

Thermochemical Values of Oxygen-Containing Compounds from *ab Initio* Calculations. 1. Enthalpies of Formation of Ethers and Alcohols

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A semitheoretical calculation of enthalpies of formation has been applied to alcohols and ethers. The calculation involves two steps. In the first step the *ab initio* energy for the conformer of lowest energy is converted into an estimate of the formal steric enthalpy (FSE). In the second step the FSE is combined with the formal bond enthalpy (FBE) to generate an estimate of ΔH_f° . The group increments for calculating the FBE values are derived from experimental enthalpies of formation. FSE values and FBE values are defined in terms of standard molecules. Calibration requires minimal calculation, and the procedure is readily generalized to other classes of compounds. The calculation is group isodesmic. Three basis sets were used: 3-21G, 6-31G*, and 6-31G**. Electron correlation was performed with single point estimates using MP2 (Moeller–Plesset, truncated at the quadratic expansion) with geometry optimized with HF 6-31G**. For a selection of molecules geometry optimizations were also performed with the MP2/6-31G** procedure. ΔH_f° values derived using the 6-31G** basis set with a single point MP2 estimation of electron correlation agree with experimental ΔH_f° values within the reasonable standard deviation of 0.55 kcal/mol for 14 molecules, including strained cyclic ethers and highly strained acyclic examples. Examination of the conformer families provides information useful for interpretation of steric effects in synthetic reactions. Average relative energy differences for four important torsional sequences expressed as gauche minus trans energy differences are 0.8 kcal/mol for C–C–C–C (literature), 1.4 for C–C–O–C, 0.6 for O–C–C–O, and –0.5 for C–C–C–O but –1.2 for the last sequence if the terminal carbon atom has an attached oxygen atom. Intramolecular hydrogen bonding effects are important (3 kcal/mol) for some conformers of 1,2-diols and reach 5 kcal/mol for 1,3-diols.

Introduction

Methods for converting *ab initio* energies to enthalpies of formation may be divided into those that calculate energies of atomization and those that do not. Energies of atomization in turn may be calculated entirely from theory or they may be calculated by hybrid methods that make limited use of experimental enthalpies of formation.

Excellent reviews of methods for theoretical calculation of thermodynamic properties may be found in the publication edited by Irikura and Frurip.¹ The article by Martin provides a particularly good summary of many of the methods used for calculating energies of atomization.² An especially clear description of computation of enthalpies of formation from energies of atomization is that of Nicolaidis et al.³ An example using the G2 (Gaussian 2) procedure gave accuracies of 1–2 kcal/mol.^{3–5} Many applications of the G2 procedure and of other procedures that aim for high accuracy have been reported recently.^{3,6,7} Accuracies of 0.25 kcal/mol have been reported for molecules containing two or three atoms by using very extensive basis sets and correlation methods.² These methods are routinely applicable only to small molecules because of the computational demands of the large basis sets and the refined methods necessary for treating electron correlation. They show great promise of providing benchmark enthalpy values that can be extrapolated by the group increment procedures described in this study.

Less computationally intensive hybrid procedures have been described for calculating energies of atomization. An example is the BAC (bond additivity correction) procedure.^{7–11} For

hydrocarbons the accuracy is about 5 kcal/mol.¹¹ A more recent hybrid procedure is the bond density function method developed by Cioslowski.¹² For carbon compounds the error of enthalpies of formation is about 4 kcal/mol.

A major advantage of methods based on energies of atomization is that they apply to all molecules, including radicals and ions, and to all types of elements within the scope of the available basis sets. The major disadvantages are that they do not yet provide the accuracies needed for making useful predictions of chemical equilibria and that they are too expensive to use except with small molecules.

Alternative methods for converting *ab initio* energies to estimates of ΔH_f° are those that employ some method of extrapolating experimental enthalpies of formation. The advantage of extrapolation is that in favorable cases the accuracy reaches that of the experimental data used for calibration, often of the order of 0.5 kcal/mol, sometimes as low as 0.2 kcal/mol. The disadvantage of most implementations is the requirement for extensive parametrization. The limitation is that extrapolation is applicable only to classes of compounds for which experimental enthalpy data are available or for which there are calculated enthalpies of sufficiently high accuracy.

To put accuracy requirements in perspective, if ΔH_f° is known within a standard deviation of 0.6 kcal/mol for a reactant and likewise for a product, then by propagation of error the standard deviation of ΔH_{eq} (for a single product formed from a single reactant) is 0.85 kcal/mol, and the standard deviation of $\log(K_{eq})$ at 298 K is 0.62; the corresponding error in K_{eq} is a factor of 4.2. For 95% confidence limits (roughly two standard

deviations) the error in K is a factor of 17. It is assumed that there is negligible error in the estimate of $T\Delta S$ for the equilibrium, and such is often true for estimates of differences of entropies of products and reactants. An error of a factor of 20 in K_{eq} (or in k_{rate}) is too large for many purposes. In practice the more usual comparisons are of relative equilibria or relative rate constants. These estimates involve double differences of ΔG . If the compounds are closely related, further cancelation of errors can bring the standard deviation of the theoretical estimates down to 0.3 in $\log K$, a factor of 3 in K for the 95% confidence estimate. Examples of such cancelations of errors among closely related compounds are to be found in the examples of the ΔH_f° values obtained in this study.

Several types of extrapolation methods are in use. The least accurate are based on formal bond isodesmic reactions.^{13–16} A formal isodesmic reaction has on each side of the formal equation the same numbers of each type of bond. An example is the formal reaction $\text{CH}_2=\text{CH}_2 + 2\text{CH}_4 \rightarrow 2\text{CH}_3\text{CH}_3$, which has two C–C bonds and 12 C–H bonds on each side. The enthalpy of formation of ethylene can be estimated with this reaction from the known enthalpies of formation of methane and ethane plus the ab initio energies of all three compounds, corrected for zero point energies and heat contents (change of enthalpy on going from 0 to 298 K).

Better results are obtained with group isodesmic methods.¹⁶ For use in calculating ΔH_f° values of organic compounds, methods based on extensions of the Benson group increment method are attractive.^{17–25} Details are presented below. Atom equivalent methods²⁶ and hydrogen equivalent methods are related.^{14,27}

Focus of the Present Study. The focus of the present study has been to examine how well we can estimate gas-phase enthalpies of formation of alcohols and ethers by a group increment method using corrections based on ab initio energies from basis sets of modest size. In this study I have used 10 combinations of basis sets and electron correlations with a representative set of alcohols and ethers for which experimental ΔH_f° values have been reported.

Group Increment Methods. Equation 1 defines the group increment method for calculating enthalpies of formation, developed extensively by Benson.^{17,18,28} The constant n_i is the number of occurrences of a given structural group present in the molecule, such as CH_3 or CH_2 or other group and b_i is the enthalpy contribution of that structural group. If branched chains or rings are present, it is necessary to include “steric” corrections. A structural group consists of an atom plus its nearest neighbors.

$$\Delta H_f^\circ = \sum n_i b_i + \text{steric corrections} \quad (1)$$

The most serious limitation of eq 1 is the difficulty of assigning steric corrections. There is a further limitation due to neglect of effects of atoms beyond nearest neighbors.²⁹ The difficulty of including these more distant atoms is that to do so leads to an almost factorial increase in the number of structural groups needed to represent a molecule, and this is impractical for the present purposes.

A possible general method for calculating the steric corrections is to use molecular mechanics, eq 2.^{30–38} SE (steric energy) is the energy obtained with a molecular mechanics calculation. SE_0 is the steric energy of the global minimum, the conformer of lowest energy. SE_0 may be considered as an estimate of the steric correction. ΔH_f° is the calculated standard enthalpy of formation of the compound in the gas phase. As with eq 1, n_i is the number of occurrences of the i th structural group and a_i

is its enthalpy increment. However, the a_i increments must be calibrated separately for each different force field since different force fields give significantly different values of SE for a given molecule. Hence, the SE value provides a workable but ambiguous measure of the steric correction.

$$\Delta H_f^\circ = \sum n_i a_i + SE_0 + \text{SM} \quad (2)$$

The first two terms on the right-hand side of eq 2 give the ΔH_f° of a hypothetical compound consisting solely of the conformer of lowest energy. The SM (statistical mechanical) term corrects for the contribution to the enthalpy by conformers other than the global minimum. SM is defined by eq 3 for a substance consisting of j conformers each having relative energy $h_j = SE_j - SE_0$ and fractional population f_j as determined by the Boltzmann distribution. The fractions are usually evaluated from energies, but there is not much difference in SM values whether calculated using energies or free energies.

$$\text{SM} = \sum h_j f_j \quad (3)$$

A modification of eq 2 is used in MM2 and MM3, eq 4. The summations of bond energy equivalents (BE) and group energy equivalents (GE) give effectively the same energy as does $\sum n_i a_i$ of eq 2. POP is equivalent to SM, although the reported values are not exactly the same. The term TORS is described as a term to account for low-frequency torsional modes. In practice TORS has apparently been treated more or less as an additional disposable parameter. The implications of calculating ΔH_f° values using this modification of eq 2 have been discussed elsewhere.³⁸

$$\Delta H_f^\circ = \sum \text{BE} + \sum \text{GE} + \text{SE} + \text{POP} + \text{TORS} + 2.4 \quad (4)$$

Wiberg used eq 5, a variant of eq 2, to convert ab initio energies to ΔH_f° values.^{19,39} The SM term was omitted since for the compounds treated the SM values are negligible. E_{AI} in eq 5 corresponds to the SE_0 term of eq 2; it is the ab initio energy of the target conformer and includes an estimate of the steric correction. E_{CH_3} and the other E_i terms are group increments in units of hartrees. They correspond to the a_i of eq 2. The constant 627.5 converts from hartrees to kcal. As with the SE_0 values of eq 2 the E_{AI} values of eq 5 depend on the basis set and on electron correlation. It is necessary, therefore, to derive a separate set of E_i increments for each basis set. Allinger used a related variant of eq 4 to get steric effects from ab initio energies.^{21–24}

$$\Delta H_f^\circ = 627.5(E_{\text{AI}} - n_{\text{CH}_3} E_{\text{CH}_3} - n_{\text{CH}_2} E_{\text{CH}_2} - \dots) \quad (5)$$

Fundamental problems arise in using eqs 2, 4, and 5 for converting SE values or ab initio energies into ΔH_f° values. A set of a_i values or of E_i values is valid only for the particular force field or basis set used in the calibration. This means that ΔH_f° values calculated with an augmented or modified force field are not valid unless a recalibration is performed. Recalibration encounters three difficulties: First, the calibration set used originally to obtain the a_i constants may not have been published. In that case a recalibration must start from the beginning. Second, conventional calibration sets tend to contain large numbers of compounds with the consequence that recalibration requires a major computational effort. Third, the calibrated values of the increments are ad hoc since they depend on details of the size and composition of the calibration set.

