

**A COMPUTATIONAL INVESTIGATION OF THE MOLECULAR GEOMETRY  
AND ROTATIONAL BARRIERS IN ETHYLMETHYL ETHER**

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## ABSTRACT

*Ab initio* (HF/6-31G(d) and MP2/6-31G(d)) and semiempirical (AM1 and PM3) molecular orbital methods were used to investigate the two equilibrium and the two transition-state conformations on the rotational potential surface of ethylmethyl ether. All levels of theory gave geometries and frequencies in accord with experimental values. *Ab initio* relative energies  $\Delta H_0$  agreed with experiment to within about 0.4 kcal mol<sup>-1</sup>, except for the gauche-gauche isomerization barrier where the error is about 3 kcal mol<sup>-1</sup>. There is little improvement at the MP2/6-311+G(3df,2p) level of theory. Semiempirical  $\Delta H_0$  values are no more accurate overall, but show more systematic deviations from experiment that arise from an underestimation of the stability of the *trans* conformer.

## INTRODUCTION

The replacement of methylene groups by oxygen atoms gives the polyalkylethers conformational properties which are vastly different from those of the parent hydrocarbons [1]. Ethylmethyl ether is one of the simplest of the alkyl ethers, whose structure and conformational energies have been well characterized, both theoretically [2] and experimentally [3-8]. Knowledge of the torsional potential of ethers is integral to comprehending structural properties of polyalkylethers as well as essential for molecular dynamics simulations [9] from which bulk properties are determined.

Tsuzuki and Tanabe [2] have recently reported the results of a high level *ab initio* molecular orbital study of the conformational geometries and structures of ethylmethyl ether. However, these methods cannot presently be employed to study properties of more complex polyalkyl ethers. Semiempirical MNDO based quantum mechanical methods permit much faster calculations since integrals are approximated empirically, either parameterized to agree with experiment or derived from experimental data on isolated atoms. The semiempirical methods are much less expensive in terms of computational time and, therefore, molecules containing significantly larger numbers of atoms may therefore be studied.

We have investigated the structure and relative conformational energies of the equilibrium and transition-state rotamers of ethylmethyl ether (EME), by means of (a) MNDO-PM3 and MNDO-AM1 semiempirical methods and (b) *ab initio* methods; the latter calculations are in agreement with those reported recently [2]. Calculated results are compared to each other and to experimental values obtained for ethylmethyl ether and for n-butane, the hydrocarbon analogue of EME.

## CALCULATIONS

The purpose of the calculations was to obtain the potential energy curve for rotational motion about the C<sub>2</sub>-O<sub>3</sub> bond (see Figure 1) in EME. *Ab initio* MO calculations were performed on a Solbourne 5E/902 computer [10] using the *Gaussian 90* [11] program. Complete geometry optimizations of the four conformations of EME (shown in Figure 1) were performed.

The two equilibrium structures are denoted as Trans (T) and Gauche (G) while the two transition states are designated (GT)<sup>‡</sup> and (GG')<sup>‡</sup>. The geometries were gradient optimized [12] at both the HF/6-31G(d) and MP2/6-31G(d) levels. This basis set was chosen for its generally good agreement with experimental molecular geometries [13]. Single point HF and MP2 calculations were also performed on the T and (GG')<sup>‡</sup> rotamers using the much larger 6-311+G(3df,2p) basis.

MNDO-AM1 [14] and MNDO-PM3 [15] semiempirical molecular orbital calculations [16] were performed on a Digital Equipment Corporation VAX 6310 computer using the program MOPAC [17]. Complete geometry optimizations of the four stationary points were performed.

Vibrational frequencies were calculated both at the *ab initio* level using the HF/6-31G(d) basis set, and at the semiempirical level using MNDO-PM3. Stationary points on the potential energy surface were verified as equilibrium geometries by the absence of imaginary frequencies, while transition states were characterized by the presence of a single imaginary frequency.

