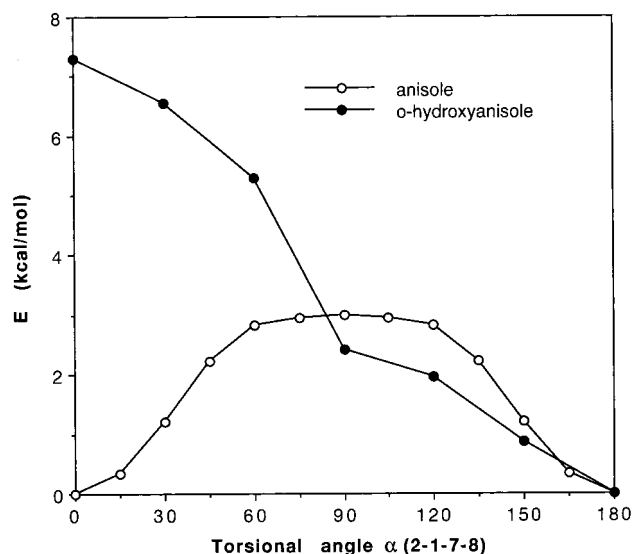
angle ( $\beta$ ) is 0° when the  $\alpha$  is 180° (conformer a). The  $\beta$  is increased by the decrease of the  $\alpha$ . The change of the  $\beta$  is not large until the  $\alpha$  reaches 60°. The optimized geometry where the  $\alpha$  is 60° is shown in Figure 2 (conformer b), in which a distorted hydrogen bond is observed ( $\beta = 33^\circ$ ). The  $\beta$  is close to 180° when  $\alpha$  is 0° (conformer c) and 30°. The  $\beta$ 's of these geometries show that the intramolecular hydrogen bond does not exist in these structures. The calculated torsional potential of methyl group is a 3-fold potential as in the case of anisole. The calculated internal rotational barrier height at the MP2/6-311G\*\*//HF/6-311G\*\* level is 3.82 kcal/mol.

**F. Torsional Potential of the Hydroxyl Group of *o*-Hydroxyanisole.** The torsional potential of the hydroxyl group of *o*-hydroxyanisole was calculated. The torsional angle  $\beta$  was fixed at 0°, 30°, 60°, 90°, 120°, 150°, and 180°, respectively, during the geometry optimization. The optimized geometries for  $\beta = 0^\circ$ , 90°, and 180° are shown in Figure 2 (conformers a, d, and e). The relative energies of the optimized geometries were calculated at the MP2/cc-pVTZ level, as shown in Table 3. The conformer e ( $\beta = 180^\circ$ ) is 4.43 kcal/mol less stable than the most stable conformer, conformer a ( $\beta = 0^\circ$ ). The calculated energy is the largest when  $\beta = 90^\circ$  (conformer d). This conformer is 6.83 kcal/mol less stable than the conformer a.

Carlson and Fateley estimated the torsional potential of hydroxyl group of *o*-hydroxyanisole from the measurements of torsional frequencies.<sup>52</sup> They reported that the  $V_1$  and  $V_2$  terms



**Figure 3.** Comparison between the calculated torsional potential of the hydroxy group of *o*-hydroxyanisole at the MP2/cc-pVTZ//HF/6-311G\*\* level and the experimental one.



**Figure 4.** Comparison between the torsional potentials of the methoxy group of anisole and *o*-hydroxyanisole calculated at the MP2/cc-pVTZ//HF/6-311G\*\* level.

of the potential were 2.00 and 5.94 kcal/mol, respectively. The torsional potential obtained by the ab initio calculations was compared with their potential as shown in Figure 3. The calculated potential agrees well with the experimental one where the torsional angle is  $0^\circ$ – $90^\circ$ . On the other hand, the agreement is not good in other regions. The information about the potential function obtained from the measurements of torsional frequencies is essentially effective for the region around the potential minimum. Thus, the curvature of the potential at the minimum can be determined with some degree of accuracy, whereas the torsional potential far from the minimum depends to a great extent on the mathematical expression selected to describe the potential.<sup>53</sup> This deficiency would be the cause of the poor agreement where the torsional angle is  $120^\circ$ – $180^\circ$ .