TABLE 1: Structural Groups and Corresponding Reference Standard Molecules

ref std molecules	conformer	structural group represented	assigned FSE value	<i>c</i> -increment of structural group	std dev of <i>c</i> -increment	SM of std compd
butane	anti, <i>C</i> ₂ <i>h</i>	C(C)(H) ₃	0.00	-10.033	0.022	0.27
octane	anti, <i>C</i> ₂ <i>h</i>	C(C) ₂ (H) ₂	0.00	-5.147	0.051	1.12
2-methylbutane		C(C) ₃ (H)	0.70	-2.258	0.077	0.09
2,2-dimethylbutane		C(C) ₄	1.40	-0.217	0.089	0.00
ethyl methyl ether	anti, <i>C</i> _s	C(O)(H) ₃	0.00	-6.819	0.057	0.25
same as C(C) ₂ (H) ₂		C(C)(O)(H) ₂		-5.147		
2-butanol	9L	C(C) ₂ (O)(H)	0.20	-4.340	0.130	0.25
2-methyl-2-butanol	3L	C(C) ₃ (O)	0.90	-3.870	0.160	0.09
1-propanol	g ⁺ g ⁺	O(C)(H)	0.00	-40.770	0.071	0.12
diethyl ether	anti, <i>C</i> ₂ <i>v</i>	O(C) ₂	0.00	-30.250	0.160	0.47

TABLE 2: FSE *d*_i Conversion Constants for Alkanes, Alcohols, and Ethers (Equation 8) for use with Uncorrected (Raw) ab Initio Energies

	3-21G	6-31G*	6-31G**	MP2/6-31G**// 6-31G**	MP2/6-31G**// MP2/6-31G**
C(C)(H) ₃	-39.397129	-39.614512	-39.619256	-39.771618	-39.771654
C(C) ₂ (H) ₂	-38.819103	-39.034692	-39.037720	-39.182029	-39.182073
C(C) ₃ (H)	-38.242701	-38.454701	-38.456060	-38.595086	-38.595270
C(C) ₄	-37.667115	-37.874096	-37.873797	-38.009990	-38.010276
C(O)(H) ₃	-39.392048	-39.609190	-39.613798	-39.766363	-39.766387
C(O)(C)(H) ₂	-38.819103	-39.034692	-39.037720	-39.182029	-39.182073
C(O)(C) ₂ (H)	-38.247140	-38.460018	-38.461461	-38.599222	-38.599286
C(O)(C) ₃	-37.675113	-37.882666	-37.882561	-38.017141	-38.017297
O(C)(H)	-75.008756	-75.426681	-75.433339	-75.615038	-75.616024
O(C) ₂	-74.429269	-74.846477	-74.846624	-75.018102	-75.019041

An example of the effects of composition of calibration set may be found in two different treatments of the same data set. In the original study, Wiberg derived the four E_i increments for alkanes from the complete set of compounds,²⁰ while in a subsequent study Allinger²¹ derived a different set of the same increments from a subset of the Wiberg data. ΔH_f° values calculated with the Wiberg increments and those calculated with the Allinger increments show differences larger than 1 kcal/mol.

In a study of alcohols and ethers by Allinger et al.,²² ab initio energies obtained with the 6-31G* basis set were converted to ΔH_f° values by fitting all 28 data values with 6 new adjustable increments. Four additional increments came from the treatment of the Wiberg data cited above.²¹ The reported standard deviation between experimental and calculated ΔH_f° for the 28 compounds is 0.5 kcal/mol. The calculation required assignment of two constants for each compound, POP and TOR. POP should be the same as the SM values reported in this study since the value is derived using eq 3, but some POP values are more than 0.5 kcal/mol larger than the corresponding SM values. Assignment of TOR values appears somewhat arbitrary, and determining the correct TOR value for a new target molecule may prove difficult.

Formal Steric Enthalpy (FSE) and Formal Bond Enthalpy (FBE). Equation 6 is an alternative expression for calculating ΔH_f° values. It separates the estimation of enthalpy into two terms (plus the SM correction). The term $\sum n_i c_i$ may be called the formal bond enthalpy (FBE). The c_i group increments are based on experimental ΔH_f° data as described below. Conceptually, FBE is the enthalpy of formation of a hypothetical "strain free" molecule (a single conformer), one for which gauche interactions and other steric effects are zero; c_i values have been published for alkanes, alkenes, alcohols, and ethers, carbonyl compounds, and acid derivatives.³⁴⁻³⁷

$$\Delta H_f^\circ = \sum n_i c_i + \text{FSE}_0 + \text{SM} \quad (6)$$

The FSE_0 term in eq 6 is the formal steric enthalpy (FSE) of the conformer that is the global minimum of energy.³⁰⁻³⁸ It is

an unambiguous estimate of the steric correction. As described below, FSE may be derived from SE values obtained by molecular mechanics³⁸ or from ab initio energies.²⁵ SM is defined in eq 3. In calculating ΔH_f° it is FSE_0 and SM that are to be calculated using a given force field or a given basis set/electron correlation procedure.

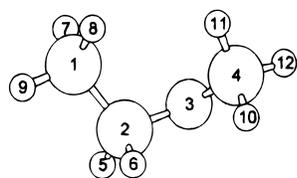
FSE is calculated from steric energies (SE) by use of eq 7 and from ab initio energies (E_{AI}) by eq 8. Both FBE and FSE are defined in terms of standard molecules. Exactly one standard molecule is needed to define the d_i and c_i constants for a given structural group. The calculation of ΔH_f° in eq 6 is group isodesmic. Standard molecules have been chosen so that the given structural group is in a representative environment. As an example, butane and octane contain CH₃ and CH₂ structural groups in typical environments while the environments of these groups in the simpler molecules ethane and propane are less typical.

$$\text{FSE} = \text{SE} - \sum n_i d_i' \quad (7)$$

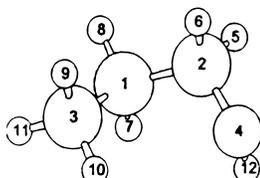
$$\text{FSE} = 627.5(E_{\text{AI}} - \sum n_i d_i) \quad (8)$$

A separate set of d_i or d_i' conversion constants is required for each force field or each basis set. However, the c_i increments are derived from experimental ΔH_f° data and are universal in the sense that they are independent of force field or basis set.

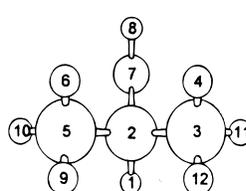
The d_i conversion constants are calculated with the use of eq 8. The independent variables for this calibration step are the set of calculated E_{AI} values (ab initio energies) of the standard molecules together with their assigned FSE values. These latter are summarized in Table 1. See also Chart 1. The ab initio energies may be found in Tables 5 and 9 in the Supporting Information. Representative d_i conversion constants are summarized in Tables 2 and 6. The number of calculations needed for calibrating a given set of d_i constants is minimal; one energy value for each standard molecule. This is in sharp contrast to the extensive calculations required to perform a calibration of the increments of eqs 2, 4, or 5.

CHART 1^a

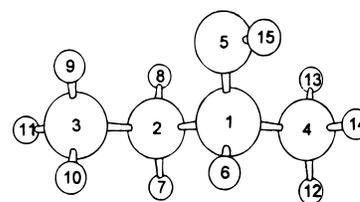
Ethyl methyl ether g



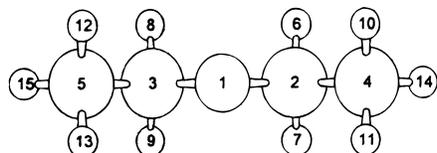
1-Propanol g+g+OH



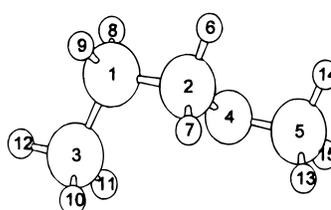
2-propanol



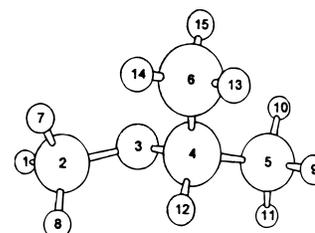
2-butanol 9L



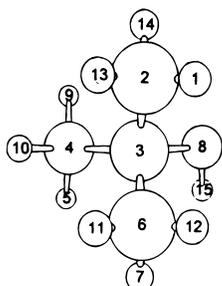
Diethyl ether t t



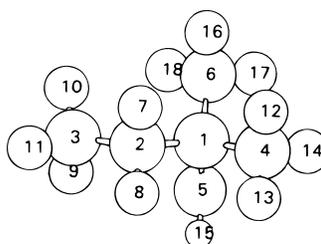
Methyl 1-propyl ether g+t



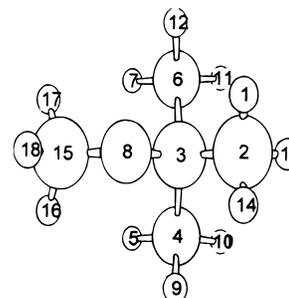
Methyl 2-propyl ether



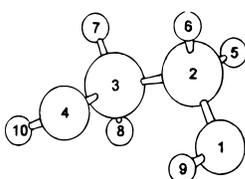
2-Methyl-2-propanol



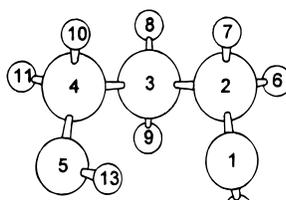
2-Methyl-2-butanol 3D



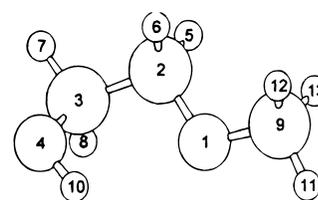
t-Butyl methyl ether



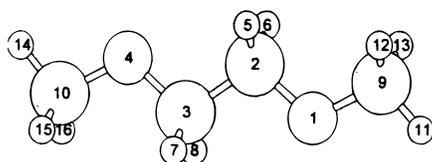
1,2-Ethandiol g+g+t



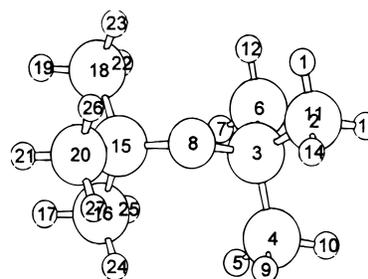
1,3-Propanediol g+g+g+



2-Methoxyethanol t g+g-



1,2-Dimethoxyethane



Di-t-butyl ether

^a See also Supporting Information.

Advantages and Characteristics of the FSE Formalism

•The FSE procedure uses no adjustable parameters. It is in fact possible algebraically to do away altogether with d_i conversion constants, replacing each with an appropriate sum of fractional quantities of the energies of the standard molecules.