## RESULTS AND DISCUSSION

### Geometries

Calculated geometric parameters of the T [ $\phi(\text{C}_4\text{O}_3\text{C}_2\text{C}_1)=180^\circ$ ] equilibrium and (GG')<sup>‡</sup> [ $\phi(\text{C}_4\text{O}_3\text{C}_2\text{C}_1)=0^\circ$ ] transition-state structures are displayed in Table 1; skeletal dihedral angles for the G rotamer are given at the bottom of Table 1A. For comparison, selected bond lengths and angles for n-butane [18] are listed in the far right-hand column. The calculated C<sub>1</sub>-C<sub>2</sub> bond lengths in the ether are very close to those of n-butane and, of course, R(C<sub>2</sub>-O<sub>3</sub>) is substantially shorter than the corresponding C<sub>2</sub>-C<sub>3</sub> bond length in the alkane. Most of the C-H bond lengths determined by either the semiempirical or *ab initio* methods are approximately independent of conformation (average values and standard deviations are given in the table). In contrast, the skeletal C-C and C-O bond lengths show significant changes upon rotation from the T ( $\phi=180^\circ$ ) to the (GG')<sup>‡</sup> ( $\phi=0^\circ$ ) conformation. Hartree-Fock and MP2 results yield a physically reasonable

C<sub>2</sub>-O<sub>3</sub> bond length increase of 0.011-0.014 Å. This lengthening is analogous to, although of lesser magnitude than, the 0.027 Å increase of the C<sub>2</sub>-C<sub>3</sub> bond length in n-butane. The *ab initio* C<sub>1</sub>-C<sub>2</sub> bond lengths also increase, by almost 0.01 Å; the O<sub>3</sub>-C<sub>4</sub> bond length remains unchanged. The semiempirical results are very different. Both the PM3 and AM1 calculations yield a physically unrealistic C<sub>2</sub>-O<sub>3</sub> bond length decrease of 0.003 Å. The C<sub>1</sub>-C<sub>2</sub> and O<sub>3</sub>-C<sub>4</sub> bonds also shorten, by 0.001-0.005 Å, using the latter methods.

The structure of EME has been determined experimentally by electron diffraction [5] and microwave spectroscopy [6]. Comparison of the calculated and experimental results (Table 1) reveals bond lengths in reasonable agreement for all methods and levels of theory.

Bond angles calculated from all methods have a mean deviation of  $\pm 2.1^\circ$ , and agree reasonably well with experimental values. Angles involving the hydrogens are approximately independent of conformation (average CCH and OCH angles, with their standard deviations, are presented in the table). Not surprisingly, the C<sub>1</sub>C<sub>2</sub>O<sub>3</sub> and C<sub>2</sub>O<sub>3</sub>C<sub>4</sub> skeletal bond angles exhibit a significant increase in the eclipsed (GG')<sup>‡</sup> structure, ranging from +4° to +12°, depending upon the computational method. The angle increases upon rotation from the T to (GG')<sup>‡</sup> conformation are larger than the +2.6° rise in the corresponding C<sub>1</sub>C<sub>2</sub>C<sub>3</sub> angle in n-butane, indicative of the shorter C-O bond lengths in the ether, which produce additional methyl-methyl repulsion.

Calculated values of the dihedral angle,  $\Phi(\text{C}_4\text{C}_3\text{O}_2\text{C}_1)$ , of the gauche rotamer range from 70° to 80°. The results from all methods fall within the range of 64° [6] to 84° [5] determined experimentally. One sees further from Table 1A that the computed skeletal dihedral angle in EME is substantially greater than that determined for n-butane. This is further evidence of the effect of the shorter C-O bonds which cause the dihedral angle of the gauche conformer to increase in order to minimize methyl-methyl non-bonded repulsions.

## Vibrations

Calculated and experimental vibrational frequencies for the G and T equilibrium conformations are listed in Table 2. *Ab initio* values derived at the HF/6-31G(d) level have been

scaled by the usual 0.9 factor [19]. The scaled frequencies exhibit an average (absolute) deviation of 1.3% and 2.5% for the G and T conformers respectively, when compared to experimental values [7,8]. The results are exceptionally accurate for frequencies above 1200  $\text{cm}^{-1}$ , where the mean deviation from experimental is 0.9% in the T conformer. In the region below 1200  $\text{cm}^{-1}$  computed results are still close, varying an average of 5.4% from experiment.

The question arises whether one should scale the semiempirical PM3 frequencies [20], since the method has already been parameterized to agree with experimental data. It was determined that a scale factor of 0.98 yielded the minimum absolute deviation between calculated and experimental frequencies, with an average error of 5.2% for all (G and T) frequencies. This is only marginally lower than the mean error of < 5.3% obtained with the unscaled theoretical frequencies. Hence, frequency scaling is not justified.

