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Thermochemical Values of Oxygen-Containing Compounds from ab Initio Calculations: 2. High Accuracy Enthalpies of Formation of Alcohols and Ethers

DeLos F. DeTar

Department of Chemistry, Florida State University, Tallahassee, Florida 32306

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The objective of this series of studies is to develop procedures for calculating high quality enthalpies of formation and differences of enthalpies of typical organic compounds. Can this be achieved using basis set/electron correlation methods (BSECMs) of modest size so that the calculations are routinely applicable to molecules having 12 or more heavy atoms? The answer is a qualified "yes." The procedure I have explored is based on conversion of ab initio energies into formal steric enthalpy (FSE) values. FSE is the difference of the energy of a target molecule and $\sum n_i d_i$, the sum of the energies of its constituent structural groups as defined by a set of standard molecules. FSE values are group isodesmic because the same numbers of each structural group appear in both the target molecule and in the summation. To a considerable extent, the isodesmic calculation cancels out errors due to limitations of BSECMs. FSE values can be converted to estimates of gas phase ΔH_f° values by a method related to the group increment method developed extensively by Benson and others. Energies derived with a number of BSECMs were explored. Of those evaluated, the most successful were MP2/6-31+G(d,p)//6-31G(d,p) and MP2/6-311+G(2df,2p)//6-31G(d,p). For 21 alcohols and ethers having a range of ring strain and steric congestion, the former gave differences between calculated ΔH_f°(g,298) values and experimental values with a standard deviation of 0.56 kcal/mol and with a maximum deviation of 1.35, whereas the latter gave a standard deviation of 0.62 with a maximum deviation of 1.74. These numbers can be compared with an estimated standard deviation of the experimental ΔH_f° data of 0.44 kcal/mol and a maximum deviation of 1.22 for the same data set. Energies derived with the popular density functional B3LYP/6-31G(d,p) gave poorer results. The standard deviation was 1.25 and maximum deviation was 2.49. An important use of FSEs is in comparing enthalpies. While comparison of ab initio energies is restricted to conformers of the same molecule, comparison of FSEs gives a valid estimate of the difference of enthalpies of isomers as well. The difference of FSEs of unrelated molecules provides an estimate of the difference of strain enthalpies, and this may be converted to an estimate of the difference of total enthalpies by correcting for the bond enthalpy terms as described in the text. These comparisons pertain to hypothetical compounds that consist solely of the molecules being compared.

Introduction

The objective of making ab initio calculation of enthalpies may be to obtain ΔH_f° values or to obtain enthalpy differences. Both types of calculation are the subject of the present study.

For any two conformers of the same molecule, the difference of their ab initio energies represents an estimate of the difference of enthalpies of formation of the two hypothetically pure substances, each consisting entirely of a single conformer. This expectation is valid insofar as the conformers have the same zero point energies and heat contents, the $\Delta H_f^\circ(0-298)$ values. The present study focuses on calculating formal steric enthalpies, FSEs. The particular advantage of working with FSE values is that comparisons are not limited just to conformers of a single molecule but may be extended to estimate differences of enthalpies of isomers and homologues, and even of unrelated molecules.

In principle, all basis set/electron correlation methods (BSECMs) should give the identical FSE value for a given conformer, but what is found in practice is a range of values. Examination of trends provides useful information about the characteristics and the reliability of the several BSECMs for estimating enthalpies.

Formal steric enthalpies can be converted to ΔH_f° values, and comparisons of calculated and experimental ΔH_f° values provide a further basis for judging the reliability of the energies obtained with a given BSECM.

The focus of the present study is to compare the performances of a set of BSECMs in calculating absolute and relative enthalpies of alcohols and ethers. The study is limited to alcohols and ethers having no more than one oxygen atom on any given carbon atom.

In a previous study (Part 1),[1] I reported calculation of ΔH_f° values for 14 alcohols and ethers from ab initio energies using the formal steric enthalpy (FSE) procedure. The compounds in the set included cyclic ethers and compounds having steric crowding. Of the several basis set/electron correlation methods (BSECMs) used in that study, MP2/6-31G(d,p)//6-31G(d,p) gave the best results: 0.55 kcal/mol standard deviation and 1.01 maximum difference.

In the present study, seven more alcohols and ethers have been included. The corresponding standard deviation obtained with MP2/6-31G(d,p)//6-31G(d,p) is 0.79. This higher standard deviation arises at least in part from the questionable reliability of some of the experimental enthalpy data for the additional compounds. The present study also includes results obtained with additional BSECMs. These results will be presented below.

It should be noted at this point that calculations for compounds having two or three oxygen atoms attached to a single

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TABLE 1: Structural Groups and Corresponding Reference Standard Molecules

reference standard molecules	conformer	structural group represented	assigned FSE value	*c*-increment of structural group	SM of standard compound
butane	anti,C_{2h}	$C(C)(H)_3$	0.00	−10.033	0.27
octane	anti,C_{2h}	$C(C)_2(H)_2$	0.00	−5.147	1.12
2-methylbutane		$C(C)_3(H)$	0.70	−2.258	0.09
2,2-dimethylbutane		$C(C)_4$	1.40	−0.217	0.00
ethyl methyl ether	anti,C_s	$C(O)(H)_3$	0.00	−6.819	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	0.25
2-methyl-2-butanol	3L	$C(C)_3(O)$	0.90	−3.870	0.09
1-propanol	g+g+	$O(C)(H)$	0.00	−40.770	0.12
diethyl ether	anti,C_{2v}	$O(C)_2$	0.00	−30.250	0.47

carbon atom, namely acetals and their derivatives and orthoacids and their derivatives, have given some ΔH_f° values that differ from experiment by several kcal/mol. The significance of these larger differences is under investigation. One difficulty with evaluating the reliability of calculated enthalpies of these molecules is the paucity of reliable experimental data.

Background. Reviews of methods for the calculation of thermodynamic properties from ab initio energies can be found in the publication edited by Irikura and Frurip.[2] Many applications of the G2, G2(MP2), G3,[3] and related procedures and of other procedures that aim for high accuracy have been reported recently.[4−14] The G2 (Gaussian 2) procedure[4] gives accuracies of 1 to 2 kcal/mol; the CBS-Q procedure[13,15,16] gives accuracies of the order of 1 kcal/mol. 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.[17] Calculations using these methods are limited to relatively small molecules.

Virtually all calculations of ΔH_f° from ab initio energies have utilized conversion of the ab initio energy to the energy of atomization of the molecule at 0 K.[5,17−19] The energy of atomization is converted to ΔH_f°(0 K) and then to ΔH_f° (*g*,298). The zero point energy and the heat content (H(298) − H(0)) are usually derived from the partition function using the rigid-rotor/harmonic-oscillator approximation with scaled calculated frequencies. Martin summarizes methods for calculating ΔH_f° from atomization energies,[17] and an especially clear description of atomization methods is that of Nicolaides et al.[5] This direct method also places serious demands on the quality of the estimated zero point energies.

Alternative methods of converting ab initio energies to ΔH_f° are based on use of isodesmic reactions.[10,12,20−23] Bond increment methods such as those of Ibrahim and Schleyer[20] or the BAC (bond adaptivity correction) method of Melius[21] require smaller calibration sets than do group increment methods, but the accuracy of the computed enthalpies is at best a few kcal/mol. A recent method has been reported by Cioslowski.[18] It uses atom equivalents with a defined set of corrections.

Mention should be made of the completely empirical group increment methods such as those developed extensively by Benson and co-workers.[24−29] These methods and variants have been used to provide accurate extrapolations of certain ΔH_f° data.[27,30] The weakness of the empirical methods lies in the requirement to apply special steric corrections for gauche effects and for ring strain that are not always well determined.

Modifications of the group increment methods have been used by Wiberg[31,32] and Allinger[33−35] to convert ab initio energies to estimates of ΔH_f°. These published methods can be described as ad hoc in that the members of the calibration sets tend to coincide with the set of compounds whose enthalpies are being calculated. These methods are inconvenient to use because calibration for each BSECM requires calculation of ab initio energies of the total set of molecules.

The FSE procedure, described below and reported previously, has similarities to the group increment methods, but it is more readily calibrated because it makes use of a minimal set of standard molecules (cf Table 1). FSE values have also been estimated from the steric energies of molecular mechanics calculations.[36,37]

An important advantage of using the energy of atomization procedure for calculating ΔH_f° is that no experimental data are needed, except for energies of atomization of elements, and the procedure is applicable to all types of molecules. The principle disadvantages are that very large basis sets are needed and that it has proved difficult to calculate zero point energies (ZPEs) to the requisite accuracy. The advantage of group increment methods is that they are applicable to relatively large molecules within limited sets. Because they depend on differences of energies, they are insensitive to certain types of errors in ZPEs.

Calculation of Formal Steric Enthalpies. Calculation of FSE values and of ΔH_f° values from FSE values is accomplished by use of eqs 1−3. A more extensive treatment may be found in previous references.[1,36−42]

$$\mathrm{FSE} = 627.5\left(E_{\mathrm{AI}} - \sum n_i d_i\right) \tag{1a}$$

$$\mathrm{FSE} = 627.5\left(E_{\mathrm{AI}} + \mathrm{ZPE} + \text{heat content} - \sum n_i d_i'\right) \tag{1b}$$

$$\Delta H_f^\circ = \sum n_i c_i + \mathrm{FSE}_0 + \mathrm{SM} \tag{2}$$

$$\mathrm{SM} = \sum(\text{over conformers}) f_j(e_j - e_o) \tag{3}$$

In eqs 1a and 1b, FSE is the difference between the energy E_{AI} of the target molecule as calculated with a given BSECM and $\sum n_i d_i$, the sum of the energies of the constituent structural groups as defined by energies of standard molecules calculated with the same BSECM. The d_i may be referred to as conversion terms. The calculation of FSE is group isodesmic. The factor 627.5 converts units of hartrees to kcal/mol.