The disadvantage of this approach is that the resultant explicit isodesmic equations are cumbersome.²⁵

•The FSE formalism provides a clearly specified definition of the steric correction component of the group increment representation of ΔH_f° . It does so in terms of sets of standard

TABLE 3: FSE Values of Alcohols and Ethers from "Raw" ab Initio Energies

compound		3-21G FSE	6-31G* FSE	6-31G** FSE	MP2 A ^a FSE	MP2 B ^b FSE	exptl FSE
cyclopropane		35.20 ^d	28.37	27.67	30.79	30.80	28.15
cyclobutane		28.30 ^{d,e}	26.04	25.82	28.79	28.55	27.17
2,2,3,3-tetramethylbutane	C ₂	8.26	8.87	8.88	6.46		6.68
methanol		1.75	0.28	0.27	0.18	0.25	-0.53
methanol	eclipsed			1.56			
oxirane				30.12	30.37		27.97
ethanol	C _s	1.45	0.09	0.10	0.37	0.43	-0.22
ethanol	g	1.30		0.20	0.28	0.34	
dimethyl ether		0.10 ^d	0.07 ^d				-0.10
oxetane			25.84 ^f	25.71	29.01		26.45
ethyl methyl ether ^g	tC _s	0.00	0.00	0.00	0.00	0.00	0.28
ethyl methyl ether	g	1.00		1.67	1.37	1.32	
1-propanol ^g	g ⁺ g ⁺ OH	0.00	0.00	0.00	0.00	0.00	-0.29
1-propanol	g ⁺ tOH			-0.05	0.20	0.21	
1-propanol	g ⁺ g ⁻ OH			0.35	0.33		
1-propanol	tg ⁺ OH	0.68		0.07	0.39		
1-propanol	ttOH	0.87		0.05	0.63	0.67	
2-propanol			0.20 ^f				0.03
2-propanol	g ⁺ OH	1.19	0.19	0.20	0.43	0.47	
2-propanol	tOH	1.10	0.42	0.42	0.58	0.61	
tetrahydrofuran	C ₂		5.52	5.51	8.07		6.82
tetrahydrofuran	C _s TS			5.94	8.50		
2-butanol ^g	9L ^c	0.20	0.20	0.20	0.20	0.20	0.14
2-butanol	8L	0.04		0.41	0.25		
2-butanol	7L	1.01		0.55	0.45		
2-butanol	4L	0.95		1.17	0.87		
2-butanol	1L	1.35		0.99	0.90		
2-butanol	3L	1.34		1.05	1.04		
2-butanol	6L	1.09		1.27	1.05		
2-butanol	2L	1.27		1.24	1.08		
2-butanol	5L	1.81		1.82	1.48		
diethyl ether ^g	ttC _{2v}	0.00	0.00	0.00	0.00	0.00	-0.13
diethyl ether	tg ⁺	0.93		1.67	1.34	1.29	
diethyl ether	g ⁺ g ⁺	1.92		3.03	2.48		
diethyl ether	g ⁺ g ⁻ TS	3.02		4.19	3.70		
1-butanol			0.12 ^f				0.25
2-methyl-1-propanol			-0.49 ^f				0.42
methyl 1-propyl ether	g ⁺ t	-1.15	-0.14	-0.14	-0.29		0.05
methyl 1-propyl ether	ttC _s	-0.50		-0.01	0.23		
methyl 1-propyl ether	tg ⁺ CCOC			1.68	1.54		
methyl 1-propyl ether	g ⁺ g ⁺			1.51	0.92		
2-methyl-2-propanol		0.94	-0.37 ^f	-0.33	0.59	0.67	0.06
methyl 2-propyl ether	gHCOC	1.13	1.95	1.92	1.41	1.36	1.17
methyl 2-propyl ether	tHCOC	2.73	4.27	4.04	3.50	3.43	
tetrahydropyran			1.28 ^f	1.32	2.87		2.60
1-pentanol			0.08 ^f				-0.51
2-methyl-2-butanol ^g	3D ^c	0.90	0.90	0.90	0.90	0.90	0.91
2-methyl-2-butanol	5D	1.02		0.96	1.07	1.08	
2-methyl-2-butanol	4m	1.80		1.35	1.40		
2-methyl-2-butanol	1D	2.01		1.48	1.51		
2-methyl-2-butanol	2m	2.01		1.51	1.62		
2-pentanol			0.25 ^f				0.14
ethyl 1-propyl ether			0.02 ^f				0.01
tert-butyl methyl ether		2.79	3.91	3.90	3.42	3.40	3.28
cyclohexanol			-0.04 ^f				1.45
diisopropyl ether			3.58 ^f				2.71
1-hexanol			0.08 ^f				-0.17
isopropyl tert-butyl ether			6.22 ^f				3.10
di-tert-butyl ether			13.49 ^f	13.55	11.12		11.33
di-tert-butyl ether	TS			14.81	12.55		
1,2-ethanediol	g ⁻ g ⁺ t			-1.81	-1.47		-0.95
1,2-ethanediol	g ⁺ g ⁺ g ⁻			-1.17	-1.27		
1,2-ethanediol	g ⁺ g ⁺ g ⁻			-0.53	-0.26		
1,2-ethanediol	g ⁺ tg ⁻			0.62	1.51		
1,2-ethanediol	ttt			0.21	1.74		
1,2-ethanediol	g ⁺ tt			0.54	1.78		
1,2-ethanediol	g ⁺ tg ⁺			0.99	1.81		
1,2-ethanediol	g ⁺ g ⁺ g ⁺			1.55	1.96		
1,2-ethanediol	tg ⁺ t			1.85	2.75		
1,2-ethanediol	g ⁺ g ⁺ t			2.29	2.93		
1,2-propanediol	g ⁻ g ⁺ t(g ⁻)			-1.76	-1.74		-1.69
1,2-propanediol	g ⁻ g ⁺ t(t)			-2.04	-1.73		
1,2-propanediol	g ⁺ g ⁺ g ⁻ (t)			-1.60	-1.64		

TABLE 3 (Continued)

compound		3-21G FSE	6-31G* FSE	6-31G** FSE	MP2 A ^a FSE	MP2 B ^b FSE	exptl FSE
1,3-propanediol	$g^-g^+g^-g^+$		-2.36	-2.24	-2.88		-1.13
1,3-propanediol	$tg^-g^-g^-$			-2.21	-2.45		
1,3-propanediol	$g^-g^+g^+g^+$			-0.85	-1.32		
1,3-propanediol	$g^-g^+g^+t$			-0.85	-1.07		
1,3-propanediol	tg^+g^+t			-0.81	-0.26		
1,3-propanediol	$g^+g^+g^+t$			-0.37	-0.11		
1,3-propanediol	g^+tg^+t			-0.07	0.67		
1,3-propanediol	ttg^+t			-0.04	0.91		
1,3-propanediol	$g^+tg^+g^+$			0.39	0.91		
1,3-propanediol	$g^-tg^+g^-$			1.35	1.71		
1,3-propanediol	g^+ttt			0.88	1.93		
1,3-propanediol	$tttt$			1.04	2.32		
1,3-propanediol	tg^-g^+t			3.99	4.65		
2-methoxyethanol	$tOMg^+g^-$			-1.74	-1.63		
2-methoxyethanol	$g^+OMg^+g^-$			0.36	-0.07		
2-methoxyethanol	$tOMtg^+$			0.57	1.59		
2-methoxyethanol	$tOMtt$			0.28	1.65		
2-methoxyethanol	g^-OMg^+t			1.96	2.06		
2-methoxyethanol	$tOMg^+t$			1.80	2.43		
2-methoxyethanol	$tOMg^+g^+$			2.14	2.51		
2-methoxyethanol	g^+OMtg^-			2.23	2.87		
2-methoxyethanol	g^+OMtt			2.13	3.15		
2-methoxyethanol	g^+OMtg^+			2.57	3.18		
2-methoxyethanol	g^+OMg^+t			3.71	3.87		
1,4-dioxane			4.02 ^f	4.13	5.96		5.70
1,2-dimethoxyethane	$tOMtt$			0.34	1.47		
1,2-dimethoxyethane	g^-OMg^+t			1.94	1.62		
1,2-dimethoxyethane	$tOMg^+t$			1.74	2.06		
1,2-dimethoxyethane	g^+OMtt			2.16	2.91		
1,2-dimethoxyethane	$g^+OMg^+g^-$			3.94	3.12		
1,2-dimethoxyethane	$g^+OMg^+g^+$			4.38	3.28		
1,2-dimethoxyethane	g^+OMg^+t			3.58	3.41		
1,2-dimethoxyethane	$g^-OMg^+g^-$			4.00	3.61		
1,2-dimethoxyethane	g^+OMtg^-			3.90	4.30		
1,2-dimethoxyethane	g^+OMtg^+			4.12	4.44		

^a MP2/6-31G**//6-31G**, ^b MP2/6-31G**//MP2/6-31G**, ^c See Supporting Information for definition, and see tables and figures for examples. ^d Reference 20. ^e References 53 and 54. ^f Reference 22. ^g Standard molecule.

molecules that have assigned FSE values. Since FSE is calculated by a procedure that is group isodesmic, errors that would arise from deficiencies or limitations of force fields or basis sets are partially canceled.

- FSE values for each given type of compound are clearly specified in terms of a *minimal* number of standard molecules. The calibration process is rigorously specified for every force field or basis set. The number of calculations required for calibration is as small as possible; it requires calculation of the energy of just one standard molecule per structural group. The resultant d_i conversion constants can be published and used by others; for the given type of compounds and given force field or basis set the calibration need be performed only once.

- Comparison of FSE values obtained for a given set of compounds with various force fields or basis sets provides an unbiased measure of the performances of the force fields or basis set/correlation procedures. All force fields and basis sets must in principle give the same FSE value for a given target molecule. Moreover, calculated FSE values should agree with experimental FSE values if these are available.

- Use of FSE values can help provide a solution for the commonly expressed concern that force fields contain so many parameters that they cannot be properly characterized. Force fields could, in principle, be characterized in terms of the FSE values they produce for some agreed upon set of test molecules.

- In some cases the FSE formalism provides a way to compute differences of enthalpies of formation even though experimental enthalpy data are not available for calculation of individual enthalpies of formation. The requirement is that the structural

group(s) for which data are not available must appear in comparable environments in several molecules so that there will be cancellation of the unavailable d_i and c_i values. The two molecules may otherwise differ as to what structural groups are present.

- The FSE values assigned to standards serve largely to provide a cosmetic indication of the “strain” present in target molecules. Although the FSE values assigned to the standards do determine the FSE values obtained for target molecules (and also the FBE values), the assigned FSE values do not affect calculated ΔH_f° values since the assigned FSE values drop out identically in combining the FBE and FSE terms of eq 6.