The average error in the calculated frequencies of the two equilibrium conformers, 5.1% and 5.3% for the G and T rotamers, respectively, are comparable. Unlike the *ab initio* results, there is no significant dependence of the accuracy of the calculated values, with errors of 6.1% and 4.9% for frequencies below and above 1200  $\text{cm}^{-1}$  for the T conformer.

From these results, it is clear that vibrational frequencies determined from the PM3 semiempirical method are somewhat less accurate than those determined with the HF/6-31G(d) basis set. An important application of computed vibrational frequency data is in the determination of thermodynamic parameters, such as heat capacities, absolute entropies and thermal contributions to conformational enthalpy differences [ $\Delta H^\circ(T)$ ]. These quantities have been calculated using scaled *ab initio* and unscaled PM3 frequencies; the results are given in Table 3.

One observes from the table that both zero point vibrational energies [ZPVE] and thermal contributions to the enthalpy [ $H(298)-H(0)$ ] are quite close for all four rotamers using the *ab initio* and semiempirical frequencies, leading to nearly identical corrections to the conformational enthalpy differences [ $\Delta[\Delta H(298)]$ ]. There is also satisfactory agreement between calculated

heat capacities [ $C_p(298)$ ] (average deviation = 1.4%) and absolute entropies [ $S(298)$ ] (avg. dev. = 1.1%). One sees larger deviations in the conformational entropy differences [ $\Delta S(298)$ ], including a reversal in sign for  $S(G)-S(T)$ ; this is not surprising since all of the entropy differences are quite small relative to the magnitudes of the absolute entropies.

From these results, it is clear that the semiempirical frequencies yield very satisfactory values for all of the thermodynamic quantities and may be used profitably in larger systems where *ab initio* frequency calculations are prohibitively time consuming.

## Energies

Displayed in Table 4 are the total *ab initio* energies (in hartrees) and the derived enthalpy differences [ $\Delta H_0$ ] (in kcal mol<sup>-1</sup>) relative to the *trans* conformation at 0 K, calculated at various *ab initio* and semiempirical levels of theory. One observes from the table that the inclusion of electron correlation has a comparatively minor effect on calculated energies of the gauche equilibrium rotamer and both transition states since relative HF/6-31G(d) and MP2/6-31G(d) energies are fairly close. A similarly small dependence of correlation effects on conformational energies was also found in the isoelectronic butane molecule [18].

Because the stationary points on the PES have similar energies it is necessary to distinguish carefully between  $\Delta H_0$  and other measures of energy [21]. In particular,  $\Delta[ZPVE]$  (see Table 3) is added to the differences in *ab initio* electronic energies  $\Delta E$  to obtain  $\Delta H_0$ , while the semiempirical data that directly yield  $\Delta H_{298}$  are corrected to 0 K by subtraction of  $\Delta[H(298)-H(0)]$  (Table 3). Experimental energies for EME [3,4,6] and n-butane [21,22,23] and calculated conformational energies for n-butane [18,21,24,25], all corrected to the common level of  $\Delta H_0$ , are given for comparison. In reviewing the relative energies, one observes that the HF/6-31G(d) and MP2/6-31G(d) *ab initio*  $\Delta H_0$  results are exclusively positive, in agreement with the experimental observation that the *trans* conformation has the lowest energy [3,4,6]. The *ab initio* results also agree well with the experimental (GT)<sup>‡</sup> energy, and predict barriers within 0.4 kcal mol<sup>-1</sup> of that measured, although the (GG')<sup>‡</sup> barrier is significantly overestimated, by about 3

kcal mol<sup>-1</sup>. A similar pattern of accord can be seen for n-butane, where the *ab initio* energies are in good accord with experiment except for the (GG')<sup>‡</sup> conformer. In contrast to the *ab initio* methods, both semiempirical methods yielded negative  $\Delta H_0$  values for the G conformer, thus predicting the incorrect conformation as the global minimum, and also predicting (GT)<sup>‡</sup> and (GG')<sup>‡</sup> energy barriers that are too small. The errors from semiempirical theory are more systematic than those in *ab initio* theory, but the root mean square deviations are slightly larger, e.g. 1.97 vs. 1.77 kcal mol<sup>-1</sup> at the PM3 and MP2/6-31G\* levels, respectively. Much of the error in the semiempirical values might be eliminated by inclusion of an extra negative correction to the energy of the T conformer; investigation of whether such a correction can be generally applied to a range of G and T isomers is a topic for future study.