In eq 1b, the sum E_{AI} + ZPE + heat content ($H_{298} - H_0$) is the “raw” ab initio energy explicitly corrected for zero point energy and heat content and the d_i' conversion terms are for use with corrected ab initio energies. In eq 1a, the ZPE and heat content are subsumed into the d_i conversion terms. The term n_i specifies the number of occurrences of the *i*th structural group in the target molecule. Table 2 lists d_i values and Table 3 lists d_i' values for the several BSECMs used in the present study.

Calculation of d_i Conversion Terms. For each BSECM used the d_i terms are calculated from the ab initio energies and the assigned FSE values of the standard molecules listed in Table 1. These values are substituted into eq 1a or 1b to get sets of equations defining the d_i terms. It should be noted that the d_i

TABLE 2: d_i-Conversion Terms for Raw ab InItio Energies

	$C(H)_3(C)$	$C(H)_2(C)_2$	$C(H)(C)_3$	$C(C)_4$	$C(H)_3(O)$	$C(H)_2(C)(O)$	$C(H)(C)_2(O)$	$C(C)_3(O)$	$O(H)(C)$	$O(C)_2$
MP2	−39.771618	−39.182029	−38.595086	−38.009990	−39.766363	−39.182029	−38.599222	−38.017141	−75.615038	−75.018102
M_S	−39.772761	−39.183356	−38.596924	−38.012521	−39.767771	−39.183356	−38.601246	−38.019261	−75.623991	−75.025446
MAS	−39.808701	−39.217466	−38.629532	−38.043747	−39.803847	−39.217466	−38.633323	−38.049441	−75.702865	−75.101640
CBM	−39.831256	−39.238729	−38.649352	−38.061920	−39.826453	−39.238729	−38.653934	−38.068595	−75.735104	−75.132756
CBQ	−39.814040	−39.226323	−38.641455	−38.058917	−39.809821	−39.226323	−38.645948	−38.066366	−75.726484	−75.130092
B6D	−39.919462	−39.316519	−38.714087	−38.111169	−39.913965	−39.316519	−38.718993	−38.119916	−75.811133	−75.205140
MPM	−39.771654	−39.182073	−38.595270	−38.010276	−39.766387	−39.182073	−38.599286	−38.017297	−75.616024	−75.019041
M__	−39.773042	−39.183666	−38.597261	−38.012971	−39.768060	−39.183666	−38.601560	−38.019630	−75.624115	−75.025540
M_O	−39.772761	−39.183356	−38.596945	−38.012545	−39.767770	−39.183356	−38.601298	−38.019303	−75.623976	−75.025472
M32	−39.490614	−38.910374	−38.333589	−37.759397	−39.485861	−38.910374	−38.337177	−37.766786	−75.124343	−74.541679
B6P	−39.920935	−39.317358			−39.915563	−39.317358				−75.210235
CBO	−39.829808	−39.238694	−38.650673	−38.063698	−39.825513	−39.238694	−38.655151	−38.072629	−75.733365	−75.131622
63S	−39.614512	−39.034692	−38.454701	−37.874096	−39.609190	−39.034692	−38.460018	−37.882666	−75.426681	−74.846477
63D	−39.619256	−39.037720	−38.456060	−37.873797	−39.613798	−39.037720	−38.461461	−37.882561	−75.433339	−74.846624
6_S	−39.619527	−39.037937	−38.456301	−37.874098	−39.614157	−39.037937	−38.461844	−37.882586	−75.437832	−74.850369
6AS	−39.628925	−39.046628	−38.464130	−37.880928	−39.623532	−39.046628	−38.469676	−37.889486	−75.463929	−74.876578
321	−39.397129	−38.819103	−38.242701	−37.667115	−39.392048	−38.819103	−38.247140	−37.675113	−75.008756	−74.429269
6__	−39.619580	−39.037977	−38.456273	−37.873992	−39.614159	−39.037977	−38.461818	−37.882502	−75.437989	−74.850482
6_O	−39.619529	−39.037936	−38.456298	−37.874092	−39.614157	−39.037936	−38.461812	−37.882571	−75.437890	−74.850389
431	−39.558087	−38.977711	−38.397746			−38.977711				

TABLE 3: d'_i-Conversion Terms for Ab InItio Energies Corrected for ZPE and Heat Content

	$C(H)_3(C)$	$C(H)_2(C)_2$	$C(H)(C)_3$	$C(C)_4$	$C(H)_3(O)$	$C(H)_2(C)(O)$	$C(H)(C)_2(O)$	$C(C)_3(O)$	$O(H)(C)$	$O(C)_2$
MP2	−39.733749	−39.153356	−38.575963	−37.999478	−39.728299	−39.153356	−38.580434	−38.008334	−75.599129	−75.011967
M_S	−39.734892	−39.154682	−38.577802	−38.002010	−39.729706	−39.154682	−38.582457	−38.010453	−75.608084	−75.019313
MAS	−39.770833	−39.188793	−38.610406	−38.033231	−39.765784	−39.188793	−38.614534	−38.040632	−75.686955	−75.095503
CBM	−39.829204	−39.237355	−38.648754	−37.880841	−39.824333	−39.237355	−38.653241	−38.068680	−75.733418	−75.131704
CBQ	−39.811989	−39.224948	−38.640855	−38.059078	−39.807701	−39.224948	−38.645253	−38.066448	−75.724799	−75.129040
B6D	−39.881594	−39.287845	−38.694962	−38.100654	−39.875901	−39.287845	−38.700203	−38.111106	−75.795225	−75.199005
MPM	−39.733785	−39.153399	−38.576148	−37.999765	−39.728322	−39.153399	−38.580497	−38.008489	−75.600117	−75.012908
M__	−39.735173	−39.154993	−38.578138	−38.002459	−39.729996	−39.154993	−38.582772	−38.010823	−75.608206	−75.019405
M_O	−39.734892	−39.154682	−38.577823	−38.002034	−39.729705	−39.154682	−38.582509	−38.010495	−75.608069	−75.019339
M32	−39.452359	−38.881498	−38.314457	−37.750233	−39.447559	−38.881498	−38.318365	−37.758086	−75.109226	−74.535909
B6P	−39.883066	−39.288685			−39.877499	−39.288685				−75.204100
CBO	−39.827757	−39.237319	−38.650073	−37.882616	−39.823393	−39.237319	−38.654456	−38.072711	−75.731680	−75.130570
63S	−39.576388	−39.005860	−38.435514	−37.864795	−39.570696	−39.005860	−38.441326	−37.874210	−75.411345	−74.841186
63D	−39.581387	−39.009046	−38.436938	−37.863286	−39.575733	−39.009046	−38.442672	−37.873753	−75.417432	−74.840491
6_S	−39.581658	−39.009263	−38.437179	−37.863587	−39.576092	−39.009263	−38.443055	−37.873778	−75.421925	−74.844236
6AS	−39.591056	−39.017955	−38.445007	−37.870416	−39.585468	−39.017955	−38.450888	−37.880679	−75.448020	−74.870443
321	−39.358875	−38.790227	−38.223566	−37.657947	−39.353747	−38.790227	−38.228327	−37.666411	−74.993638	−74.423497
6__	−39.581711	−39.009304	−38.437150	−37.863480	−39.576095	−39.009304	−38.443030	−37.873695	−75.422080	−74.844347
6_O	−39.581661	−39.009262	−38.437173	−37.863577	−39.576093	−39.009262	−38.443022	−37.873761	−75.421982	−74.844254
431	−39.558087	−38.977711	−38.397746			−38.977711				

term for every $d[C(C)(H)_2X]$ is to be set equal to $d[C(H)_2(C)_2]$. Because there is only one molecule per d_i term, it is possible to obtain the d_i terms by a simple stepwise process.

Calculation of ΔH_f°. The FSE_o value for the conformer that has the lowest energy, the global minimum, is combined with the formal bond enthalpy term, $\sum n_i c_i$ and with SM as shown in eq 2 to give a calculated estimated of ΔH_f° for the target *compound*. The formal bond enthalpy is the ΔH_f° of a hypothetical "strain-free" compound consisting of a single conformer and containing the same structural groups as the target compound. The c_i values of the structural groups for alcohols and ethers are listed in Table 1. Their derivation is described elsewhere.[1,38,40]

SM is a statistical mechanical correction for the energies contributed by conformers other than the global minimum. It is defined by eq 3 in terms of a summation over j of terms consisting of the Boltzmann fraction of conformer j and the difference in energy of conformer j and the energy of the global minimum.

ΔH_f° Values of Alcohols and Ethers. Table 4(a,b) summarizes a selection of the results of the calculation of ΔH_f° values for 21 alcohols and ethers by use of several BSECMs, both with and without explicit treatment of zero point energy (ZPE) and heat content. Results are presented as the experimental $\Delta H_f^\circ(g,298)$ minus the calculated ΔH_f°. Calculations of ΔH_f° for Table 4 were derived by the FSE procedure. The single exception is that CBS-Q (CBQ) energies were processed by both the heat of atomization procedure (entries in column 6) and by the FSE procedure (entries in column 11). The complete version of Table 4(a,b) is provided as Table 1S in the Supporting Information. Table 1S contains data obtained with additional BSECMS. The BSECM abbreviations at the heads of columns are summarized in Table 5; a terminal "Z" signifies that the ZPE and heat content values have been treated explicitly using eq 1b to calculate FSE. For entries without the terminal "Z" ZPE and heat content are included implicitly through use of eq 1a to calculate FSE.