FSE Values of Alcohols and Ethers Derived from *ab Initio* Energies. FSE values based on “raw” *ab initio* energies are summarized in Table 3, those based on “corrected” *ab initio* energies are in Table 7. A “raw” *ab initio* energy pertains to a fictional vibrationless molecule at 0 K. A “corrected” *ab initio* energy is the “raw” energy plus the zero point energy (ZPE) and the heat content at 298 K ($H_{298} - H_0$) and pertains to an actual molecule at 298 K. “Raw” energies are given in Tables 5 and 9 (Supporting Information) and values of ZPE and of heat content are given in Table 7. The FSE values in Table 3 have been derived from the “raw” *ab initio* energies listed in Table 5 (Supporting Information) and the d_i conversion constants in Table 2 by use of eq 8. The FSE values in Table 7 have been derived from “corrected” energies and the d_i conversion constants in Table 6. It may be noted that the required ZPE and heat content corrections are subsumed in the d_i conversion constants in Table 2, but not in those of Table 6.

TABLE 4: ΔH_f° Values of Alcohols and Ethers from “Raw” ab Initio Energies

compound	conform	3-21G ΔH_f°	6-31G* ΔH_f°	6-31G** ΔH_f°	MP2 A ^a ΔH_f°	MP2 B ^b ΔH_f°	exptl ^c ΔH_f°	Benson		SM
								corr ⁿ	ΔH_f°	
cyclopropane		19.76	12.93	12.23	15.35	15.36	12.71	27.60	12.81	0.00
cyclobutane		7.71	5.49	5.23	8.20	7.96	6.58	26.20	6.48	0.00
2,2,3,3-tetramethylbutane	C ₂	-52.37	-51.76	-51.75	-54.17		-53.96	4.80	-57.40	0.00
methanol		-45.84	-47.31	-47.32	-47.41	-47.34	-48.12	0.00	-47.98	0.00
oxirane				-10.42	-10.17		-12.58	26.90	-12.50	0.00
ethanol	C _s	-54.50	-55.86	-55.85	-55.58	-55.52	-56.17	0.00	-56.20	0.00
dimethyl ether		-43.79	-43.82				-43.99	0.00	-43.36	0.00
oxetane			-19.85	-19.98	-16.68		-19.24	25.70	-18.63	0.00
ethyl methyl ether ^f	tC _s	-52.00	-52.00	-52.00	-52.00	-52.00	-51.73	0.00	-51.58	0.25
1-propanol ^f	g ⁺ g ⁺ OH	-60.98	-60.98	-60.98	-60.98	-60.98	-61.27	0.00	-61.13	0.12
2-propanol	g ⁺ OH	-63.99	-64.99	-64.98	-64.75	-64.71	-65.15	0.00	-65.50	0.00
tetrahydrofuran	C ₂		-45.32	-45.33	-42.77		-44.02	5.90	-43.36	0.00
2-butanol ^f	9L	-69.87	-69.87	-69.87	-69.87	-69.87	-69.93	0.50	-69.93	0.25
diethyl ether ^f	ttC _{2v}	-60.14	-60.14	-60.14	-60.14	-60.14	-60.27	0.00	-59.80	0.47
1-butanol			-65.79				-65.66	0.00	-66.06	0.33
2-methyl-1-propanol			-68.68				-67.77	0.50	-67.80	0.05
methyl 1-propyl ether	g ⁺ t	-58.07	-57.06	-57.06	-57.21		-56.88	0.00	-56.51	0.48
2-methyl-2-propanol		-73.80	-75.11	-75.07	-74.15	-74.07	-74.68	0.00	-75.10	0.00
methyl 2-propyl ether	gHCOC	-60.27	-59.45	-59.48	-59.99	-60.04	-60.24	0.80	-60.08	0.08
tetrahydropyran			-54.70	-54.66	-53.12		-53.39	0.50	-53.69	0.00
1-pentanol			-70.78				-71.37	0.00	-70.99	0.53
2-methyl-2-butanol ^f	3D	-78.90	-78.90	-78.90	-78.90	-78.90	-78.90	0.80	-79.23	0.09
2-pentanol			-74.76				-74.87	0.50	-74.86	0.46
ethyl 1-propyl ether			-65.05				-65.06	0.00	-64.73	0.69
tert-butyl methyl ether		-68.25	-67.13	-67.14	-67.62	-67.64	-67.76	1.60	-68.88	0.00
cyclohexanol			-70.89				-69.40	0.00	-69.75	0.00
diisopropyl ether			-75.37				-76.25	1.60	-76.80	0.11
1-hexanol			-75.67				-75.92	0.00	-75.92	0.79
isopropyl tert-butyl ether			-82.41				-85.54	3.20	-84.80	0.00
di-tert-butyl ether			-84.70	-84.64	-87.07		-86.86	4.70	-92.90	0.00
1,2-ethanediol			-93.53				-92.61	0.00	-92.00	0.18
1,2-ethanediol	g ⁻ g ⁺ t			-93.47	-93.13		-92.61	0.00	-92.00	0.17
1,2-propanediol ^d			-103.14	-102.79	-102.77		-102.72	0.00	-101.30	0.03
1,3-propanediol ^e	g ⁻ g ⁺ g ⁻ g ⁺		-99.05	-98.73	-99.36		-97.61	0.00	-96.93	0.50
2-methoxyethanol	tOMg ⁺ g ⁻			-89.72	-89.61			0.00	-87.38	
1,4-dioxane			-77.07	-76.96	-75.13		-75.39	3.30	-75.50	0.00
1,2-dimethoxyethane	ttt			-83.66	-82.53			0.00	-82.76	

^a MP2/6-31G**//6-31G**. ^b MP2/6-31G**//MP2/6-31G**. ^c References 55 and 29. ^e Reference 56 error is 1.0. ^d Reference 57 error is 1.2. ^f Standard molecule.

TABLE 6: FSE d_i Conversion Constants for Alkanes, Alcohols, and Ethers (Equation 8) for Use with Corrected ab Initio Energies (ab Initio Energy + ZPE + Heat Content, 298 K)

structural group	3-21G	6-31G*	6-31G**	MP2/6-31G**//6-31G**	MP2/6-31G**//MP2/6-31G**
C(C)(H) ₃	-39.358871	-39.576388	-39.581387	-39.733749	-39.733785
C(C) ₂ (H) ₂	-38.790231	-39.005860	-39.009046	-39.153356	-39.153399
C(C) ₃ (H)	-38.223574	-38.435514	-38.436938	-38.575963	-38.576148
C(C) ₄	-37.657959	-37.864795	-37.864465	-38.000657	-38.000944
C(O)(H) ₃	-39.353189	-39.572131	-39.575733	-39.728299	-39.728322
C(O)(C)(H) ₂	-38.790231	-39.005860	-39.009046	-39.153356	-39.153399
C(O)(C) ₂ (H)	-38.228335	-38.441151	-38.442672	-38.580434	-38.580497
C(O)(C) ₃	-37.666423	-37.873875	-37.873753	-38.008334	-38.008489
O(C)(H)	-74.993634	-75.410883	-75.417432	-75.599129	-75.600117
O(C) ₂	-74.423545	-74.840293	-74.840491	-75.011967	-75.012908

Entries in the tables labeled with asterisks are for the lowest energy conformers of the standard molecules. In the Supporting Information may be found more extensive tables that cross-reference FSE values, ab initio energies, and geometries.

One important factor to be analyzed is the consistency of the several estimates of FSE for a given target molecule and of sets of target molecules. Each basis set and each force field must in principle give the same FSE value of the target molecule. The extent of agreement among the several estimates of the FSE value is, therefore, a measure of the effectiveness of the basis sets or force fields in representing the energy of the molecule and the effectiveness of the isodesmic compensation of errors that arise from limitations of the basis set or the

force field. If experimental ΔH_f° data are available, the experimental FSE value can be obtained, and this should agree with the calculated value.

The consistency of the several estimates of FSE values may be judged by comparing the entries in Table 3 for FSE values calculated from “raw” ab initio energies and in Table 7 for those calculated from “corrected” ab initio energies. These pairs of values are generally the same within about 0.2 kcal/mol for acyclic molecules. That is, for acyclic molecules the FSE values are the same whether based on implicit or explicit corrections for ZPE. The differences are much larger for cyclic molecules. The reason is straightforward. All standard molecules are acyclic, and a given acyclic molecule has a higher ZPE than

TABLE 7: FSE Values of Alcohols and Ethers from ab Initio Energies Corrected by Adding ZPE and Heat Content