As found here for EME, most *ab initio* estimates of  $\Delta H_0[(GG')^{\ddagger}-T]$  for n-butane are also substantially greater than the experimental value, 4.37 kcal mol<sup>-1</sup> [23,26] (see, for example, the HF/6-31G(d)//HF/6-31G(d) energy barrier in Table 4). Allinger *et al.* [21] observed a significant improvement only if the basis set was enlarged to triple zeta with two sets of polarization functions on carbon and one set on hydrogen; e.g. an MP2 calculation at the TZ(2d,p) level yielded  $\Delta E = 5.37$  kcal mol<sup>-1</sup> and thus  $\Delta H_0 = 5.55$  kcal mol<sup>-1</sup>, which is still more than 1 kcal mol<sup>-1</sup> above the experimental value. In order to determine whether an enlarged basis can provide similar improvement in the calculated (GG')<sup>‡</sup> barrier of EME, we performed single point HF and MP2 calculations (at the MP2/6-31G(d) geometries) on the T and (GG')<sup>‡</sup> conformers using a large 6-311+G(3df,2p) basis. As shown in Table II, one finds improvements of only 0.1 and 0.5 kcal mol<sup>-1</sup> (relative to the 6-31G(d) energies) at the HF and MP2 levels, respectively. Allinger *et al.* found that the degree of correction for electron correlation had little effect on  $\Delta H_0$  in n-butane [21], as may also be seen in the data of Tsuzuki and Tanabe for EME [2].

Displayed in Figure 2 are the rotational potential energy curves for EME and n-butane. As seen in the figure and in Table 1B, the equilibrium dihedral angle of the G rotamer in EME is



greater than in the alkane. As noted above, a possible explanation is that the C<sub>2</sub>-O<sub>3</sub> bond length is shorter than the analogous C<sub>2</sub>-C<sub>3</sub> bond in n-butane, and therefore the dihedral angle increases to reduce the 1,4 methyl-methyl repulsion.

We note that the G and (GG')<sup>‡</sup> conformations of EME are of higher energy relative to the T conformer than in n-butane. This could be due to the C<sub>2</sub>-O<sub>3</sub> bond polarity and resistance to lengthening as compared to the C<sub>2</sub>-C<sub>3</sub> bond, and the greater deformation of bond angles. The observation that the (GT)<sup>‡</sup> structure of n-butane is of higher energy than in EME is explained by the fact that this conformation contains three eclipsing interactions of atoms compared to one such interaction in EME.

## SUMMARY AND CONCLUSIONS

*Ab initio* and semiempirical molecular orbital methods have been used to calculate the rotational potential about the C<sub>2</sub>-O<sub>3</sub> bond in ethylmethyl ether. A good description of the geometries of the two equilibrium and two transition-state conformations of EME may be obtained both by *ab initio* methods using the 6-31G(d) basis set and by the semiempirical PM3 and AM1 methods. Bond lengths and angles are in close agreement with experimental results.

Scaled vibrational frequencies calculated at the Hartree-Fock level using the 6-31G(d) basis set are in good accord with experiment, and agree exceptionally well for vibrations over 1200 cm<sup>-1</sup>. Vibrational frequencies obtained semiempirically using PM3 are also reasonably representative of experimental frequencies, and semiempirical methods appear to be suitable for estimating thermodynamic quantities such as S and C<sub>p</sub>.

The calculated energy differences relative to the T conformation, ΔH<sub>0</sub>, obtained by MP2 calculations are in agreement with experiment, with the exception of ΔH<sub>0</sub>[(GG')<sup>‡</sup>-T]. Use of the large 6-311+G(3df,2p) basis set leads to little improvement, similar to difficulties previously reported in the computation of the analogous barrier height in n-butane. The semiempirical barriers overall are no more accurate, but show more systematic deviations that arise mainly

from underestimation of the stability of the T conformer relative to the G form. Future studies will investigate whether this is a systematic effect over a wide range of molecules.

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26. As argued in ref. 21, the zero-point vibrational energy of the torsional mode is subtracted from the spectroscopic barrier height of 4.54 kcal mol<sup>-1</sup> to obtain  $\Delta H_0$ .