Calculated ΔH_f° values are also presented at the bottom of Table 4 (a,b) for 2-methoxyethanol and 1,2-dimethoxyethane, but no experimental data are available for these two compounds.

The results are summarized by two sets of statistics. The upper set is based on values for all 21 alcohols and ethers. The lower set is for 19 alcohols and ethers, omitting data for 1,3-propanediol and cyclohexanol. Conflicting experimental ΔH_f° values are reported for all three of the glycols, and all calculated ΔH_f° values for cyclohexanol differ appreciably from the reported experimental value.

For the 21 compounds, the standard deviations are: experimental data 0.45, M_SZ 0.57, MASZ 0.62, MP2Z 0.79 kcal/mol. If the data for 1,3-propanediol and cyclohexanol are

TABLE 4: Experimental $\Delta H_f^\circ - \Delta H_f^\circ$ Calculated by FSE Procedure (except for CBS-Q by atomization; kcal/mol)

Table 4(a)

compound	conformer	exp ΔH_f°	ref	error of exp ΔH_f°	CBQ atomiz.	M_SZ	MASZ	MP2Z	CB4	CBQ FSE	B6DZ	MPMZ
methanol	Cs	−48.16	43	0.07	0.16	−0.10	−0.05	−0.71	0.48	0.67	−1.24	−0.78
oxirane		−12.57	43	0.14	0.22	0.38	0.24	0.08	1.90	−0.66	1.44	0.47
ethanol	Cs	−56.21	43	0.10	−0.20	0.06	0.05	−0.62	0.46	0.56	−0.82	−0.68
dimethyl ether		−44.00	43	0.12	0.43	−0.09	−0.14	−0.10	−0.10	−0.10	−0.18	
1,2-ethanediol	g−g+t	−94.26	45	0.67	−0.40	−0.55	−0.84	−1.14	−0.61	−0.68	−1.31	
oxetane	C2	−19.24	43	0.14	−0.28	−0.75	−1.00	−0.67	−0.07	−1.49	2.24	−0.53
methyloxirane		−22.63	43	0.14	−0.08	−0.37	−0.54	−0.23	1.27	−1.60		
2-propanol	g+OH	−65.20	43	0.12	−0.24	−0.22	−0.30	−0.47	−0.03	−0.22	−0.32	−0.52
1,2-propanediol	t g+g-(t)	−102.72	45	0.98	0.68	−0.15	−0.41	−0.48	−0.19	−0.42	−0.32	
1,3-propanediol	g+g+g−g+	−97.61	44	1.22	1.22	1.20	0.81	1.76	0.37	0.52	2.09	
tetrahydrofuran	C2	−44.02	43	0.19	−0.75	0.08	−0.22	0.17	0.02	−2.35	1.38	0.20
1,4-dioxane	chair	−75.48	43	0.19	1.04	0.54	0.20	0.92	0.54	−1.93	2.10	0.98
methyl 1-propyl ether	g+t (COCC)	−56.93	43	0.17	0.24	0.12	0.11	0.41	−0.18	−0.33	0.24	
2-methyl-2-propanol		−74.69	43	0.19	0.25	−0.27	−0.32	−0.47	0.13	−0.55	−0.04	−0.56
methyl 2-propyl ether	g HCOC	−60.23	43	0.24	−0.07	−1.00	−0.60	−0.25	−0.60	−0.83	−0.35	−0.19
tetrahydropyran	chair	−53.40	43	0.24	−0.33	0.38	0.33	0.94	0.12	−2.49	1.59	0.99
3,3-dimethyloxetane		−35.42	43	0.41	0.06	0.11	−0.59	0.32		−1.52		
cyclopentanol		−57.98	43	0.41	−0.09	0.54	0.59	0.87		−2.12		
tert-butyl methyl ether		−67.76	43	0.26	0.77	−0.22	−0.25	−0.19	−0.12	−0.75	−0.49	−0.17
cyclohexanol	eq g	−68.40	43	0.50	1.34	1.35	1.74	1.81	1.34	−1.32		
di-*tert*-butyl ether		−86.52	43	0.29	0.00	0.37	0.52	0.40	−0.17	0.00	−1.04	
statistics, all values: number of values				21	20	21	21	21	19	20	17	11
average				0.32	0.20	0.07	−0.03	0.11	0.24	−0.88	0.29	−0.07
standard deviation				0.45	0.56	0.57	0.62	0.79	0.65	0.95	1.24	0.64
mean absolute deviation				0.32	0.44	0.42	0.47	0.62	0.46	1.06	1.01	0.55
max absolute deviation				1.22	1.34	1.35	1.74	1.81	1.90	2.49	2.24	0.99
statistics omitting values for 1,3-propanediol and cyclohexanol:												
average				0.27	0.08	−0.06	−0.17	−0.06	0.17	−0.93	0.18	−0.07
standard deviation				0.35	0.45	0.42	0.44	0.59	0.63	0.94	1.19	0.64
mean absolute deviation				0.27	0.35	0.33	0.38	0.50	0.41	1.07	0.94	0.55
Max Absolute Deviation				0.98	1.04	1.00	1.00	1.14	1.90	2.49	2.24	0.99
ΔH°_f values:												
2-methoxyethanol	OMg+g-OM	0.00		0.00	−90.11	−89.35	−89.05	−89.32	−88.90	−90.11	−89.22	
1,2-dimethoxyethane	t OMt t OM	0.00		0.00	−83.76	−82.28	−82.26	−82.64	−82.20	−83.76	−82.82	

Table 4(b)

compound	MP2	MPM	M_S	M__	MAS	B6D	63SZ	63DZ	6_SZ	6__Z	6ASZ
methanol	−0.75	−0.82	−0.14	−0.16	−0.09	−1.28	−0.91	−0.80	−0.31	−0.33	−0.14
oxirane	−2.40	−2.01	−2.10	−2.22	−2.23	−1.04		0.32	0.54	0.53	1.32
ethanol	−0.65	−0.71	0.03	0.01	0.02	−0.85	−0.44	−0.35	0.19	0.16	0.22
dimethyl ether	−0.10		−0.09	−0.10	−0.14	−0.18	−0.17	−0.18	−0.19	−0.20	−0.18
1,2-ethanediol	−1.11		−0.52	−0.54	−0.81	−1.28		−0.80	−0.32	−0.38	−0.62
oxetane	−2.56	−2.42	−2.63	−2.80	−2.89	0.35	2.27	2.63	2.78	2.79	2.83
methyloxirane	−2.42		−2.57		−2.74			0.79	0.81		1.62
2-propanol	−0.49	−0.53	−0.24	−0.25	−0.31	−0.34	−0.33	−0.25	−0.02	−0.02	0.01
1,2-propanediol	−0.41		−0.08	−0.09	−0.34	−0.25		−0.02	0.27	0.24	−0.05
1,3-propanediol	1.96		1.40	1.35	1.01	2.29	0.82	1.12	0.84	0.78	0.31
tetrahydrofuran	−1.25	−1.22	−1.34	−1.53	−1.64	−0.04	2.15	2.73	2.78	2.75	2.69
1,4-dioxane	−0.35	−0.29	−0.72	−1.00	−1.07	0.82	2.19	2.75	2.54	2.44	2.22
methyl 1-propyl ether	0.45		0.16		0.15	0.28	0.37	0.26	0.03		−0.06
2-methyl-2-propanol	−0.57	−0.65	−0.26	−0.29	−0.42	−0.14	0.39	0.45	0.68	0.66	0.81
methyl 2-propyl ether	−0.19	−0.14	−0.53	−0.56	−0.56	−0.31	−0.78	−0.75	−1.40	−1.39	−1.03
tetrahydropyran	−0.28	−0.24	−0.84	−1.10	−0.89	0.37		2.49	2.33	2.27	2.15
3,3-dimethyloxetane	−2.46		−2.66		−3.37			5.63	5.82		6.12
cyclopentanol	−0.50		−0.84		−0.78			3.13	3.23		3.14
tert-butyl methyl ether	−0.14	−0.12	−0.17	−0.20	−0.20	−0.44	−0.68	−0.67	−0.73	−0.72	−0.80
cyclohexanol	0.56		0.10		0.49			3.62	3.78		3.79
di-*tert*-butyl ether	0.55		0.52		0.67	−0.88	−1.98	−2.03	−2.36		−2.41
number	21	11	21	15	21	17	13	21	21	15	21
average	−0.62	−0.83	−0.64	−0.63	−0.77	−0.17	0.22	0.96	1.01	0.64	1.04
standard deviation	1.13	0.76	1.07	1.00	1.19	0.87	1.32	1.90	1.93	1.32	1.96
mean absolute deviation	0.96	0.83	0.85	0.81	0.99	0.66	1.04	1.51	1.52	1.04	1.55
max absolute deviation	2.56	2.42	2.66	2.80	3.37	2.29	2.27	5.63	5.82	2.79	6.12
statistics omitting values for 1,3-propanediol and cyclohexanol											
average	−0.82	−0.83	−0.79	−0.77	−0.93	−0.33	0.17	0.81	0.88	0.63	0.94
standard deviation	0.97	0.76	1.00	0.87	1.13	0.62	1.37	1.90	1.93	1.37	1.95
mean absolute deviation	0.93	0.83	0.87	0.78	1.02	0.55	1.05	1.42	1.44	1.06	1.50
max absolute deviation	2.56	2.42	2.66	2.80	3.37	1.28	2.27	5.63	5.82	2.79	6.12
2-methoxyethanol	−89.41		−89.44	−89.41	−89.13	−89.31		−89.43	−89.47	−89.43	−89.13
1,2-dimethoxyethane	−82.67		−82.31	−82.32	−82.28	−82.84		−83.86	−83.60	−83.60	−83.29

[a] See Table 5 for abbreviations of BSECMs.