compound		3-21G			6-31G**			MP2/6-31G**	
		ZPE	heat content	FSE	ZPE	heat content	FSE	FSE	exptl FSE
cyclopropane					49.02	2.73	25.44	28.56	28.15
cyclobutane					66.71	3.25	23.81	26.78	26.96
2,2,3,3-tetramethylbutane	C ₂	148.49	7.30	8.52	147.23	7.34	9.16	6.74	6.68
methanol		30.77	2.69	1.33	31.14	2.69	0.23	0.14	-0.53
methanol	eclipsed				31.14	2.69	1.53		
oxirane					34.79	2.57	27.65	27.89	27.97
ethanol	C _s	48.19	3.35	1.37	48.38	3.33	0.07	0.34	-0.22
ethanol	g	48.38	3.33	1.39	48.39	3.31	0.16	0.27	
oxetane					52.75	3.19	23.82	27.12	26.45
ethyl methyl ether ^c	tC _s	65.91	4.19	0.00	65.35	4.14	0.00	0.00	0.28
ethyl methyl ether	g	65.61	4.17	0.68	65.38	4.15	1.71	1.41	
1-propanol ^c	g ⁺ g ⁺ OH	65.70	4.03	0.00	65.66	4.07	0.00	0.00	-0.29
1-propanol	g ⁺ tOH				65.62	4.10	-0.06	0.19	
1-propanol	g ⁺ g ⁻ OH				65.65	4.09	0.35	0.34	
1-propanol	tg ⁺ OH	65.65	4.09	0.69	65.58	4.13	0.05	0.38	
1-propanol	ttOHC	65.51	4.16	0.81	65.55	4.15	0.02	0.60	
2-propanol	g ⁺ OH	65.14	4.12	1.14	65.20	4.08	0.19	0.41	0.03
2-propanol	tOH	65.14	4.11	1.05	65.20	4.08	0.41	0.56	
tetrahydrofuran	C ₂				70.67	3.73	4.09	6.65	6.82
2-butanol ^c	9L	82.49	4.93	0.20	82.36	4.93	0.20	0.20	0.14
2-butanol	8L	82.37	4.92	-0.09	82.37	4.92	0.41	0.25	
2-butanol	7L	82.39	4.93	0.91	82.39	4.93	0.58	0.48	
2-butanol	4L	82.51	4.89	0.93	82.51	4.89	1.28	0.98	
2-butanol	1L	82.42	4.92	1.27	82.42	4.92	1.04	0.95	
2-butanol	3L	82.41	4.92	1.25	82.41	4.92	1.09	1.08	
2-butanol	6L	82.48	4.91	1.06	82.48	4.91	1.37	1.15	
2-butanol	2L	82.40	4.93	1.18	82.40	4.93	1.28	1.12	
2-butanol	5L	82.49	4.91	1.79	82.49	4.91	1.93	1.59	
diethyl ether ^c	ttC _{2v}	82.83	5.01	0.00	82.40	4.96	0.00	0.00	-0.13
diethyl ether	tg ⁺	82.86	5.01	0.96	82.43	4.96	1.70	1.37	
diethyl ether	g ⁺ g ⁺	82.86	4.98	1.92	82.45	4.92	3.04	2.49	
methyl 1-propyl ether	g ⁺ t	83.04	4.94	-1.39	82.45	4.92	-0.25	-0.25	0.05
methyl 1-propyl ether	ttC _s	82.50	4.99	-1.22	82.50	4.99	0.00	0.24	
methyl 1-propyl ether	tg ⁺				82.54	5.00	1.73	1.60	
methyl 1-propyl ether	g ⁺ g ⁺				82.59	4.93	1.54	0.95	
2-methyl-2-propanol		81.88	4.93	0.78	81.81	4.89	-0.43	0.49	0.06
methyl 2-propyl ether	gHCOC	82.49	5.03	0.86	82.11	4.99	1.97	1.46	1.17
methyl 2-propyl ether	tHCOC	82.60	5.00	2.54	82.22	4.98	4.19	3.65	
tetrahydropyran					88.48	4.11	0.09	1.64	2.60
2-methyl-2-butanol ^c	3D	99.35	5.73	0.90	99.06	5.73	0.90	0.90	0.91
2-methyl-2-butanol	5D	99.03	5.75	0.72	99.03	5.75	0.95	1.06	
2-methyl-2-butanol	4m	99.06	5.75	1.53	99.06	5.75	1.37	1.42	
2-methyl-2-butanol	1D	99.26	5.78	1.97	99.06	5.74	1.49	1.52	
2-methyl-2-butanol	2m	99.25	5.78	1.96	99.06	5.74	1.52	1.63	
<i>tert</i> -butyl methyl ether		99.31	5.86	2.51	98.77	5.83	3.95	3.47	3.28
di- <i>tert</i> -butyl ether					149.51	8.12	13.70	11.27	11.33
di- <i>tert</i> -butyl ether	TS				149.51	8.12	14.96	12.70	
1,2-ethanediol	g ⁻ g ⁺ t				52.18	3.80	-1.78	-1.44	-0.95
1,2-ethanediol	g ⁺ g ⁺ g ⁻				52.22	3.76	-1.14	-1.24	
1,2-ethanediol	g ⁻ g ⁺ g ⁻				51.95	4.01	-0.52	-0.25	
1,2-ethanediol	g ⁺ tg ⁻				51.93	3.96	0.56	1.45	
1,2-ethanediol	ttt				51.84	4.01	0.11	1.64	
1,2-ethanediol	g ⁺ tt				51.87	3.99	0.46	1.69	
1,2-ethanediol	g ⁺ tg ⁺				51.91	3.96	0.91	1.72	
1,2-ethanediol	g ⁺ g ⁺ g ⁺				51.68	4.10	1.38	1.79	
1,2-ethanediol	tg ⁺ t				51.68	4.08	1.66	2.56	
1,2-ethanediol	g ⁺ g ⁺ t				51.80	3.97	2.11	2.75	
1,2-propanediol					69.02	4.61	-1.63	-1.62	-1.69
1,2-propanediol	g ⁻ g ⁺ t(t)				68.94	4.64	-1.97	-1.66	
1,2-propanediol	g ⁺ g ⁺ g ⁻ (t)				68.99	4.61	-1.51	-1.55	
1,3-propanediol	g ⁻ g ⁺ g ⁻ g ⁺				69.68	4.46	-2.04	-2.68	-1.13
1,3-propanediol	tg ⁻ g ⁺ g ⁻				69.58	4.51	-2.06	-2.31	
1,3-propanediol	g ⁻ g ⁺ g ⁺ g ⁺				69.55	4.57	-0.68	-1.14	
1,3-propanediol	g ⁻ g ⁺ g ⁺ g ⁺ t				69.52	4.60	-0.67	-0.89	
1,3-propanediol	tg ⁺ g ⁺ t				69.21	4.72	-0.82	-0.28	
1,3-propanediol	g ⁺ g ⁺ g ⁺ t				69.24	4.69	-0.38	-0.12	
1,3-propanediol	g ⁺ tg ⁺ t				69.16	4.75	-0.10	0.63	
1,3-propanediol	ttg ⁺ t				69.14	4.76	-0.08	0.86	
1,3-propanediol	g ⁺ tg ⁺ g ⁺				69.15	4.75	0.34	0.86	
1,3-propanediol	g ⁻ tg ⁺ g ⁻				69.11	4.78	1.29	1.66	
1,3-propanediol	g ⁺ ttt				69.08	4.81	0.82	1.88	
1,3-propanediol	tttt				69.03	4.83	0.96	2.24	
1,3-propanediol	tg ⁻ g ⁺ t				68.88	4.87	3.80	4.46	

TABLE 7 (Continued)

compound		3-21G			6-31G**			MP2//6-31G**	exptl FSE
		ZPE	heat content	FSE	ZPE	heat content	FSE	FSE	
2-methoxyethanol	tOMg ⁺ g ⁻			69.14	4.65	-1.65	-1.54		
2-methoxyethanol	g ⁺ OMg ⁺ g ⁻			69.14	4.66	0.46	0.03		
2-methoxyethanol	tOMtg ⁺			68.86	4.82	0.55	1.56		
2-methoxyethanol	tOMtt			68.82	4.85	0.25	1.62		
2-methoxyethanol	g ⁻ OMg ⁺ t			68.89	4.80	1.94	2.05		
2-methoxyethanol	tOMg ⁺ t			68.75	4.83	1.68	2.30		
2-methoxyethanol	tOMg ⁺ g ⁺			68.78	4.79	2.01	2.38		
2-methoxyethanol	g ⁺ OMtg ⁻			68.88	4.83	2.23	2.88		
2-methoxyethanol	g ⁺ OMtt			68.82	4.86	2.11	3.12		
2-methoxyethanol	g ⁺ OMtg ⁺			68.86	4.82	2.55	3.16		
2-methoxyethanol	g ⁺ OMg ⁺ t			68.82	4.81	3.64	3.80		
1,4-dioxane				74.47	3.93	2.86	4.69	5.70	
1,2-dimethoxyethane	tOMtt			85.78	5.70	0.37	1.50		
1,2-dimethoxyethane	g ⁻ OMg ⁺ t			85.85	5.64	1.98	1.66		
1,2-dimethoxyethane	tOMg ⁺ t			85.77	5.62	1.67	2.00		
1,2-dimethoxyethane	g ⁺ OMtt			85.80	5.63	2.14	2.89		
1,2-dimethoxyethane	g ⁺ OMg ⁺ g ⁻			85.88	5.62	3.99	3.16		
1,2-dimethoxyethane	g ⁺ OMg ⁺ g ⁺			86.10	5.50	4.53	3.43		
1,2-dimethoxyethane	g ⁺ OMg ⁺ t			85.80	5.63	3.55	3.38		
1,2-dimethoxyethane	g ⁻ OMg ⁺ g ⁻			85.79	5.71	4.04	3.66		
1,2-dimethoxyethane	g ⁺ OMtg ⁻			85.80	5.74	3.99	4.39		
1,2-dimethoxyethane	g ⁺ OMtg ⁺			85.81	5.71	4.18	4.50		

^a MP2/6-31G**//6-31G**, ^b MP2/6-31G**//MP2/6-31G**, ^c Standard molecule.

TABLE 8: ΔH_f° Values of Alcohols and Ethers from ab Initio Energies Corrected by Adding ZPE and Heat Content

compound		3-21G ΔH_f°	6-31G* ΔH_f°	6-31G** ΔH_f°	MP2 A ^a ΔH_f°	MP2 B ^b ΔH_f°	exptl ^c ΔH_f°	Benson		
								corn	ΔH_f°	SM
cyclopropane			10.66	10.00	13.12	13.13	12.71	27.60	12.81	0.00
cyclobutane				3.22	6.19	5.95	6.37	26.20	6.48	0.00
2,2,3,3-tetramethylbutane	C ₂	-52.11	-51.46	-51.47	-53.89		-53.96	4.80	-57.40	0.00
methanol		-46.26	-46.53	-47.36	-47.45	-47.38	-48.12	0.00	-47.98	0.00
oxirane				-12.89	-12.65		-12.58	26.90	-12.50	0.00
ethanol	g	-54.56		-55.79	-55.68	-55.63	-56.17	0.00	-56.20	0.00
oxetane			-22.07	-21.87	-18.57		-19.24	25.70	-18.63	0.00
ethyl methyl ether ^f	tC _s	-52.00	-52.00	-52.00	-52.00	-52.00	-51.73	0.00	-51.58	0.25
1-propanol ^f	g ⁺ g ⁺ OH	-60.98	-60.98	-60.98	-60.98	-60.98	-61.27	0.00	-61.13	0.12
2-propanol	tOH	-64.13	-65.08	-64.77	-64.62	-64.59	-65.15	0.00	-65.50	0.00
tetrahydrofuran	C ₂		-46.73	-46.75	-44.19		-44.02	5.90	-43.36	0.00
2-butanol ^f	9L	-69.87	-69.87	-69.87	-69.87	-69.87	-69.93	0.50	-69.93	0.25
diethyl ether ^f	ttC _{2v}	-60.14	-60.14	-60.14	-60.14	-60.14	-60.27	0.00	-59.80	0.47
methyl 1-propyl ether	g ⁺ t	-58.31	-56.23	-57.17	-57.17		-56.88	0.00	-56.51	0.48
methyl 2-propyl ether	gHCOC	-60.54	-58.61	-59.43	-59.94	-59.99	-60.24	0.80	-60.08	0.08
tetrahydropyran				-55.89	-54.34		-53.39	0.50	-53.69	0.00
2-methyl-2-butanol ^f	3D	-78.90	-78.90	-78.90	-78.90	-78.90	-78.90	0.80	-79.23	0.09
tert-butyl methyl ether		-68.53	-66.29	-67.09	-67.57	-67.59	-67.76	1.60	-68.88	0.00
di-tert-butyl ether				-84.49	-86.92		-86.86	4.70	-92.90	0.00
1,2-ethanediol	g ⁻ g ⁺ t			-93.44	-93.10		-92.61	0.00	-92.00	0.17
1,2-propanediol ^d				-102.66	-102.65		-102.72	0.00	-101.30	0.03
1,3-propanediol ^e	g ⁻ g ⁺ g ⁻ g ⁺			-98.52	-99.16		-97.61	0.00	-96.93	0.50
2-methoxyethanol	tg ⁺ g ⁻ OH			-89.63	-89.52			0.00	-87.38	
1,4-dioxane				-78.23	-76.40		-75.39	3.30	-75.50	0.00
1,2-dimethoxyethane	ttt			-83.63	-82.50			0.00	-82.76	

^a MP2/6-31G**//6-31G**, ^b MP2/6-31G**//MP2/6-31G**, ^c References 55 and 29. ^e Reference 56. ^d Reference 57. Estimated errors of the glycols are 0.5–1 kcal/mol, and differences among various reported values are larger. ^f Standard molecule.

does a cyclic molecule of the same carbon content because of the two extra C–H bonds present in the acyclic molecule. If cyclic molecules are to be included, then explicit ZPE corrections must be used.