**G. Effects of Intramolecular Hydrogen Bond.** The calculated torsional potential of the methoxy group of *o*-hydroxyanisole is considerably different from that of anisole as shown in Figure 4. Anisole prefers the planar structure ( $\alpha = 0^\circ$  and  $180^\circ$ ). The perpendicular structure ( $\alpha = 90^\circ$ ) is the saddle point. The planar structure ( $\alpha = 180^\circ$ ) of *o*-hydroxyanisole, which

has intramolecular hydrogen bond, is the energy minimum structure, whereas the other planar structure ( $\alpha = 0^\circ$ ) is the saddle point of the torsional potential of the methoxy group of *o*-hydroxyanisole. The difference of the shapes of the torsional potentials indicates that the ortho hydroxyl group has a substantial effect on the torsional potential of the methoxy group. The calculated internal rotational barrier height of *o*-hydroxyanisole (7.30 kcal/mol) is considerably larger than that of anisole (2.99 kcal/mol), which shows that the energy minimum structure (conformer a) is significantly stabilized by the hydrogen bond.

The calculated barrier height between the two energy minima ( $\alpha = 0^\circ$  and  $180^\circ$ ) of anisole is only 2.99 kcal/mol, which indicates that the hindrance of the rotation of the methoxy group is not large. On the other hand, *o*-hydroxyanisole has only one energy minimum ( $\alpha = 180^\circ$ ), and the internal rotational barrier height (7.30 kcal/mol) is considerably higher than that of anisole. The large torsional energy (5.30–7.30 kcal/mol) when  $\alpha = 0^\circ$ – $60^\circ$  shows that the conformational flexibility of the methoxy group is strictly restricted by the hydrogen bond with the ortho hydroxy group.

The calculated torsional potential of methoxy group of *o*-hydroxyanisole is close to that of anisole when  $\alpha = 90^\circ$ – $180^\circ$ , whereas the torsional energy of *o*-hydroxyanisole is considerably larger than that of anisole when  $\alpha = 60^\circ$ , as shown in Figure 4. The  $\beta$  of *o*-hydroxyanisole is  $0^\circ$ – $15^\circ$  when  $\alpha = 90^\circ$ – $180^\circ$ , which indicates that *o*-hydroxyanisole has an intramolecular hydrogen bond. On the other hand,  $\beta$  increased up to  $33^\circ$  when  $\alpha$  was  $60^\circ$ . The structure of conformer b ( $\alpha = 60^\circ$  and  $\beta = 33^\circ$ ) in Figure 2 clearly illustrates that the steric repulsion between the methyl and hydroxyl groups breaks the hydrogen bond. Apparently, the breaking of the hydrogen bond is the cause of the larger torsional energy of *o*-hydroxyanisole when  $\alpha = 60^\circ$ .

Whereas the torsional energy of anisole decreases substantially when  $\alpha$  decreases from  $60^\circ$  to  $0^\circ$ , the torsional energy of *o*-hydroxyanisole further increases. The increase of steric repulsion between methyl and hydroxyl group would be the cause of the increase of the torsional energy of *o*-hydroxyanisole. The HF/6-311G\*\*-optimized geometries indicates the existence of substantial steric repulsion when  $\alpha = 0^\circ$  and  $30^\circ$ . The calculated  $C_2$ – $C_1$ – $O_7$  angles are  $127.3^\circ$ ,  $125.8^\circ$ , and  $122.1^\circ$ , respectively, when  $\alpha$  is  $0^\circ$ ,  $30^\circ$ , and  $60^\circ$ . These values are considerably larger than  $120^\circ$ . On the other hand, the  $C_2$ – $C_1$ – $O_7$  angle is smaller than  $120^\circ$  ( $114.2^\circ$ – $118.3^\circ$ ) when  $\alpha = 90^\circ$ – $180^\circ$ . Apparently, attractive intramolecular hydrogen bond is the cause of the small bond angle.

Conformer a ( $\beta = 0^\circ$ ) of *o*-hydroxyanisole is 4.43 kcal/mol more stable than conformer e ( $\beta = 180^\circ$ ). The large energy difference between these conformers also shows that conformer a is stabilized with the intramolecular hydrogen bond. The energy difference between the two conformers is close to the bonding energy of a water dimer (about 5 kcal/mol).<sup>54–56</sup>

The calculated internal rotational barrier height of the hydroxyl group of *o*-hydroxyanisole (about 7 kcal/mol) is considerably larger than that of phenol (3.56 kcal/mol). The calculated conformational energy is large (4.43–6.83 kcal/mol) when the  $\beta = 60^\circ$ – $180^\circ$ . These geometries do not have the intramolecular hydrogen bond. These results indicate that the intramolecular hydrogen bond has a significant effect on the torsional potential of the hydroxyl group.