TABLE 5: Abbreviations for Basis Set/Electron Correlation Methods

321	3-21G
M32	MP2/3-21G//3-21G
431	4-31G
63S	6-31G(d)//6-31G(d)
63D	6-31G(d,p)//6-31G(d,p)
MP2	MP2/6-31G(d,p)//6-31G(d,p)
MPM	MP2/6-31G(d,p)//MP2/6-31G(d,p)
6_S	6-31+G(d,p)//6-31G(d,p)
6__	6-31++G(d,p)//6-31G(d,p)
M__	MP2/6-31++G(d,p)//6-31G(d,p)
M_S	MP2/6-31+G(d,p)//6-31G(d,p)
6_O	6-31+G(d,p)//6-31+G(d,p)
M_O	MP2/6-31+G(d,p)//6-31+G(d,p)
6AS	6-311+G(2df,2p)//6-31G(d,p)
MAS	MP2/6-311+G(2df,2p)//6-31G(d,p)
B6D	B3LYP/6-31G(d,p)//B3LYP/6-31G(d,p)
B6P	B3LYP/6-31+G(d,p)//B3LYP/6-31G(d,p)
CB4	CBS-4M
CBQ	CBS-Q
G2	G2
G2M	G2M

omitted, the corresponding standard deviations are: experimental 0.35, M_SZ 0.42, MAS 0.44, MP2 0.59. The ratio of the variances of the calculated enthalpies to the variances of the experimental data are little changed by omission of values of the two compounds. The statistics indicate that for simple alcohols and ethers, the BSECMs MP2/6-31+G(d,p)//6-31G(d,p) (M_SZ) and MP2/6-311+G(2df,2p)//6-31G(d,p) (MASZ) give calculated ΔH_f° values by the FSE procedure that agree with experimental values, with standard deviations of about 0.5 kcal/mol.

Other BSECMs give somewhat poorer agreement between calculated and experimental ΔH_f° values. For example, the standard deviations of ΔH_f° values derived from energies obtained with the density functional B3LYP/6-31G(d,p) (B6DZ) are two times larger than those obtained with the faster MP2/6-31+G(d,p)/6-31G(d,p) BSECM.

From the results shown in Table 4 and 1S, we reach the following conclusions: (1) Electron correlation has to be used, at least at the MP2 level. RHF energies give poorer estimates of ΔH_f°. (2) The basis set must include polarization terms, and core electrons must be treated adequately. MP2/3-21G gives poor results (Table 1S). MP2/6-31+G(d,p) is better than MP2/6-31G(d,p), so we may conclude that diffuse orbitals are important. But MP2/6-31++G(d,p) is not much better than MP2/6-31+G(d,p), which suggests that having diffuse functions on hydrogen may not be important. Adding extra polarization is only slightly better, that is, MP2/6-311+G(2df,2p) is not much better than the simpler and more than 10 times faster MP2/6-31+G(d,p). (3) More complete basis sets are not necessarily better than simpler ones. It is curious that CBS-Q gives rather inferior results with the FSE procedure; its standard deviation is some two times larger than is obtained with MP2/6-31+G(d,p). And the simpler CBS-4M[15] is quite good in the FSE procedure. Evidently the 3-21G* geometries obtained with CBS-4M give as good FSE values as do the 6-31G(d,p) geometries. Also MP2/6-31G(d,p) geometries give about the same standard deviations as do 6-31G(d,p) geometries.

A recurring question in comparing calculated and experimental ΔH_f° values concerns the accuracy of the experimental data. Some are clearly of high quality, with standard deviations of 0.3 kcal/mol or possibly less, but others may be less accurate.

Except as noted, all experimental ΔH_f° values have been taken from the consistent set of estimates by Pedley et al.[43] The reported "uncertainties" of the ΔH_f° values have been treated as standard deviations. The overall average of the standard deviations for the set of 27 compounds, calculated as the square root of the average of the variances, is 0.43 kcal/mol. The ΔH_f° data for the diols cover a considerable range. The values shown in Table 4 are those of Knauth[44,45] rather than those of Pedley,[43] which differ by several kcal/mol. Comparisons of different approaches to deriving standard deviations of experimental ΔH_f° values have been presented elsewhere.[1]

Empirical Group Increment Procedures. Equation 4 is used to calculated ΔH_f° values by the empirical group increment procedure.

$$\Delta H_f^\circ = \sum n_i b_i + \text{steric correction} \qquad (4)$$

In Table 6 are presented values of ΔH_f° experimental minus ΔH_f° calculated by the Benson[46] and Cohen[29] increments for the alcohols and ethers treated in this study.

A problem with the empirical group increment procedure is that of deciding on the best values for the steric corrections used to account for steric crowding and for ring "strain." Examples of these corrections are be found in Table 6. Considering that some corrections are based on just two experimental enthalpies, as is true for oxetane, tetrahydrofuran, and 1,4-dioxane rings, as examples, the agreement between calculated and experimental data for strained compounds might be somewhat fortuitous. The Cohen correction for di-*tert*-butyl ether is based on di-*tert*-butyl ether alone. The correction for di-*tert*-butyl ether in the Benson column represents the value that is obtained by applying the gauche rules.

Cohen was unable to derive consistent steric correction values for use with compounds having internal hydrogen bonding as occurs in the glycols. The omission of corrections for glycols makes calculated ΔH_f° values too positive. An average value of the FSEs of the global minima of glycols as derived below may provide a usable value for the glycol correction.

Marsi et al.[47] have used CBS-4O energies to obtain group increments applicable to alkyl radicals.

The FSE procedure, in principle, completely solves the problem of obtaining the steric and ring corrections for any compound. The problem is reduced to that of getting consistent FSE values for a given set of compounds. FSE values can be estimated from molecular mechanics calculations or from ab initio energies, as is done in the present study.

Examples of Calculation of ΔH_f° with Eq 2. Table 6 provides the values of $\sum n_i c_i$ and of SM for the alcohols and ethers. Also reported are values of ZPE and of heat content. These several values together with the FSE values in Table 7 permit calculation of ΔH_f° for the entries in Table 4. The data can also be used with other BSECMs providing that the requisite d_i terms are calculated. The geometries of the global minimum conformers of 2-butanol and of 2-methyl-2-butanol have been reported previously.[1]

ZPE, SM, and Heat Content Issues. Zero point energy corrections can be a major source of uncertainty in calculated ΔH_f° values obtained from heats of atomization. Problems of getting accurate ZPE values have been examined by several authors.[5,17,48]

The reported ZPE and heat content ($H_{298} - H_0$) values in Table 6 were obtained from scaled values of frequencies calculated with the basis set 6-31G(d,p)//6-31G(d,p) using the rigid rotor-harmonic oscillator approximation. The scaling factor used was 0.90. The effect of using 0.91 as the scale factor was evaluated. There was almost no difference in the resultant FSE values; the largest differences were less than 0.04 kcal/mol. This result is a consequence of the isodesmic cancellation of errors.

TABLE 6: Terms for Equation 2 and ΔH_f° from Empirical Group Increments

					correction		ΔH_f° exp − calc	
compound	$\sum n_i c_i$	SM	ZPE	heat content	Benson	Cohen	Benson	Cohen
methanol	−47.59	0.00	31.14	2.69	0.00	0.00	−0.06	−0.26
oxirane	−40.54	0.00	34.68	2.61	26.90	27.00	−0.07	0.43
ethanol	−55.95	0.02	48.19	3.35	0.00	0.00	−0.01	−0.26
dimethyl ether	−43.89	0.00	48.32	3.38	0.00	0.00	−0.40	−0.22
1,2-ethanediol	−91.83	0.15	51.56	3.76	0.00	0.00	−2.26	−2.24
oxetane	−45.69	0.00	52.70	3.19	25.70	25.00	−0.61	0.76
methyloxirane	−49.77	0.00	51.81	3.39	26.90	27.00	−0.83	−0.60
2-propanol	−65.18	0.04	65.14	4.12	0.00	0.00	0.30	−0.22
1,2-propanediol	−101.06	0.35	68.42	4.64	0.00	0.00	−1.42	−1.67
1,3-propanediol	−96.98	0.29	69.27	4.38	0.00	0.00	−0.68	−0.59
tetrahydrofuran	−50.84	0.00	70.67	3.73	5.90	5.90	−0.66	0.08
1,4-dioxane	−81.09	0.00	74.29	4.03	3.30	3.50	0.02	1.02
methyl 1-propyl ether	−57.40	0.31	83.04	4.94	0.00	0.00	−0.30	−0.10
2-methyl-2-propanol	−74.74	0.03	81.88	4.93	0.00	0.00	0.41	−0.36
methyl 2-propyl ether	−61.48	0.03	82.49	5.03	0.80	0.80	−0.03	−0.17
tetrahydropyran	−55.98	0.00	88.81	4.16	0.50	1.10	0.29	0.50
3,3-dimethyloxetane	−60.83	0.00	86.30	4.88	25.70	25.00	−1.82	−0.44
cyclopentanol	−65.70	0.00	87.80	4.57	6.30	7.10	0.54	0.02
tert-butyl methyl ether	−71.04	0.00	99.30	5.86	1.60	1.60	1.24	0.85
cyclohexanol	−70.84	0.15	105.45	5.04	0.00	0.70	1.35	1.00
di-*tert*-butyl ether	−98.19	0.00	150.48	8.21	7.80	10.50	3.28	−0.38
number							21.00	21.00
average							−0.08	−0.14
standard deviation							1.17	0.80
mean absolute deviation							0.79	0.58
max absolute deviation							3.28	2.24
2-methoxyethanol	−88.13	0.35	68.91	4.65	0.00	0.00	−87.50	−87.90
1,2-dimethoxyethane	−84.43	0.29	85.84	5.79	0.00	0.00	−83.00	−83.78

The same compensation effect largely eliminates errors in the estimation of the heat content.