Another comparison is among FSE values obtained with different basis set/electron correlation methods. Examination of the FSE entries in Table 3 for a given conformer (that is, across a row of entries) shows that there are sometimes considerable differences. Examples of nearly the same FSE values are those calculated with MP2/6-31G**//6-31G** (column header MP2 A) and those calculated with geometries optimized with MP2/6-31G** (column header MP2 B); the differences are mostly less than 0.1 kcal/mol. Also nearly the same are values

calculated with 6-31G* and 6-31G**; these are mostly within 0.2 kcal/mol.

In making further comparisons it is convenient to select one set of FSE values to serve as the reference set. Those calculated with MP2/6-31G**//6-31G** are closest to the experimental FSE values. Comparison with FSE values calculated with RHF 3-21G shows that the latter tend to be higher than the reference values, but there are exceptions among the ethers. Differences between values calculated with RHF 6-31G** and MP2/6-31G**//6-31G** are erratic and sometimes exceed 3 kcal/mol. The conclusion is that RHF energies are inadequate for calculating correct FSE values and enthalpies and that electron correlation must be used.

TABLE 10: Calculated ΔH_f° Values Minus Experimental ΔH_f° Values

compound	acyclics				all cpds				Benson
	6-31G**		MP2 A		6-31G** raw	MP2A raw	6-31G** ZPE corr	MP2A ZPE corr	
	raw	ZPE corr	raw	ZPE corr					
methanol	0.80	0.76	0.71	0.67	0.80	0.71	0.76	0.67	0.14
ethanol	0.32	0.29	0.59	0.56	0.32	0.59	0.29	0.56	-0.03
2-propanol	0.17	0.16	0.40	0.38	0.17	0.40	0.16	0.38	-0.35
methyl 1-propyl ether	-0.18	-0.29	-0.33	-0.29	-0.18	-0.33	-0.29	-0.29	0.37
2-methyl-2-propanol	-0.39	-0.49	0.53	0.43	-0.39	0.53	-0.49	0.43	-0.42
methyl 2-propyl ether	0.76	0.81	0.25	0.30	0.76	0.25	0.81	0.30	0.16
<i>tert</i> -butyl methyl ether	0.62	0.67	0.14	0.19	0.62	0.14	0.67	0.19	1.12
di- <i>tert</i> -butyl ether	2.22	2.37	-0.21	-0.06	2.22	-0.21	2.37	-0.06	5.48
1,2-ethanediol	-0.88	-0.85	-0.54	-0.51	-0.88	-0.54	-0.85	-0.51	0.61
oxirane					2.16	2.41	-0.31	-0.07	0.08
oxetane					-0.74	2.56	-2.63	0.67	0.61
tetrahydrofuran					-1.31	1.25	-2.73	-0.17	0.66
tetrahydropyran					-1.27	0.27	-2.50	-0.95	-0.30
dioxane					-1.57	0.26	-2.84	-1.01	-0.11
std dev from 0	0.98	1.03	0.48	0.44	1.20	1.11	1.69	0.55	1.59
omitting di- <i>tert</i> -butyl ether									0.50

Comparisons may also be made among the relative ab initio energies of sets of conformers of a given compound. Since each conformer of a given compound has the identical $\sum n_i d_i$, the difference between the FSE values of two conformers and between the energies of two conformers will be identical. Accordingly, it becomes possible to compare relative conformer energies with data from other laboratories. Pertinent examples are studies of conformers of 1,2-ethanediol^{40,41} and 1,2-dimethoxymethane⁴² with various levels of basis sets and various correlation methods. For conformers of 1,2-ethanediol the MP2/6-31G**//6-31G** energies are mostly within 0.5 kcal/mol or less of the composite averages.⁴⁰ For 1,2-dimethoxyethane the differences are somewhat less.⁴² Although these differences do not correspond directly to the errors introduced into the estimation of enthalpies derived from ab initio energies, they provide further indication that MP2/6-31G**//6-31G** energies are a reasonable choice as reference values.

c_i Increments and Experimental FSE Values. The c_i increments have been derived with the use of eq 6 and have been published.³⁴⁻³⁷ The independent variables for these estimates are the experimental ΔH_f° values, the estimated SM values, and the assigned FSE values. The published c_i estimates are based on a least squares treatment using all compounds for which reliable a priori assignments could be made of their FSE values. Errors expressed as standard deviations of the c_i increments are summarized in Table 1 for the c_i values needed for this study. These errors arise primarily from errors in the experimental ΔH_f° values. Table 11 gives specific examples.

Based on propagation of error, it is possible to estimate the standard deviation of the FBE for any desired molecule. As examples, the estimated standard deviation of the calculated FBE value for methyl 1-propyl ether is 0.17, for di-*tert*-butyl ether is 0.28, for tetrahydropyran is 0.16, and for 1,2-ethanediol is 0.10.

Equation 6 is also used to obtain experimental FSE values. For this calculation the independent variables are the experimental ΔH_f° value and an estimate of the SM value. The above calculated c_i increments are also needed. The experimental FSE value is FSE₀, the formal steric enthalpy of the conformer that is the global minimum. Differences between calculated and observed experimental FSE values arise from uncertainties in the enthalpies of formation and from limitations of the group increment procedure. Increments of ΔH_f° between initial members of a series tend to differ from increments appropriate for later members. Thus application of the general increments

TABLE 11: Calculated FSE Values for Unexceptional Compounds Having No Obvious Steric Strain (Expected Experimental FSE = 0)

	exptl FSE	Benson $\Delta H_f^\circ(\text{calc}) - \Delta H_f^\circ(\text{obsd})$
ethanol	-0.26	0.14
dimethyl ether	-0.09	0.63
ethyl methyl ether	0.28	-0.15
1-propanol	0.01	0.14
2-propanol	-0.02	0.35
diethyl ether	-0.11	0.47
1-butanol	0.18	0.40
methyl 1-propyl ether	-0.01	0.13
1-pentanol	0.43	-0.38
1-hexanol	0.27	0.00
ethyl 1-propyl ether	0.01	-0.33
count	11.00	11.00
std dev from 0	0.21	0.35

to ethane, 2-methylpropane, or methanol, for example, gives estimates of experimental FSE values and calculated ΔH_f° values that have larger errors than are found for later members of the series.

The difference between the experimental FSE₀ value and the FSE value calculated for the conformer that is the global minimum of energy is necessarily the same as the difference between the experimental ΔH_f° value and the calculated ΔH_f° value. It is, therefore, equally valid to compare experimental and calculated FSE values of the global minimum or the experimental and calculated ΔH_f° values in evaluating the reliability of the calculations.

Calculated ΔH_f° Values. ΔH_f° values calculated from "raw" ab initio energies are reported in Table 4. These were obtained with eq 6 using the FSE values in Table 3, the SM values in Table 4, and the c_i increments in Table 1. ΔH_f° values calculated from "corrected" ab initio energies are reported in Table 8. These were calculated with eq 6 using FSE values in Table 7, SM values in Table 8, and the c_i increments reported in Table 1. Note that the ΔH_f° values shown for the reference standards are FBE + SM + FSE and are the same for each basis set since the separate terms are the same.

Table 10 compares experimental ΔH_f° values with those calculated with the several basis sets. The best results for the total set of 14 compounds including rings and crowded molecules is obtained with the MP2/6-31G**//6-31G** energies corrected for ZPE and heat content. For all compounds the

standard deviation is 0.55 kcal/mol; for acyclic molecules alone it is 0.44 kcal/mol. Experimental ΔH_f° values for a few of the compounds have reported standard deviations of 0.5 kcal/mol or greater.

The results that are obtained with the Benson increments (eq 1) are also provided. Overall agreement between calculated and experimental values provides an indication of the accuracy attainable by the group increment procedure. The data for di-*tert*-butyl ether illustrate the difficulties of assigning appropriate steric corrections in using the Benson procedure.

Sensitivity to Estimates of SM Values. For compounds that exist as a mixture of conformers, the SM value is not zero. A given scalar error in SM (eq 3) introduces the same scalar error into the calculated ΔH_f° (eq 6). The simplest way to estimate SM, and the way used in previous studies, is to calculate the Boltzmann distribution from SE values based on molecular mechanics. Since molecular mechanics calculations tend to give somewhat confusing sets of conformers for alcohols, a better alternative is to use ab initio energies. In principle the Boltzmann fractions should be based on free energies, but in fact, the difference between the two ways of calculating fractions is negligible.

Relative energies of conformers depend somewhat on the basis set/correlation procedure. Examples of different energies of conformers of alkanes have been reported in the literature.^{34,43,44} Energies of most of the conformers reported in this study are different for different basis sets and also differ whether correlation has been used.⁴⁵ Although relative energies of the conformers differ, SM values calculated from the differing sets show smaller deviations owing to compensation. The larger is the energy of a given conformer, the smaller is its contribution to SM.^{25,34,38}

As indicated in the tables, the SM values selected for this study differ slightly from published values for three compounds. For the standard molecules the differences between the published SM values and those derived from complete conformer data using 6-31G** energies are less than 0.1 kcal/mol except for one compound, which differs by 0.17 kcal/mol. SM values for the standard compounds are used only in the calibration of the c_i increments, and since the calibration involves some 40 compounds, the effect of updating these few SM values is found to be negligible.

Sensitivity to Calculated Zero Point Energies. Problems of obtaining accurate estimates of zero point energies have been discussed frequently.^{2,3,25,46} For the present study the need is for reliable relative ZPE values. All values summarized in the tables were derived from frequency calculations with the 6-31G** basis set with frequencies scaled by 0.90, a value comparable to those cited. Other factors sometimes used are 0.905 and 0.91.^{46,47}

An error in the relative ZPE value translates directly to the same error in the calculated ΔH_f° value. ZPE values depend almost entirely on the high frequencies.