#### IV. Conclusion

We have calculated the internal rotational barrier heights of phenol and anisole by the MP2 method using several basis sets



to evaluate the basis set effects. The effects of the improvement of the basis set beyond the cc-pVTZ are very small. Although the electron correlation substantially increases the barrier heights of phenol and anisole, the effects of the correction beyond the MP2 method are not large. The barrier heights calculated with the CCSD(T) method are close to those with the MP2 method. Phenol and anisole prefer planar structure, and the perpendicular structure is the saddle point of the internal rotation. The calculated barrier heights at the MP2/cc-pVTZ//HF/6-311G\*\* level agree well with the experimental barrier heights.

*o*-Hydroxyanisole also prefers planar structure, in which the hydroxyl group has an intramolecular hydrogen bond with the methoxy oxygen atom. The calculations show that the torsional potential has the maximum when the methoxy group rotates 180° from the energy minimum structure, in which the hydroxyl group does not have the hydrogen bond. The internal rotational barrier height calculated at the MP2/cc-pVTZ//HF/6-311G\*\* level is 7.30 kcal/mol, which is substantially larger than that of anisole (2.99 kcal/mol). The larger barrier height indicates that the stabilization of the energy minimum structure by the intramolecular hydrogen bond has a considerable effect on the torsional potential of the methoxy group. The conformational flexibility of the methoxy group is strictly restricted by the ortho hydroxyl group.