As for errors in SM values, these will be directly reflected as errors in calculated ΔH_f° values. The SM values listed in Table 6 were obtained consistently with the MP2/6-31G(d,p)//6-31G(d,p) energies of all low-energy conformers whenever available, or else with HF 6-31G(d,p)//6-31G(d,p) energies. These energies were processed by eq 3. Previously reported SM values were obtained with energies of conformers estimated by molecular mechanics;[49] a few differ by up to 0.3 kcal/mol.

Formal Steric Enthalpies: Consistency and Accuracy. Four types of BSECM energies were used for calculating formal steric enthalpies. These were (a) restricted Hartree−Fock (RHF) energies, (b) MP2 corrected RHF energies, (c) density functional energies, and (d) energies obtained using the complete basis set procedures CBS-Q, CBS-4M,[15] and CBS-4O of Petersson as implemented in the Gaussian G98W program.[15,50−52] Preliminary calculations with G2 and G2(MP2) showed large errors in calculated ΔH_f° together with very long computational times; these BSECMs were not pursued further. Note that a single-point MP2 calculation with a given basis set also yields the corresponding single-point RHF energy for the same basis set.

The FSE calculations used two variants for converting ab initio energies to FSE values: (1) raw ab initio energies were used to calculate the FSEs (eq 1a) or (2) the raw ab initio energies were first corrected for zero point energies and heat contents (eq 1b).

Table 2S in the Supporting Information includes all FSE values computed together with the ab initio energies on which they are based. Table 7 contains an abstract of the data of Table 2S, including complete data for the MP2-Z energies along with experimental FSE values[38−41] and certain averages. FSE values for calculations based on B3LYP/6-31G(d,p) and those based on complete basis set energies are reported in Table 2S but not in Table 7. Examples of results obtained with the latter two types of calculations are summarized in part in Table 4.

The FSE values in Table 7 are organized into three classes. The first class consists of acyclic alcohols and ethers. The second consists of cyclic alcohols and ethers. The third consists of cycloalkanes included for purposes of comparison.

The abbreviations used for the BSECMs in the headers of Table 2S and Table 7 are summarized in Table 5. A terminating Z signifies use of ab initio energies corrected for ZPE and heat content, and the absence of Z signifies that raw ab initio energies were used in calculations of FSEs.

Three types of comparisons of FSE values can be made. These are (1) evaluation of the error estimates based on deviations of individual FSE values from group averages, (2) comparisons among the average FSE values obtained with the different methods of calculation, and (3) comparisons of calculated FSE averages (and individual values) with the experimental FSEs. Experimental values of FSE have been derived in previous studies. They were obtained from experimental ΔH_f° values by use of eq 2.[38−41] Comparisons 1 and 3 will be considered in this section, whereas comparison 2 is considered in the next section.

In evaluating the FSE results, it is convenient to compute averages of selected groupings of FSEs. The groupings used are, respectively, AVGHF for FSEs based on raw HF energies, AVGM for FSEs based on raw MP2 energies, AVGHFZ for FSEs based on HF energies corrected for ZPE and heat content, and AVGMZ for FSEs based on MP2 energies corrected for ZPE and heat content. Table 7 reports values for these four types of averages for each conformer. The AVGMZ values are derived from the entries in columns 4 to 8 of Table 7. The other averages were obtained from data in Table 2S of the Supporting Information.

An overall estimate of the standard deviation of an FSE value within one of the four groupings can be calculated by averaging

TABLE 7: FSE Values of Conformers of Alcohols and Ethers

compound	conformer	FSE exp	M_SZ	MASZ	MP2Z	MPMZ	M__Z	AVGMZ[a]	AVGHFZ[b]	AVGM[c]	AVGHF[d]
methanol	C_s	−0.57	−0.47	−0.52	0.14	0.21	−0.45	−0.22	−0.18	−0.18	−0.14
ethanol	g		−0.19	−0.17	0.25	0.32	−0.18	0.01	−0.10	0.04	−0.06
dimethyl ether		−0.11	−0.02	0.03	−0.01		−0.01	−0.00	0.08	−0.00	0.08
1,2-ethanediol	g−g+t	−2.58	−2.03	−1.74	−1.44		−2.01	−1.81	−2.05	−1.84	−2.08
1,2-ethanediol	g+g+g-		−1.35	−1.24	−1.24		−1.37	−1.30	−1.24	−1.33	−1.27
1,2-ethanediol	g−g+g-		−0.78		−0.25		−0.79	−0.61	−0.82	−0.62	−0.83
1,2-ethanediol	g+t g-		1.17		1.45		1.15	1.26	0.36	1.32	0.42
1,2-ethanediol	t t t		0.82		1.64		0.85	1.10	−0.37	1.20	−0.27
1,2-ethanediol	g+t t		1.12		1.69		1.11	1.31	0.10	1.40	0.19
1,2-ethanediol	g+t g+		1.48		1.72		1.47	1.56	0.69	1.64	0.80
1,2-ethanediol	g+g+g+		1.43		1.79		1.42	1.55	1.16	1.72	1.33
1,2-ethanediol	t g+t		1.49		2.56		1.47	1.84	1.11	2.03	1.30
1,2-ethanediol	g+g+t		2.26		2.83		2.22	2.44	1.85	2.54	1.95
ethyl methyl ether	t C_s	0.30	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
ethyl methyl ether	g		1.48		1.41	1.36		1.42	1.75	1.38	1.71
1-propanol	g+g+OH	−0.09	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
1-propanol	g+t OH		−0.24	−0.22	0.19	0.20	−0.21	−0.06	−0.27	−0.05	−0.26
1-propanol	g+g-OH		0.17	0.11	0.33		0.21	0.21	0.22	0.21	0.23
1-propanol	t g+OH		0.06	0.02	0.37		0.05	0.13	−0.17	0.15	−0.15
1-propanol	t t OH		0.05	−0.03	0.60	0.64	0.04	0.26	−0.33	0.29	−0.30
2-propanol	g+OH	−0.06	0.16	0.24	0.41	0.46	0.18	0.29	0.01	0.30	0.02
2-propanol	t OH		0.58	0.56	0.55	0.59	0.58	0.57	0.33	0.60	0.35
1,2-propanediol	t g+g-(t)	−2.01	−1.86	−1.60	−1.53		−1.85	−1.71	−2.12	−1.78	−2.19
1,2-propanediol	g−g+t (t)		−1.69	−1.40	−1.66		−1.66	−1.60	−1.95	−1.67	−2.03
1,2-propanediol	g−g+t (g-)		−1.32	−1.35	−1.62		−1.31	−1.40	−1.41	−1.52	−1.53
1,2-propanediol	g+g+g-(t)		−1.35	−1.26	−1.55			−1.39	−1.45	−1.48	−1.54
1,2-propanediol	t g+g-(g-)		−0.81	−0.64	−0.90		−0.80	−0.79	−1.08	−0.89	−1.18
1,2-propanediol	g+g+g-(g-)		−0.23	−0.21	−0.79		−0.25	−0.37	−0.33	−0.49	−0.45
1,3-propanediol	g+g+g−g+	−0.92	−2.12	−1.73	−2.68		−2.08	−2.15	−1.68	−2.35	−1.88
1,3-propanediol	g−g+g−t		−2.53	−2.10	−2.31		−2.49	−2.36	−2.05	−2.51	−2.20
1,3-propanediol	g+g+g+g-		−0.83		−1.14			−0.99	−0.59	−1.17	−0.77
1,3-propanediol	t g+g+g-		−1.17		−0.89		−1.14	−1.07	−0.80	−1.24	−0.98
1,3-propanediol	t g+g+t		−1.18		−0.28		−1.14	−0.87	−1.28	−0.85	−1.27
1,3-propanediol	t g+g+g+		−0.51		−0.12		−0.54	−0.39	−0.60	−0.37	−0.59
1,3-propanediol	t g+t g+		−0.04		0.63			0.30	−0.39	0.33	−0.36
1,3-propanediol	t g+t t		−0.11		0.86		−0.11	0.21	−0.59	0.26	−0.55
1,3-propanediol	g+t g+g+		1.06		0.86		0.64	0.85	0.17	0.90	0.21
1,3-propanediol	g−g+t g-				1.66			1.66	1.29	1.71	1.35
1,3-propanediol	t t t g+				1.88			1.88	0.82	1.93	0.88
1,3-propanediol	t t t t				2.24			2.24	0.96	2.32	1.04
1,3-propanediol	t g+g−t				4.46			4.46	3.80	4.65	3.99
2-methoxyethanol	t OMg+g-OM		−1.57	−1.27	−1.54		−1.54	−1.48	−1.59	−1.57	−1.67
2-methoxyethanol	g+OMg+g-OH		0.24		0.03		0.27	0.18	0.56	0.08	0.46
2-methoxyethanol	t OMt g+OH		1.59		1.56		1.57	1.57	0.50	1.60	0.52
2-methoxyethanol	t OMt t OH		1.40		1.62		1.40	1.47	0.07	1.50	0.10
2-methoxyethanol	g-OMg+t OH		1.81		2.05		1.85	1.90	1.87	1.91	1.88
2-methoxyethanol	t OMg+t OH		1.88		2.30		1.84	2.01	1.47	2.13	1.59
2-methoxyethanol	t OMg+g+OH		2.42		2.38		2.37	2.39	1.97	2.52	2.11
2-methoxyethanol	g+OMt g-OH		2.97		2.88		2.98	2.94	2.25	2.93	2.25
2-methoxyethanol	g+OMt t OH		2.93		3.12		2.93	2.99	2.00	3.02	2.02
2-methoxyethanol	g+OMt g+OH		3.30		3.17		3.31	3.26	2.60	3.27	2.61
2-methoxyethanol	g+OMg+t OH		3.60		3.80		3.60	3.67	3.53	3.74	3.60
2-butanol	9L	−0.12	0.20	0.20	0.20	0.20	0.20	0.20	0.20	0.20	0.20
2-butanol	8L		0.68	0.55	0.25		0.64	0.53	0.59	0.53	0.59
2-butanol	7L		0.49	0.42	0.48		0.48	0.47	0.55	0.44	0.52
2-butanol	4L		1.13				1.08	1.11	1.36	1.00	1.25
2-butanol	1L		0.77		0.95		0.80	0.84	0.94	0.79	0.89
2-butanol	3L		0.92		1.08		0.96	0.99	1.00	0.95	0.96
2-butanol	6L		1.17		1.15		1.18	1.17	1.38	1.07	1.28
2-butanol	2L		1.24		1.12		1.23	1.20	1.29	1.16	1.25
2-butanol	5L		1.84		1.59		1.87	1.77	2.00	1.66	1.89
diethyl ether	t t C_{2v}	−0.08	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
diethyl ether	t g+		1.44		1.35	1.32	1.48	1.40	1.75	1.38	1.74
diethyl ether	g+g+ C_2		2.77		2.49		2.82	2.69	3.22	2.68	3.21
diethyl ether	g+g- TS				3.70			3.70	4.19	3.70	4.19
methyl 1-propyl ether	g+t (COCC)	0.16	0.04	0.05	−0.25			−0.05	0.08	−0.09	0.04
methyl 1-propyl ether	t t C_s		0.37	0.31	0.24			0.31	0.05	0.30	0.04
methyl 1-propyl ether	g+g+(COCC)		1.36		1.00			1.18	1.95	1.10	1.87
methyl 1-propyl ether	t g+(COCC)		1.77		1.60			1.69	1.79	1.63	1.74
2-methyl-2-propanol		0.02	0.29	0.34	0.49	0.58	0.32	0.40	−0.63	0.46	−0.59
methyl 2-propyl ether	g HCOC	1.22	2.21	1.82	1.46	1.41	2.24	1.83	2.36	1.61	2.10
methyl 2-propyl ether	t HCOC		3.98	3.94	3.65	3.58	3.99	3.83	4.66	3.68	4.51