**Table 1. Calculated Geometry Parameters for Ethylmethyl Ether<sup>a,b</sup>**

**A. TRANS**

	HF 6-31G(d)	MP2 6-31G(d)	PM3	AM1	EXPERIMENT		n-Butane <sup>c</sup> MP2/6-31G(d)
					ED <sup>c</sup>	MW <sup>d</sup>	
R(C <sub>1</sub> C <sub>2</sub> )	1.516	1.512	1.516	1.511	1.520(4)	1.520(4)	1.523
R(C <sub>2</sub> O <sub>3</sub> )	1.397	1.419	1.423	1.428	1.422(7)	1.404(7)	1.528
R(O <sub>3</sub> C <sub>4</sub> )	1.392	1.415	1.402	1.416	1.413(9)	1.415(6)	1.523
R(CH) <sup>f</sup>	1.087 (0.003)	1.096 (0.005)	1.099 (0.005)	1.119 (0.003)			
$\theta$ (C <sub>1</sub> C <sub>2</sub> O <sub>3</sub> )	108.6	107.8	107.3	106.9	109.4(3)	108.2(5)	113.8
$\theta$ (C <sub>2</sub> O <sub>3</sub> C <sub>4</sub> )	114.2	111.5	113.6	112.5	111.9(5)	111.8(5)	113.8
$\theta$ (CCH) <sup>g</sup>	110.5 (0.1)	110.4 (0.3)	111.4 (0.6)	110.3 (0.5)			
$\theta$ (CCO) <sup>g</sup>	110.2 (1.6)	110.0 (1.9)	109.4 (3.6)	108.9 (2.6)			
<b>GAUCHE</b>							
$\phi$ (C <sub>4</sub> O <sub>3</sub> C <sub>2</sub> C <sub>1</sub> )	77.8	73.9	80.0	69.8	84(6)	64	65.2

**B. (GG')<sup>+</sup>**

	HF 6-31G(d)	MP2 6-31G(d)	PM3	AM1	n-Butane <sup>c</sup> MP2/6-31G(d)
R(C <sub>1</sub> C <sub>2</sub> )	1.525	1.521	1.514	1.506	1.528
R(C <sub>2</sub> O <sub>3</sub> )	1.408	1.433	1.420	1.425	1.555
R(O <sub>3</sub> C <sub>4</sub> )	1.392	1.415	1.401	1.412	1.528
R(CH) <sup>f</sup>	1.085 (0.002)	1.095 (0.002)	1.099 (0.004)	1.120 (0.003)	
$\theta$ (C <sub>1</sub> C <sub>2</sub> O <sub>3</sub> )	117.3	117.5	118.9	116.8	116.4
$\theta$ (C <sub>2</sub> O <sub>3</sub> C <sub>4</sub> )	120.8	118.2	118.3	116.9	116.4
$\theta$ (CCH) <sup>g</sup>	110.5 (1.8)	110.4 (1.7)	111.3 (1.1)	110.4 (0.8)	
$\theta$ (CCO) <sup>g</sup>	109.7 (3.0)	109.5 (3.5)	109.6 (4.2)	109.1 (3.1)	
$\phi$ (C <sub>4</sub> O <sub>3</sub> C <sub>2</sub> C <sub>1</sub> )	0.0	0.0	-0.1	0.3	0.0

### Table 1. Footnotes

- a) Bond lengths are in angstroms and bond angles are in degrees.
- b) Atom numbering illustrated in Figure 1.
- c) From electron diffraction; Ref. 5.
- d) From microwave spectroscopy; Ref. 6.
- e) From Ref. 18.
- f) Average bond length. Value in parenthesis is standard deviation.
- g) Average bond angle. Value in parenthesis is standard deviation.