**Acknowledgment.** We thank the Tsukuba Advanced Computing Center for the provision of the computational facilities

## References and Notes

- Garg, S. K.; Smyth, C. D. *J. Chem. Phys.* **1967**, *46*, 373.
- Owen, N. L.; Hester, R. E. *Spectrochim. Acta* **1969**, *25A*, 343.
- Lister, D. G.; Owen, N. L. *J. Chem. Soc., Faraday Trans. 2* **1973**, *68*, 1304.
- Seip, H. M.; Seip, R. *Acta Chem. Scand.* **1973**, *27*, 4024.
- Grindley, T. B.; Katritzky, A. R.; Topsom, R. D. *J. Chem. Soc., Perkin Trans. 2* **1974**, 289.
- Allen, G.; Fewster, S. *Internal Rotations in Molecules*; Orville-Thomas, W. J., Ed.; Wiley: New York, 1974; Chapter 8.
- Goulon, J.; Canet, D.; Evans, M.; Davies, G. J. *Mol. Phys.* **1975**, *30*, 973.
- Tylli, H.; Korschin, H. *J. Mol. Struct.* **1977**, *42*, 7.
- Klessinger, M.; Rademacher, P. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 826.
- Friege, H.; Klessinger, M. *Chem. Ber.* **1979**, *112*, 1614.
- Korschin, H.; Tylli, H.; Grundfetl-Forsius, C. *J. Mol. Struct.* **1981**, *77*, 51.
- Schaefer, T.; Penner, G. H. *Can. J. Chem.* **1988**, *66*, 1635.
- Schaefer, T.; Penner, G. H. *Can. J. Chem.* **1988**, *66*, 1641.
- Schaefer, T.; Sebastian, R. *Can. J. Chem.* **1989**, *67*, 1148.
- Allinger, N. L.; Maul, J. J.; Hickey, M. J. *J. Org. Chem.* **1971**, *36*, 2747.
- Hehre, W. J.; Radom, L.; Pople, J. A. *J. Am. Chem. Soc.* **1972**, *94*, 1496.
- Matsushita, T.; Osamura, Y.; Misawa, N.; Nishimoto, K.; Tsuno, Y. *Bull. Chem. Soc. Jpn.* **1979**, *52*, 2521.
- Anderson, G. M., III.; Kollman, P. A.; Domelsmith, L. N.; Houk, K. N. *J. Am. Chem. Soc.* **1979**, *101*, 2344.
- Schaefer, T.; Wildman, T. A.; Sebastian, R. *J. Mol. Struct. (THEOCHEM)* **1982**, *89*, 93.
- Klessinger, M.; Zywiets, A. J. *J. Mol. Struct. (THEOCHEM)* **1982**, *90*, 341.
- Korschin, H. *J. Mol. Struct. (THEOCHEM)* **1983**, *105*, 213.
- Schaefer, T.; Penner, G. H. *J. Mol. Struct. (THEOCHEM)* **1987**, *152*, 179.
- Spellmeyer, D. C.; Grootenhuis, P. D. J.; Miller, M. D.; Kuyper, L. F.; Kollman, P. K. *J. Phys. Chem.* **1990**, *94*, 4483.
- Vincent, M. A.; Hillier, I. H. *Chem. Phys.* **1990**, *140*, 35.
- Simon, J. P.; Eriksson, K.-E. L. *J. Mol. Struct.* **1996**, *384*, 1.
- Koenig, K. E.; Lein, G. M.; Stuckler, P.; Kaneda, T.; Cram, D. J. *J. Am. Chem. Soc.* **1979**, *101*, 3553.
- Cram, D. J.; Kaneda, T.; Helgeson, R. C.; Lein, G. M. *J. Am. Chem. Soc.* **1979**, *101*, 6752.
- Shulgin, A. T.; Sargent, T.; Naranjo, C. *Nature* **1969**, *221*, 537.
- Domelsmith, L. N.; Munchausen, L. L.; Houk, K. N. *J. Am. Chem. Soc.* **1977**, *99*, 4311.
- Borisenko, K. B.; Bock, C. W.; Hargittai, I. *J. Phys. Chem.* **1994**, *98*, 1442.
- Borisenko, K. B.; I. Hargittai, I. *J. Mol. Struct.* **1996**, *382*, 171.
- Raghavachari, K. *J. Chem. Phys.* **1984**, *81*, 1383.
- Wiberg, K. B.; Murcko, M. A. *J. Am. Chem. Soc.* **1988**, *110*, 8029.
- Allinger, N. L.; Grev, R. S.; Yates, B. F.; Schafer, H. F., III. *J. Am. Chem. Soc.* **1990**, *112*, 114.
- Tsuzuki, S.; Tanabe, K. *J. Chem. Soc., Faraday Trans.* **1991**, *87*, 3207.
- Tsuzuki, S.; Tanabe, K. *J. Chem. Soc., Perkin Trans. 2* **1991**, 181.
- Tsuzuki, S.; Uchimaru, T.; Tanabe, K.; Hirano, T. *J. Phys. Chem.* **1993**, *97*, 1346.
- Smith, G. D.; Jaffe, R. L. *J. Phys. Chem.* **1996**, *100*, 18718.
- Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T.; Petersson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Laham, M. A.; Zakrzewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Cioslowski, J.; Stefanov, B. B.; Nanayakkara, A.; Challacombe, M.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andres, J. L.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; Defrees, D. J.; Baker, J.; Stewart, J. J. P.; Head-Gordon, M.; Gonzalez, C.; Pople, J. A. *Gaussian 94*; Gaussian, Inc.: Pittsburgh, PA, 1994.
- Krishnan, R.; Binkley, J. S.; Seeger, R.; Pople, J. A. *J. Chem. Phys.* **1980**, *72*, 650.
- Woon, D. E.; Dunning, T. H., Jr. *J. Chem. Phys.* **1993**, *98*, 1358.
- Dunning, T. H., Jr. *J. Chem. Phys.* **1989**, *90*, 1007.
- Møller, C.; Plesset, M. S. *Phys. Rev.* **1934**, *46*, 618.
- Krishnan, R.; Pople, J. A. *Int. J. Quantum Chem.* **1978**, *14*, 91.
- Pople, J. A.; Head-Gordon, M.; Raghavachari, K. *J. Chem. Phys.* **1987**, *87*, 5968.
- Tsuzuki, S.; Uchimaru, T.; Matsumura, K.; Mikami, M.; Tanabe, K. *J. Chem. Phys.* **1999**, *110*, 2858.
- Feller, D. *J. Chem. Phys.* **1992**, *96*, 6104.
- Berden, G.; Meerts, W. L.; Schmitt, M.; Kleinermanns, K. *J. Chem. Phys.* **1996**, *104*, 972.
- Torsional potential of anisole  $V(\phi)$  can be expressed as  $V(\phi) = 1/2 [\Sigma V_2(1 - \cos 2\phi) + V_4(1 - \cos 4\phi) + V_6(1 - \cos 6\phi) + \dots]$ . Previous calculations suggest that torsional potential of anisole has larger  $V_4$  term.
- Tsuzuki, S.; Tanabe, K. *J. Chem. Soc.* **1991**, 181.
- Kasai, P. H.; Myers, R. J. *J. Chem. Phys.* **1959**, *30*, 1096.
- Carlson, G. L.; Fateley, W. G. *J. Phys. Chem.* **1973**, *77*, 1157.
- Bastiansen, O.; Samdal, S. *J. Mol. Struct.* **1985**, *128*, 115.
- Curtiess, L. A.; Frurip, D. J.; Blander, M. *J. Chem. Phys.* **1979**, *71*, 2703.
- Reimers, J.; Watts, R.; Klein, M. *Chem. Phys.* **1982**, *64*, 95.
- Feyereisen, M. W.; Feller, D.; Dixon, D. A. *J. Phys. Chem.* **1996**, *100*, 2993.