TABLE 7: (Continued)

compound	conformer	FSE exp	M_SZ	MASZ	MP2Z	MPMZ	M__Z	AVGMZ[a]	AVGHFZ[b]	AVGM[c]	AVGHF[d]
1,2-dimethoxyethane	t OMt t OM		1.86	1.88	1.50		1.84	1.77	0.55	1.75	0.55
1,2-dimethoxyethane	g-OMg+t OM		2.02		1.66		2.04	1.91	2.22	1.87	2.19
1,2-dimethoxyethane	t OMg+t OM		2.21		2.00		2.14	2.12	1.83	2.18	1.86
1,2-dimethoxyethane	g+OMt t OM		2.06		2.70		1.99	2.25	1.85	2.46	2.00
1,2-dimethoxyethane	g+OMg+g-OM		3.77		3.16		3.81	3.58	4.37	3.54	4.33
1,2-dimethoxyethane	g+OMg+g+OM		4.08		3.43		4.07	3.86	4.59	3.71	4.44
1,2-dimethoxyethane	g+OMg+t OM		3.81		3.38		3.79	3.66	3.76	3.68	3.79
1,2-dimethoxyethane	g-OMg+g-OM		3.98		3.66		3.97	3.87	4.36	3.82	4.31
1,2-dimethoxyethane	g+OMt g-OM		4.92		4.39		4.95	4.75	4.27	4.67	4.18
1,2-dimethoxyethane	g+OMt g+OM		5.01		4.50		5.04	4.85	4.47	4.78	4.41
tert-butyl methyl ether		3.28	3.50	3.53	3.47	3.45	3.53	3.50	4.01	3.45	3.96
di-*tert*-butyl ether		11.67	11.30	11.15	11.27			11.24	13.94	11.09	13.79
di-*tert*-butyl ether	TS				12.70			12.70	14.96	12.55	14.81
oxirane		27.97	27.59	27.73	27.89	27.50	27.72	27.69	27.29	30.16	29.77
oxetane	C_2	26.45	27.20	27.45	27.12	26.98	27.36	27.22	23.69	29.11	25.58
methyloxirane		27.14	27.51	27.68	27.37			27.52	26.07	29.72	28.26
tetrahydrofuran	C_2	6.82	6.74	7.04	6.65	6.62	6.93	6.80	4.08	8.22	5.50
tetrahydrofuran	C_s TS		7.05	7.25	7.09			7.13	4.47	8.55	5.89
1,4-dioxane	chair	5.61	5.07	5.41	4.69	4.63	5.34	5.03	3.12	6.30	4.39
1,4-dioxane	twist boat		12.78	12.40	11.95			12.38	9.93	13.65	11.20
tetrahydropyran	chair	2.59	2.20	2.26	1.64	1.59	2.47	2.03	0.27	3.26	1.50
tetrahydropyran	twist boat		8.32	8.17	7.72			8.07	6.37	9.19	7.49
3,3-dimethyloxetane		25.41	25.30	26.00	25.09			25.46	19.55	28.24	22.33
3,3-dimethyloxetane	T.S		25.31	25.98	25.10			25.46	19.46	28.33	22.32
cyclopentanol		7.72	7.18	7.13	6.85			7.05	4.55	8.43	5.92
cyclohexanol	eq g	2.29	0.94	0.55	0.48			0.66	−1.44	1.91	−0.20
cyclohexanol	eq t		1.29	0.79	0.58			0.89	−1.17	2.13	0.08
cyclohexanol	ax t		1.25	0.94	0.22			0.80	−0.87	2.05	0.38
cyclohexanol	ax g		2.43	1.80	1.48			1.90	0.40	3.15	1.64
cyclohexanol	tw bt 60.60		7.41		6.96			7.19	5.49	8.43	6.73
cyclohexanol	tw bt 30.30		8.01		7.65			7.83	5.81	9.08	7.06
cyclobutane	C2v	26.96	26.84	27.33	26.78	26.54		26.87	23.69	28.88	25.70
cyclobutane	D_{4h} TS		29.18	29.44	29.06			29.23	24.70	31.24	26.71
cyclopentane		7.27	6.61	6.60	6.35			6.52	4.04	8.52	6.04
cyclohexane	chair	1.45	0.94	0.69	0.25			0.63	−1.15	1.85	0.08
cyclohexane	twist boat		7.64	7.20	7.05			7.30	5.78	8.39	6.88

[a] Average of M_SZ, MASZ, MP2Z, MPMZ, and M__Z. [b] Average of 6_SZ, 6ASZ, 63DZ, 6__Z. [c] Average of M_S, MAS, MP2, MPM, and M__. [d] Average of 6_S, 6AS, 63D, 6__.

variances for the several group averages listed in Table 7. The overall standard deviation of an FSE value derived from the two groupings of MP2 energies is 0.25 kcal/mol and that for an FSE value derived from the two RHF groupings of RHF energies is 0.19. These estimates have about 300 degrees of freedom. The standard deviation of a *difference* of two FSE values within the same grouping of FSE values is, therefore, 0.35 for FSEs based on MP2 BSECMs and 0.27 for FSEs based on HF energies. The standard deviation of the difference between FSEs derived from M_SZ energies and from MASZ energies is 0.18 kcal/mol. These are measures of attainable precision.

The calculated FSE for a conformer that is the global minimum should equal the experimental FSE for the conformer. Consideration of eq 2 shows that the difference between the experimental and the calculated FSE for the global minimum is equal to the difference between the experimental and the calculated ΔH_f° for the compound. The accuracy of the FSE estimates can therefore be evaluated in terms of the standard deviation of the corresponding ΔH_f° values as reported in Table 4 and 1S for each BSECM. For M_SZ and MASZ the standard deviation of an FSE value (or of a ΔH_f° value) is about 0.5 kcal/mol.

It should be noted that FSE values reported in Table 7 for the global minimum conformer of a standard molecule will be the same for all BSECMs.

Formal Steric Enthalpies: Trends Among Averages. The group averages are based on from 1 to 5 FSE values, generally 3 values. In general, the standard deviation of a difference of two averages is about 0.25 kcal/mol. For most of the acyclic alcohols and ethers, differences between all pairs of averages are within two standard deviations. Differences among averages for di-*tert*-butyl ether are outside of these limits. Several differences among averages for 1,2-ethanediol and for 1,2-dimethoxyethane are outside of the range, but for 2-methoxy1−1-ethanol and for conformers of 1,2- and 1,3-propanediol, most differences are within the range. The first four entries for 1,2-ethanediol are for conformers that have intramolecular hydrogen bonding.