Overall Analysis of Effects of the Several Sources of Error. Two estimates may be made of errors that arise from each source, a likely minimum value and a high value. These are in terms of standard deviations and in units of kcal/mol: FBE 0.15–0.3, SM 0–0.2, ZPE 0.05–0.1, errors due to limitations of energies used to calculate FSE 0.1–0.4. By propagation of error these lead to an estimated minimum error of calculated ΔH_f° of 0.2 and a likely maximum error of 0.55 kcal/mol. The errors of experimental ΔH_f° are probably 0.1–0.5 kcal/mol and sometimes even larger. The overall error in differences between calculated and experimental ΔH_f° values may be estimated as

TABLE 12: Analysis of Trans/Gauche Energy Differences, kcal/mol

C–C–C–O	
1-propanol, methyl 1-propyl ether, av of 4	–0.48
1,3-propanediol, av of 3	–1.26
C–C–O–C	
ethyl methyl ether, methyl 1-propyl ether, diethyl ether, 1,2-dimethoxyethane, 2-methoxyethanol av of 9	1.36
O–C–C–O	
1,2-dimethoxyethane, 2-methoxyethanol, av of 4 for 1,2-dimethoxyethane with g^+ central torsion	0.58
C–C–O–C	0.05
O–C–C–O	–1.07

0.2–0.74. The values of 0.44 and 0.55 summarized in Table 10, therefore, fall within the expected range.

Geometries and Relative Energies of Conformers. Geometries of the conformers of lowest energy are reported in the geometry tables. Figures are included for selected conformers. All geometries were optimized with HF 6-31G** and all conformer energies are reported as FSE values calculated with MP2/6-31G**//6-31G**. More complete sets may be found in the Supporting Information.

Of particular interest are the relative energies of gauche and trans conformers of the standard torsional sequences C–C–C–C, C–C–O–C, C–C–C–O, and O–C–C–O since these occur frequently in organic molecules containing oxygen.

For the C–C–C–C sequence, a single gauche interaction gives a conformer about 0.8 kcal/mol higher in energy than observed for the trans conformer.^{17,48} This energy difference arises primarily from nonbonded interactions of C–H hydrogen atoms.

The data for the oxygen-containing torsions are summarized in Table 12. The FSE values are those based on calculations using MP2/6-31G**//6-31G**. A summary of the individual torsions and their FSE values may be found in the Supporting Information.

For the C–C–O–C sequence, a single gauche interaction results in a 1.4 kcal/mol higher energy for the gauche form as compared with the trans form. The larger gauche–trans difference than observed for C–C–C–C can be ascribed to the effect of the short C–O bonds, which bring the terminal groups closer than occurs with the all carbon sequence.

For the C–C–C–O sequence a small or zero gauche–trans difference might be expected since an oxygen atom has no hydrogen atoms to interfere with those on the terminal carbon atom. What is found is that the gauche form is actually lower in energy by 0.5 kcal/mol. In 1,3-propanediol the terminal CH₃ has been replaced by a terminal HOCH₂ group and the gauche–trans difference for the sequence HOC–C–C–O is even larger; the gauche form is lower in energy by 1.2 kcal/mol.

Although there are no hydrogen atoms at either terminus of the O–C–C–O sequence, the gauche form is higher in energy by 0.6 kcal/mol. This may be a consequence of repulsion of the opposing dipoles.

There are some peculiar effects in the MeO–C–C–OMe sequence. If the internal torsion is gauche, then the trans–gauche difference for the C–C–O–C sequence is zero and for the O–C–C–O sequence the gauche sequence is lower in energy by 1.1 kcal/mol.

With unsubstituted alkanes the all trans conformer has an FSE of zero by definition. For ethers and alcohols the all trans conformer might also have been expected to have an FSE of zero. The assumption proves to be correct for diethyl ether and ethyl methyl ether. However, energies of the all trans conformers of 1-propanol and of methyl 1-propyl ether are about 0.5 kcal/

TABLE 13: Geometries of Conformers (See Chart 1)

1-Propanol													
		g ⁺ g ⁺ OH	g ⁺ tOH	g ⁻ g ⁻ OH	tg ⁺ OH	ttOH		g ⁺ g ⁺ OH	g ⁺ tOH	g ⁻ g ⁻ OH	tg ⁺ OH	ttOH	
FSE		0.00	0.19	0.34	0.38	0.60	CCO	1-2-4	112.99	108.71	113.10	112.68	108.30
CC	1-3	1.527	1.527	1.528	1.528	1.527	COH	2-4-12	109.52	109.95	109.94	109.59	109.91
CC	1-2	1.524	1.519	1.524	1.523	1.518	CCCO	3-1-2-4	60.0	62.8	62.3	177.7	180.0
CO	2-4	1.404	1.404	1.404	1.402	1.403	CCOH	1-2-4-12	65.5	-177.3	-73.8	64.6	180.0
OH	4-12	0.943	0.942	0.942	0.943	0.942	C ^{•••} O	3 ^{•••} 4	3.00	2.94	3.03	3.79	3.74
CCC	2-1-3	113.23	113.29	113.70	112.65	112.63							
2-Butanol ^a													
		9L	8L	7L	4L	1L		9L	8L	7L	4L	1L	
FSE		0.20	0.25	0.48	0.98	0.95	CCO	2-1-5	107.12	111.38	111.58	111.40	110.29
CC	2-3	1.527	1.527	1.529	1.529	1.528	CCO	4-1-5	110.69	110.73	108.66	106.54	106.10
CC	1-2	1.524	1.529	1.529	1.532	1.530	CCCC	3-2-1-4	176.7	176.5	179.7	-60.9	65.2
CC	1-4	1.524	1.525	1.519	1.520	1.520	CCCCO	3-2-1-5	-61.6	-58.5	-60.9	59.8	-175.6
CO	1-5	1.409	1.409	1.409	1.409	1.409	CCCH	3-2-1-6 Z	56.4	56.2	59.7	179.4	-55.7
CCC	1-2-3	113.47	113.38	113.90	115.03	114.68	HCOH	6-1-5-15 Y	56.8	177.9	-50.0	-69.3	-59.8
CCC	2-1-4	112.31	112.41	112.14	114.11	113.78	C ^{•••} O	3 ^{•••} 5	2.91	2.96	3.00	3.01	3.79
Diethyl Ether													
		tt	tg ⁺	g ⁺ g ⁺	g ⁺ g ⁻ TS			tt	tg ⁺	g ⁺ g ⁺	g ⁺ g ⁻ TS		
FSE		0	1.37	2.49	3.7	CCO	1-2-3	108.63	108.31	111.98	113.3		
CC	1-2	1.516	1.516	1.522	1.522	COC	2-3-4	114.73	116.2	116.54	118.78		
CO	2-3	1.397	1.398	1.402	1.400	OCC	3-4-5	108.63	113.21	111.99	113.31		
OC	3-4	1.397	1.400	1.402	1.401	CCOC	1-2-3-4	180.0	176.1	89.1	-95.1		
CC	4-5	1.516	1.523	1.522	1.522	COCC	2-3-4-5	180.0	79.9	89.1	94.9		
Methyl 1-Propyl Ether													
		g ⁺ t	tt	tg ⁺	g ⁺ g ⁺			g ⁺ t	tt	tg ⁺	g ⁺ g ⁺		
FSE		-0.25	0.24	1.60	0.95	CCC	2-1-3	113.29	112.52	112.02	113.02		
CC	1-3	1.527	1.527	1.528	1.527	CCO	1-2-4	109.17	108.8	113.36	113.83		
CC	1-2	1.519	1.518	1.525	1.526	COC	2-4-5	114.36	114.31	115.86	115.77		
CO	2-4	1.397	1.396	1.399	1.400	CCCCO	3-1-2-4	62.7	180.0	176.0	57.9		
OC	4-5	1.391	1.391	1.393	1.393	CCOC	1-2-4-5	-179.0	180.0	81.1	78.0		
2-Methyl-2-butanol ^b													
		class 3							class 3				
		3D	5D	4m	1D	2m			3D	5D	4m	1D	2m
FSE		0.90	1.06	1.37	1.49	1.63	CCO	4-1-6	110.14	110.20	110.07	110.64	110.72
CC	2-3	1.528	1.528	1.530	1.529	1.529	CCO	5-1-6	105.19	109.60	109.57	104.67	109.19
CC	1-2	1.539	1.534	1.540	1.539	1.534	COH	1-5-15	109.67	109.75	110.07	109.69	109.01
CC	1-4	1.531	1.531	1.526	1.531	1.531	CCCC	3-2-1-4 Y	-178.3	-177.7	-174.6	62.2	62.6
CC	1-6	1.526	1.516	1.531	1.526	1.531	CCOH	4-1-5-15 Z	58.5	-62.8	-171.1	61.5	-60.5
CO	1-5	1.415	1.415	1.415	1.416	1.416	CCCCO	3-2-1-5	-58.0	-60.0	-59.6	-177.7	180.0
OH	5-15	0.944	0.943	0.943	0.944	0.944	CCOH	2-1-5-15	-62.1	179.3	71.0	-60.6	180.0
CCC	1-2-3	115.38	115.52	115.96	116.94	116.63	CCOH	6-1-5-15 Y	176.7	58.1	-53.0	179.8	60.5
CCC	2-1-4	109.76	109.64	109.53	112.18	112.08	CCCC	3-2-1-6 Z	58.8	59.5	62.8	-62.9	-62.6
CCC	4-1-5	109.28	109.24	104.99	108.98	109.01	C ^{•••} O	3 ^{•••} 5	2.98	2.92	3.01	3.80	3.75
CCO	2-1-5	109.99	105.70	110.16	107.94	103.64							
1,2-Ethanediol ^c													
		g ⁻ g ⁺ t	g ⁺ g ⁺ g ⁻	g ⁻ g ⁺ g ⁻	g ⁺ tg ⁻	ttt		g ⁻ g ⁺ t	g ⁺ g ⁺ g ⁻	g ⁻ g ⁺ g ⁻	g ⁺ tg ⁻	ttt	
FSE		-1.44	-1.24	-0.25	1.45	1.64	HOC	2-1-9	107.86	109.85	108.86	109.90	109.96
OC	1-2	1.396	1.408	1.404	1.400	1.402	OCH	3-4-10	110.46	108.07	108.86	109.90	109.98
CC	2-3	1.513	1.517	1.516	1.522	1.513	HOCC	3-2-1-9	-53.9	76.1	-81.3	73.7	180.0
CO	3-4	1.406	1.395	1.404	1.400	1.402	OCOC	1-2-3-4	60.8	57.8	57.3	180.0	180.0
HO	1-9	0.945	0.943	0.943	0.943	0.942	CCOH	2-3-4-10	-169.8	-45.4	-81.3	-73.7	180.0
OH	4-10	0.942	0.945	0.943	0.943	0.942	O ^{•••} H	4 ^{•••} 9	2.37	3.28	2.69	3.96	4.27
OCC	1-2-3	111.38	110.64	111.13	111.64	107.31	O ^{•••} O	1 ^{•••} 4	2.78	2.82	2.84	3.65	3.56
CCO	2-3-4	106.88	111.22	111.13	111.64	107.31	H ^{•••} O	1 ^{•••} 10	3.58	2.36	2.69	3.96	4.27
1,2-Dimethoxyethane ^c													
		ttt	g ⁻ g ⁺ t	tg ⁺ t	g ⁺ tt	g ⁺ g ⁺ g ⁻		ttt	g ⁻ g ⁺ t	tg ⁺ t	g ⁺ tt	g ⁺ g ⁺ g ⁻	
FSE		1.5	1.66	2	2.89	3.16	CCO	2-3-4	107.79	110.09	109.34	107.49	113.67
CO	1-9	1.393	1.399	1.392	1.395	1.394	COC	3-4-10	114.34	114.23	114.21	114.49	116.48
OC	1-2	1.395	1.395	1.393	1.398	1.401	COCC	3-2-1-9	180.0	-86.7	-175.4	90.1	84.8
CC	2-3	1.513	1.510	1.510	1.520	1.522	OCOC	1-2-3-4	180.0	73.6	72.1	179.3	72.6
CO	3-4	1.395	1.397	1.393	1.394	1.395	CCOC	2-3-4-10	180.0	-177.8	-175.4	-178.2	-81.7
OC	4-10	1.393	1.393	1.392	1.393	1.399	C9 ^{•••} O4	4 ^{•••} 9	4.69	3.13	4.12	4.35	4.02
COC	2-1-9	114.34	116.46	114.21	115.71	115.66	O1 ^{•••} O4	1 ^{•••} 4	3.56	2.99	2.88	3.60	3.06
OCC	1-2-3	107.70	113.68	109.34	111.40	114.30	O1 ^{•••} C10	1 ^{•••} 10	4.69	4.25	4.12	4.75	3.15