**Table 2. Calculated and Experimental Vibrational Frequencies.<sup>a</sup>**

HF/6-31G(d)	GAUCHE PM3	EXP'T	APPROX. DESCR.	HF/6-31G(d)	TRANS PM3	EXP'T <sup>b</sup>
78	91		Tors.	106(A")	73	
187	151		Tors.	201(A")	153	
238	199		Tors.	255(A")	192	238
370	392	381 <sup>b</sup>	CCO Bd. + COC Bd.	278(A')	316	308
443	510		COC Bd. + CCO Bd.	449(A')	528	472
781	839	816 <sup>c</sup>	CCH Bd.	800(A")	838	820
838	926	843 <sup>c</sup>	CC Str. + CO Str.	855(A')	920	855
979	1011	980 <sup>c</sup>	OCH Bd.	1005(A')	1015	920
1073	1025	1070 <sup>c</sup>	HCH Bd.	1099(A')	1033	1019
1123	1059	1110 <sup>c</sup>	CO Str. + CCH Bd.	1155(A")	1049	1094
1166	1108	1165 <sup>c</sup>	CC Str. + OCH Bd.	1161(A')	1120	1118
1205	1117		CCH Bd.	1185(A")	1133	1149
1233	1157		CO Str. + OCH Bd.	1238(A')	1166	1219
1319	1196	1303 <sup>c</sup>	CO Str. + CC Str.	1284(A")	1196	1275
1384	1324		CCH Bd. + CO Str.	1389(A')	1330	1367
1415	1358		HCH Bd. + OCH Bd.	1427(A')	1359	1394
1467	1366		HCH Bd.	1466(A")	1366	1471
1472	1369		OCH Bd. + CO Str.	1472(A')	1370	1477
1477	1392		HCH Bd. + CO Str.	1481(A")	1397	1479
1487	1403		HCH Bd.	1481(A')	1402	1485
1495	1412		HCH Bd. + CCH Bd.	1492(A')	1412	1487
1505	1413		HCH Bd. + CC Str.	1518(A')	1422	1494
2856	2944		CH Str.	2843(A')	2918	2836
2867	3031		CH Str.	2860(A')	2978	2874
2887	3038		CH Str.	2869(A")	3036	2891
2909	3075		CH Str.	2891(A')	3073	2927
2933	3083		CH Str.	2898(A")	3087	2939
2945	3092		CH Str.	2949(A')	3091	2976
2957	3146		CH Str.	2961(A")	3145	2983
2972	3186		CH Str.	2972(A')	3186	2993

a) Ab initio frequencies scaled by a factor of 0.9.

b) From Ref. 8.

c) From Ref. 7.

**Table 3. Thermodynamic Quantities****A. HF/6-31G(d)**

Quantity	T	G	(GT) <sup>‡</sup>	(GG') <sup>‡</sup>
ZPVE (kcal mol <sup>-1</sup> )	65.82	65.84	65.67	65.83
H(298)-H(0) (kcal mol <sup>-1</sup> )	4.13	4.14	3.67	3.63
Δ[ZPVE] (kcal mol <sup>-1</sup> )	0.00	0.02	-0.15	0.01
Δ[H(298)-H(0)] (kcal mol <sup>-1</sup> )	0.00	0.01	-0.46	-0.50
Δ[ΔH(298)] (kcal mol <sup>-1</sup> )	0.00	0.03	-0.61	-0.49
C <sub>p</sub> (298) (cal mol <sup>-1</sup> )	20.13	20.14	18.22	18.16
S(298) (cal mol <sup>-1</sup> K <sup>-1</sup> )	72.56	73.23	69.31	69.08
ΔS(298) (cal mol <sup>-1</sup> K <sup>-1</sup> )	0.00	0.67	-3.25	-3.48

**B. MNDO-PM3**

Quantity	T	G	(GT) <sup>‡</sup>	(GG') <sup>‡</sup>
ZPVE (kcal mol <sup>-1</sup> )	66.19	66.35	66.12	66.13
H(298)-H(0) (kcal mol <sup>-1</sup> )	4.23	4.16	3.72	3.70
Δ[ZPVE] (kcal mol <sup>-1</sup> )	0.00	0.16	-0.07	-0.06
Δ[H(298)-H(0)] (kcal mol <sup>-1</sup> )	0.00	-0.07	-0.51	-0.53
Δ[ΔH(298)] (kcal mol <sup>-1</sup> )	0.00	0.09	-0.58	-0.59
C <sub>p</sub> (298) (cal mol <sup>-1</sup> )	20.44	20.34	18.46	18.47
S(298) (cal mol <sup>-1</sup> K <sup>-1</sup> )	74.02	73.44	69.96	69.78
ΔS(298) (cal mol <sup>-1</sup> K <sup>-1</sup> )	0.00	-0.58	-4.06	-4.24



**Table 4. Calculated Conformational Energies.<sup>a</sup>****A. Total *Ab Initio* Energies (hartrees)**

METHOD	T	G	(GT) <sup>†</sup>	(GG') <sup>‡</sup>
HF/6-31G(d)	-193.10487	-193.10221	-193.10080	-193.09397
MP2/6-31G(d)	-193.69148	-193.68926	-193.68717	-193.68032
HF/6-311+G(3df,2p) <sup>b</sup>	-193.17607	-	-	-193.16533
MP2/6-311+G(3df,2p) <sup>b</sup>	-193.94127	-	-	-193.93094