For cyclic alcohols and ethers and for cycloalkanes, there are significant differences among averages for most of the conformers. In principle, calculation of FSEs of cyclic molecules requires use of corrected ab initio energies because implicit ZPE corrections in the d_i conversion terms used for raw ab initio energies are based on acyclic molecules and are therefore not appropriate for cyclic molecules. The differences in ZPE treatment can be seen by comparing pairwise the AVGMZ averages with the AVGM averages or the AVGHFZ averages with the AVGHF averages.

For cyclic compounds, there tend to be significant differences between FSEs based on RHF energies and those based on MP2 energies.

Interpretations of FSE Values. An FSE value represents a rigorously defined estimate of “strain.” It is, therefore, valid to compare FSE values among molecules that are not conformers of a single molecule. Four cases can be treated.

(1) The set consists of conformers of a single compound; all members of the set are constructed of the same structural groups arranged in the identical sequence. The difference in the FSE values of any two members of the set is equal to the $\Delta\Delta H_f^\circ$ for the hypothetical compounds. The difference of ab initio energies is mathematically equivalent to comparison of FSE values.

(2) The set consists of isomers that have the same numbers of each structural group, but the order of arrangement may be different. Examples would be 2-methyl-1-butanol and 3-methyl-1-butanol. As with case 1, the numerical value of a difference of FSE values of two molecules of the set is an estimate of the difference in $\Delta\Delta H_f^\circ$ of the hypothetical compounds. The difference of the ab initio energies of two isomers is a valid estimate of the difference of enthalpies.

(3) The set consists of molecules that are not isomers. The difference of FSE values is an estimate of the difference of the strain enthalpy component of $\Delta\Delta H_f^\circ$. To calculate the total $\Delta\Delta H_f^\circ$ it is necessary to include the differences in $\sum n_i c_i$ values of the two molecules. It is not necessary to include SM terms because the hypothetical compounds consist solely of single conformers. Consider, for example, the comparison between tetrahydropyran (chair) (FSE = 2.20, based on M_SZ, and $\sum n_i c_i = -55.98$) and methyl 1-propyl ether (g + t) (FSE = 0.04, and $\sum n_i c_i = -57.40$). The difference in strain energy is $2.20 - 0.04 = 2.16$ kcal/mol, and the total $\Delta\Delta H_f^\circ$ is $2.16 + 1.42 = 3.58$.

(4) Use of FSE values to estimate $\Delta\Delta H_f^\circ$ for pairs of compounds for which there are no experimental data and for which values for some structural groups are not available. As an illustration, suppose we need an estimate of the difference of ΔH_f° values for 2,2-dimethylcyclopropylamine and 3-methyl-2-butyalamine. The former is composed of six groups: 2 $C(C)(H)_3$, 1 $C(C)_2(H)_2$, 1 $C(C)_4$, 1 $C(C)_2(N)(H)$, and 1 $N(C)(H)_2$. The latter is also composed of six groups: 3 $C(C)(H)_3$, 1 $C(C)_3(H)$, 1 $C(C)_2(N)(H)$, and 1 $N(C)(H)_2$. Given the ab initio energies of the global minimum conformer of each of the two compounds, there are then sufficient data to calculate the difference of strain enthalpy because there is cancellation of terms for which the c_i and d_i values are not available, viz for the $C(C)_2(N)(H)$, and the $N(C)(H)_2$. groups. This case is an extension of case 3. It is applicable if the structural groups for which d_i and c_i data are not available are present in equal numbers in the two molecules so that the unknown values cancel.

Analysis of FSEs of Selected Sets of Molecules. Three examples will be treated: (1) the FSEs of conformers of alcohols and ethers, (2) the FSEs of glycols, and (3) the FSEs of cyclic ethers.

For acyclic molecules, a common structure for the conformer of lowest energy, the global minimum, is the extended conformer. Examples are ethyl methyl ether and diethyl ether. However, for several molecules the global minimum has a gauche backbone. For 1-propanol, all conformers have the same energy within the error limits of the FSEs. Truax and Wieser[53] report that the gauche form has the lower energy by the small difference 0.3 kcal/mol with a standard deviation of 0.15.

Structures of the conformers of 2-butanol have been reported previously.[1] There are three sets of conformers. Conformers 7, 8, and 9 have the C−C−C−C torsion t or anti and the C−C−C−O torsion g−. Conformers 1, 2, and 3 have C−C−C−C g+ and C−C−C−O t. For conformers 4, 5, and 6, the two torsions are g− and g+. The differences within the sets lie in the orientation of the OH group. The global minimum has the hydrogen of the OH group pointing away from the alkyl groups and an anti C−C−C−C conformation, while the conformers of highest energy have C−C−C−C g− and C−C−C−O g+. The FSE value of the conformer of 2-butanol that is the global minimum is defined to be 0.20 kcal/mol. This will be the FSE value of that conformer for all BSECMS.

For methyl *n*-propyl ether, the FSE of the conformer having g C−C−C−O and t C−C−O−C, the gt conformer, is about 0.3 kcal/mol less than that of the t t conformer based on MP2 BSECMs. The energy of the g+g+ conformer is about 0.5 kcal/mol less than that of the t t conformer. The gauche C−C−O−C interaction is about 1.2 kcal/mol, a value appreciably higher than the roughly 0.8 kcal/mol gauche interaction energy for alkanes. This is a consequence of closer approach of the terminal C−Hs in the ether owing to the short C−O bond (1.4 vs 1.52 for alkanes).

Analysis of Glycols. There have been many studies of 1,2-ethanediol. Schäfer[54] used two MP2 BSECMs, viz MP2/6-311G(d,p)//6-311G(d,p) and MP2/6-311G(d,p)//MP2/6-311G(d,p). These gave the same relative conformer energies within 0.05 kcal/mol. These energies are all within 0.1 kcal/mol of the "MP2" (MP2/6-31G(d,p)//6-31G(d,p)) values reported in Table 4, except for the g−g+g− conformer, which shows a 0.5 difference. Csonka and Csizmdia[55] used a variety of BSECMs on six of the ten conformers. The MP2-based BSECMs gave energies comparable to the "MP2" values in Table 4. Cramer and Truhlar[56] report relative energies for all ten conformers of with a variety of BSECMs, and they also studied solvation effects.

Comparisons of FSE values for the global minimum conformers of glycols provide definitive estimates of the energy stabilization due to intramolecular hydrogen bonding in these compounds. Consider, for example, the FSE values of the global minima for the following compounds: 1-propanol 0 (−0.1), 1,2-ethanediol −1.9 (−2.6), 1,2-propanediol −1.6 (−2.0), 1,3-propanediol −1.9 (−0.9), and 2-methyoxyethanol −1.4 (−). The numbers are averages of the values obtained with M_S and MAS. The values in parentheses are experimental FSE values. The standard deviation of averages of FSE values is about 0.45. The overall average for the four glycols is −1.7. Within the error limits, all of the glycols have the same FSE. These data provide an estimate of the steric correction applicable to glycols, corrections which could not be obtained from experimental ΔH_f° values.[29] The six-membered ring in 1,3-propanediol (6 including the hydrogen bonded H atom) does not provide additional stabilization over that which is present in the five-membered rings of the other three glycols.

For 1,2-dimethoxyethane, the global minimum is the t t C2h conformer. It is almost 1.9 kcal/mol higher in strain energy than is the extended form of diethyl ether (C_{2v}). This relationship may reflect the repulsion of two unfavorably oriented dipoles. The net stabilization found for the hydrogen-bonded conformers of 1,2-ethanediol and of 1,2-propanediol has had to overcome similar repulsions.

Cyclic Ethers and Cyclic Alkanes. In the lower section of Table 7 are presented data for cyclic ethers and for related cycloalkanes. For the unsubstituted rings the FSEs are a definitive measure of ring strain. The standard molecules for the cycloalkanes are C_{2h} butane and C_{2h} octane, and the standards for the unsubstituted cyclic ethers are butane, octane, and C_{2v} diethyl ether. The reference compounds all have assigned FSE of 0; they are considered to be unstrained. The experimental value reported for the FSEs is also referenced to the same standards. The calculated FSE values based on the

TABLE 8: Experimental Values of Elements kcal/mol[5,59]

ΔH_T(C)(298)	0.251
$\Delta H_T(H_2)$(298)	2.024
$\Delta H_T(O_2)$(298)	2.075
$\Delta H°_f$(C)(0)	169.98
$\Delta H°_f$(H)(0)	51.63
$\Delta H°_f$(O)(0)	58.98

BSECMs M_SZ and MASZ are considered to be the best of the calculated values.