TABLE 13 (Continued)

2-Methoxyethanol ^c															
		tg ⁺ g ⁻	g ⁺ g ⁺ g ⁻	ttg ⁺	ttt	g ⁻ g ⁺ t	tg ⁺ t			tg ⁺ g ⁻	g ⁺ g ⁺ g ⁻	ttg ⁺	ttt	g ⁻ g ⁺ t	tg ⁺ t
FSE		-1.54	0.03	1.56	1.62	2.05	2.30	CCO	2-3-4	111.45	111.03	111.30	107.22	109.59	108.94
CO	1-9	1.394	1.397	1.393	1.392	1.399	1.391	COH	3-4-10	107.89	108.05	109.89	109.97	109.95	109.96
OC	1-2	1.399	1.405	1.393	1.394	1.395	1.393	COCC	3-2-1-9	-175.8	88.7	-178.4	179.9	-87.6	-174.8
CC	2-3	1.514	1.518	1.518	1.513	1.515	1.510	OCCO	1-2-3-4	60.7	88.7	179.9	180.0	73.0	72.2
CO	3-4	1.396	1.397	1.401	1.402	1.404	1.400	CCOH	2-3-4-10	-53.8	-47.3	74.9	179.9	-173.3	-167.1
OH	4-10	0.945	0.945	0.943	0.942	0.942	0.942	C9...O4	4...9	4.06	3.79	4.75	4.69	3.12	4.11
COC	2-1-9	114.69	115.73	114.53	114.32	116.49	114.22	O1...O4	1...4	2.78	2.78	3.60	3.56	2.98	2.88
OCC	1-2-3	107.32	110.88	107.98	107.77	113.56	109.34	O1...H10	1...10	2.38	2.37	3.92	4.27	3.78	3.19
1,3-Propanediol ^c															
		g ⁺ g ⁻ g ⁺ g ⁺	g ⁻ g ⁺ g ⁻ t	g ⁺ g ⁺ g ⁺ g ⁻	tg ⁺ g ⁺ g ⁻	tg ⁺ g ⁺ t			g ⁺ g ⁻ g ⁺ g ⁺	g ⁻ g ⁺ g ⁻ t	g ⁺ g ⁺ g ⁺ g ⁻	tg ⁺ g ⁺ g ⁻	tg ⁺ g ⁺ t		
FSE		-2.68	-2.31	-1.14	-0.89	-0.28	COH	4-5-13	108.43	110.36	108.57	108.23	109.81		
OC	1-2	1.410	1.396	1.408	1.408	1.407	OCCC	1-2-3-4	59.0	-49.4	67.2	175.7	-172.3		
CC	2-3	1.525	1.528	1.535	1.520	1.519	CCCO	2-3-4-5	-68.7	73.9	46.8	48.8	64.6		
CC	3-4	1.527	1.520	1.528	1.528	1.519	HOCC	3-2-1-12	69.0	-58.2	49.2	49.0	64.6		
CO	4-5	1.398	1.410	1.401	1.403	1.407	CCOH	3-4-5-13	56.7	177.7	-77.1	-78.8	-172.3		
HO	1-12	0.944	0.945	0.943	0.942	0.942	O...H	5...12	3.09	2.75	3.84	3.67	4.17		
OH	5-13	0.945	0.942	0.944	0.943	0.942	O...O	1...5	2.86	2.83	3.12	3.14	3.58		
OCC	1-2-3	113.00	113.21	112.82	108.75	108.35	H...O	1...13	2.15	3.67	2.62	2.61	4.17		
CCC	2-3-4	113.81	113.83	112.74	112.98	113.30	C...O	1...4	3.00	3.14	2.81	2.87	2.95		
CCO	3-4-5	113.17	108.95	112.65	112.66	108.35	C...O	2...5	3.09	2.92	2.89	2.89	2.95		
HOC	2-1-12	109.55	108.48	109.97	109.94	109.81									
1,2-Propanediol															
		g ⁻ g ⁺ t(t)	g ⁻ g ⁺ t(g ⁻)	g ⁺ g ⁺ g ⁻ (t)			g ⁻ g ⁺ t(t)	g ⁻ g ⁺ t(g ⁻)	g ⁺ g ⁺ g ⁻ (t)						
FSE		-1.62	-1.66	-1.55	HOC	2-1-9	107.68	107.79	109.86						
OC	1-2	1.395	1.397	1.408	COH	3-4-10	110.35	110.41	108.27						
CC	2-3	1.519	1.521	1.522	HOCC	3-2-1-9	-52.8	-55.0	76.6						
CO	3-4	1.413	1.412	1.400	OCCC	1-2-3-4	58.9	60.1	55.7						
CC	3-7	1.521	1.522	1.518	CCOH	2-3-4-10	-167.4	-175.3	-43.1						
HO	1-9	0.945	0.945	0.943	CCCC	1-2-3-7	-179.5	-61.5	176.0						
OH	4-10	0.943	0.943	0.945	H...O	4...9	2.31	2.35	3.25						
OCC	1-2-3	111.51	111.92	110.76	O...O	1...4	2.74	2.76	2.78						
CCO	2-3-4	105.39	105.18	109.73	O...H	1...10	3.54	3.60	2.30						
CCC	2-3-7	112.64	112.97	112.49	C...O	1...7	3.76	2.98	3.76						

^a See Supporting Information for geometries of other conformers and Table A2 for conformer designations. ^b See Table A2 of Supporting Information for definitions of conformer labels. ^c See Supporting Information for geometries of other conformers.

mol higher than energies of the lowest energy gauche forms. The effect is larger if there are two oxygen atoms in the chain. The energy all trans 1,2-dimethoxyethane is 1.50 kcal/mol higher than the lowest energy gauche form. This effect carries over into conformers of 1,2-ethanediol, 1,3-propanediol, and 2-methoxyethanol, omitting from consideration the low-energy hydrogen-bonded conformers.

Many conformers of 1,3-propanediol show strong intramolecular hydrogen bonding. The lowest energy conformer, g⁻g⁺g⁺g⁺, (FSE -2.88) is lower in energy than the all trans conformer (FSE 2.32) by 5.2 kcal/mol. The highest energy conformer of those listed in the tables is the tg⁺g⁻t conformer (FSE 4.65), which has two oxygen atoms pointed toward each other with no intervening hydrogen-bonded hydrogen atom.

Several conformers of 1,2-ethanediol and 2-methoxyethanol also show effects of intramolecular hydrogen bonding. For 1,2-ethanediol the lowest energy conformer, g⁻g⁺t, (FSE -1.44) has a much lower energy than the all trans conformer (FSE +1.74). This conformer has the hydrogen attached to one oxygen atom pointing toward the second oxygen atom, serving as donor. The hydrogen atom on the donor oxygen atom is oriented away from the hydrogen atom of the hydrogen bond. For 2-methoxyethanol the lowest energy conformer is t OMg⁺g⁻ (FSE -1.63), and the all trans conformer, t OMt t (FSE +1.65), has a much higher energy.

α-Fucose (5-deoxygalactopyranose) in some conformations forms several intramolecular hydrogen bonds.⁴⁹ The lowest

energy conformer has two hydrogen-bonded pairs, but there is an additional hydrogen bond between oxygen atoms located on carbons 2 and 3. In effect there are three cooperating hydrogen bonds. However, the conformer listed as having nearly the same energy (g⁺g⁺g⁺g⁺) has interfering hydrogens at the hydrogen bond between oxygen atoms projecting from carbon atoms 3 and 4 and might have been expected instead to be a high-energy conformer. The related g⁺g⁺g⁺ conformer of 1,2-ethanediol is of high energy, 3.5 kcal/mol higher than the tg⁺g⁻t conformer, as reported in both this study and in the Truhlar study.⁴⁰

Calculations. Calculations were performed on a Cray-Y-MP/432 and on a Silicon Graphics Power Challenge computer at Florida State University using the Gaussian 90,⁵⁰ Gaussian 92,⁵¹ and Gaussian 94⁵² programs. A few calculations were performed on other university computers. Ab initio energies of many of the smaller molecules were computed with Gaussian 92 and Gaussian 94 on PC's. I gratefully acknowledge support by Florida State University through allocation of computer resources.

Supporting Information Available: The Supporting Information includes full tables including the identification code for each run, a complete set of figures, "arc" files and Alchemy "mol" files which give Cartesian coordinates of all structures. All information about molecules is cross referenced by the identification code of the run. Tables 5 and 9, ab initio energies, are included in the Supporting Information but are not in the article. Also to be found in the Supporting Information is a

description of the procedure used in assigning conformer labels such as the 9L label for the global minimum of 2-butanol. Conformers of the compounds in this study are summarized in tables, and figures show the arbitrary atom numbering schemes. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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