**B. Relative Energies,  $\Delta H_o$  (kcal mol<sup>-1</sup>)**

METHOD	T	G	(GT) <sup>†</sup>	(GG') <sup>‡</sup>
HF/6-31G(d)	0.00	1.69	2.41	6.85
MP2/6-31G(d)	0.00	1.41	2.55	7.01
HF/6-311+G(3df,2p) <sup>b</sup>	0.00	-	-	6.74
MP2/6-311+G(3df,2p) <sup>b</sup>	0.00	-	-	6.48
PM3 <sup>c</sup>	0.00	-1.03	1.09	2.45
AM1 <sup>d</sup>	0.00	-0.35	1.34	2.49
EXP'T	0.00	1.5 <sup>e</sup>	2.82 <sup>f</sup>	3.96 <sup>e</sup>
<b>n-Butane</b>				
HF/6-31G(d) <sup>g</sup>	0.00	1.05	3.66	6.39
EXP'T	0.00	0.89 <sup>h</sup>	3.46 <sup>i</sup>	4.37 <sup>i</sup>

a) Computed energies and geometry optimizations at the same level  
except where otherwise specified

b) Calculated using the MP2/6-31G(d) geometries

c) Energies are  $\Delta H_f - \Delta H_f(T)$ , where  $\Delta H_f(T) = -52.93$  kcal mol<sup>-1</sup>; corrected to 0 K

d) Energies are  $\Delta H_f - \Delta H_f(T)$ , where  $\Delta H_f(T) = -58.78$  kcal mol<sup>-1</sup>; corrected to 0 K.

e) From Ref. 3.

f) From Ref. 4.

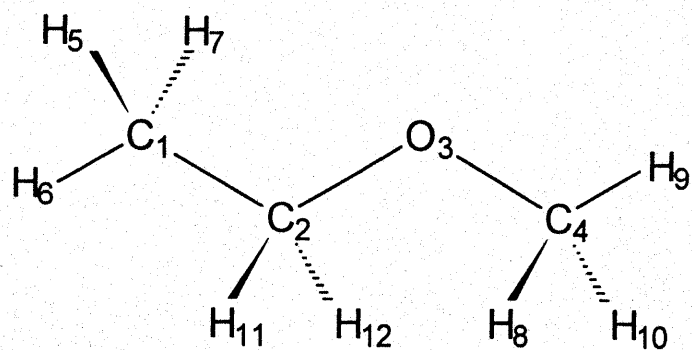
g) From Ref. 18.

h) From Refs. 21 and 22.

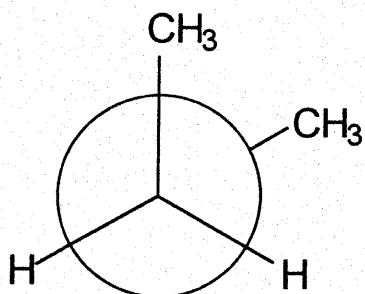
i) From Ref. 20.

## FIGURE CAPTIONS

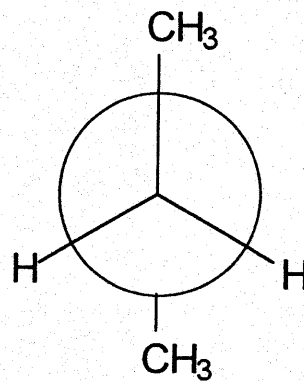
1. Atom numbering and stationary point conformations in ethylmethyl ether.
2. The calculated torsional potential in (A) EME - ● and (B) n-Butane - ■. The curves have been computed at the HF/6-31G(d) level.



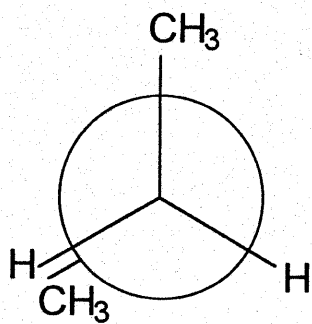
## Atom Numbering



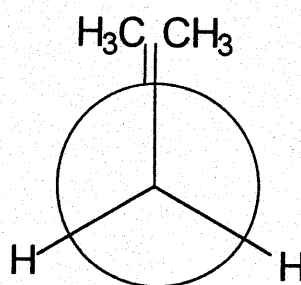
**G**



**T**



**(GT)<sup>‡</sup>**



**(GG')<sup>‡</sup>**