Consider the FSE values for typical cyclic molecules. The calculated FSE values are averages of those obtained with M_S and MAS, and experimental FSE values are in parentheses: cyclobutane 27.08 (26.96) and oxetane 27.32 (26.45); cyclopentane 6.60 (7.27) and tetrahydrofuran 6.89 (6.82) and cyclopentanol 7.15 (7.72); cyclohexane 0.82 (1.45) and tetrahydropyran 2.23 (2.59) and 1,4-dioxane 5.24 (5.61) and cyclohexanol-eqg 0.74 (2.29). Except for cyclohexanol, the agreement between calculated and experimental FSEs is within the estimated standard deviation of 0.45. For four- and five-membered rings, the carbocycles and the oxacarbocycles have the same FSE values. However, the presence of oxygen atoms in a six-membered ring leads to increased ring "strain." This may be due to an effect of ring shrinkage arising from C−O bonds being shorter than C−C bonds, thus causing increased interference of the gauche C−O−C−C sequences. The further increase in "strain" in dioxane probably arises from dipole−dipole repulsion. Incidentally, the calculation of ring strain is often based on estimates of contributions of CH_2 groups derived from acyclic compounds. This approach does not take into proper account the fact that cyclohexane, for example, has only one low-energy conformer whereas acyclic *n*-alkanes have many conformers that contributed to the enthalpy; in short, the importance of the SM term of eq 2 has been ignored.

Cyclohexanol, cyclopentanol, methyloxirane, and dimethyloxetane are referenced to standards with nonzero FSEs. However, the "strain" assigned to the standards is small and reasonable, and the reported total strain is clearly defined.

The FSE ring strain values may be compared with the steric corrections used by Benson and by Cohen, Table 6. The FSE "strain" and the corrections are quite similar, but in general the FSE values indicate a larger value of the ring strain.

Table 7 provides relative energies of twist boat conformers. For cyclohexane the twist boat conformer is calculated to be 6.8 kcal/mol higher in energy than the chair conformer; for tetrahydropyran the difference is 6.1; for 1,4-dioxane it is 7.2. In a summary of experimental results, Eliel et al. report a range of 4.7 to 6.2 for cyclohexane.

Calculation of ΔH_f° from Energies of Atomization.[5] Equation 6 is the expression for the energy of atomization $E_{at}(b)$(CPD)(0) of compound CPD = $C_iH_jO_k$ at 0 K using BSECM *b* to obtain the ab initio energies for the terms of eq 6. $E(b)$(C)(0) is the ab initio energy at 0 K of an atom of C calculated with BSECM *b*, and similarly for energies of H and O atoms, $E(b)$(CPD)(0) + ZPE(CPD) is the ab initio energy of the compound at 0 K calculated with BSECM *b*. ZPE(CPD) is based on the optimized geometry calculated with the 6-31G(d,p)//6-31G(d,p) basis set and frequencies with the same basis set scaled by 0.90.

The calculated energy of atomization, $E_{at}(b)$(CPD)(0), is equated to the energy of atomization E_{at}(CPD)(0) that would be obtained from ΔH_f°(CPD)(0), the enthalpy of formation of the compound at 0 K, eq 7. Experimental values are used for the enthalpies of formation of several atoms. ΔH_f°(CPD)(0) is converted to ΔH_f°(CPD)(298), eq 9, by adding algebraically the heat content terms, eq 8. The heat content for the compound is obtained from the same set of scaled vibrational frequencies as is used to calculate ZPE(CPD). The heat content values of the elements are experimental values. Experimental values are listed in Table 8.

$$\mathrm{CPD} = \mathrm{C}_i\mathrm{H}_j\mathrm{O}_k \rightarrow i\mathrm{C} + j\mathrm{H} + k\mathrm{O} \tag{6a}$$

$$E_{at}(b)(\mathrm{CPD})(0) = iE(b)(\mathrm{C})(0) + jE(b)(\mathrm{H})(0) + kE(b)(\mathrm{O})(0) - E(b)(\mathrm{CPD})(0) + \mathrm{ZPE}(\mathrm{CPD}) \tag{6b}$$

$$\Delta H_f^\circ(\mathrm{CPD})(0) = i\Delta H_{fat}^\circ(\mathrm{C})(0) + j\Delta H_{fat}^\circ(\mathrm{H})(0) + k\Delta H_{fat}^\circ(\mathrm{O})(0) - E_{at}(\mathrm{CPD})(0) \tag{7}$$

$$\Delta H_T = H(T) - H(0) = H(298) - H(0) \tag{8}$$

$$\Delta H_f^\circ(\mathrm{CPD})(298) = \Delta H_f^\circ(\mathrm{CPD})(0) + \Delta H_T(\mathrm{CPD}) - i\Delta H_T(\mathrm{C}) - (j/2)\Delta H_T(\mathrm{H_2}) - (k/2)\Delta H_T(\mathrm{O_2}) \tag{9}$$

Calculations. Calculations were performed with Gaussian G94, G94W,[57] and G98W.[58] Most of the calculations were run on a PC using G98W. Some were run on SG computers supervised by Academic Computing and Networking services of Florida State University. I wish to acknowledge my appreciation for the ACNS support.

Conclusions

Formal steric enthalpy (FSE) is the difference between the energy of a target molecule and the sum of the energies of its constituent structural groups as defined by standard molecules, eqs 1a and 1b. The calculation of FSE is group isodesmic, and thus provides extensive cancellation of deficiencies of basis set/electron correlation methods (BSECMs). The FSE of a molecule is also a rigorously defined estimate of the strain energy of the molecule. The FSE of the conformer that is the global minimum of energy may be converted to ΔH_f° by eq 2.

The overall steps of converting the ab initio energy of a *molecule* that is a global minimum conformer into the FSE of that conformer and then by eq 2 into the ΔH_f° of the corresponding *compound* is designated the "FSE procedure" for deriving ΔH_f° of a compound from the ab initio energy of a conformer.

Calculations have been performed for 21 alcohols and ethers plus five standard alcohols and ethers. A reasonable sampling has been made of BSECMs likely to be applicable to molecules of medium size, about 15 or more heavy atoms. Several BSECMs give ΔH_f° values that agree moderately well with experimental values. The best of the BSECMs are with MP2/6-31+G(d,p)//6-31G(d,p) (M_S) and with MP2/6-311+G(2df,-2p)//6-31G(d,p) (MAS), which give standard deviations of about 0.5 kcal/mol. The estimated standard deviation of the experimental ΔH_f° values of these same compounds is about 0.4 kcal/mol.

The optimized geometry appears not to be a critical factor. Geometries optimized with MP2/6-31G(d,p) are slightly different than those optimized with 6-31G(d,p), but there is little difference in the calculated values of ΔH_f°. It is interesting that ΔH_f° values calculated by the FSE procedure from energies obtained with CBS-4M also agree well with experiment. The geometry optimization for CBS-4M uses the 3-21G* basis set; and the geometries are significantly different from 6-31G(d,p) geometries.

Treatment of electron correlation by QCISD(T) as is done in CBS-Q does not give as good results as does the MP2 treatment.

That is, treatment of CBS-Q energies by the FSE procedure gives mediocre estimates of ΔH_f°. However, treatment of CBS-Q energies by the heat of atomization procedure gives generally good estimates of ΔH_f°. The standard deviation is about 0.5 kcal/mol, the same as is obtained with M_S and MAS BSECMs. The heat of atomization procedure gives poor estimates of ΔH_f° with all other BSECMs investigated.

The density functional energy from B3LYP/6-31G(d,p) gives mediocre estimates of ΔH_f° by either the FSE or the atomization procedures.

With currently available desktop computers, a molecule having about 13 CHO atoms requires slightly more than one hour per iteration in a geometry optimization. The time required for an MP2/6-31+G(d,p) calculation is modest, but the larger MP2/6-311+G(2df,2p) basis set begins to require several days. CBS-Q calculations become unduly time-consuming on a desktop computer for molecules with more than 12 heavy atoms. Moreover, CBS-Q calculations with G98W version 5.2 tend to fail with large molecules because disk limitations are not enforced. CBS-4M occasionally fails at the extrapolation stage. Therefore, the FSE procedure with M_S and MAS BSECMs provides the best alternatives for calculating ΔH_f° from among those BSECMs examined.

FSEs provide a valuable tool for estimating differences of enthalpies. For example, the difference of the FSEs of two molecules that are isomers or conformers provides directly an estimate of the difference of the enthalpies of hypothetical compounds consisting entirely of those pure molecules. The difference of the FSEs of molecules that are unrelated provides an estimate of the difference of the strain enthalpy of the molecules, and this may readily be converted to an estimate of the difference of the total enthalpy by incorporating the difference in formal bond enthalpy increments, the $\Delta n_i c_i$ values of eq 2.

Examples of the application of FSE values are the finding that the intramolecular hydrogen bonds of 1,2-ethanediol, 1,2-propanediol, and 1,3-propanediol all have FSE values that average −1.8 kcal/mol and are the same for five-membered and six-membered rings including the H-bonded hydrogen atom. These numbers are not available from considerations of ΔH_f° values. Analysis of FSE values of ring compounds shows that carbocylic and oxacarbocylic four-membered rings have the same strain enthalpy, and likewise for five-membered rings. However, for six-membered rings the strain enthalpy ranges from about 1 kcal/mol for cyclohexane, 2.5 for tetrahydropyran, and 5.5 for 1,4-dioane. These differences can be attributed in part to the effect of short C−O bonds in bringing additional interference between gauche H atoms. For 1,4-dioxane the oxygen dipoles are oriented so as to repel each other.

Supporting Information Available: Further details of data in Tables 4 and 7, including ab initio energies for all molecules, are available. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) DeTar, DeL. F. *J. Phys. Chem. A* **1999**, *103*, 7055−68.

(2) Irikura, K. K., Frurip, D. J., Eds.; *Computational Thermochemistry*, ACS Synposium Series 677 ed.; American Chemical Society: Washington, D.C., 1997.

(3) Curtiss, L. A.; Raghavachari, K.; Redfern, P. C.; Pople, J. A. *J. Chem. Phys.* **2000**, *112*, 7374−83.

(4) Curtiss, L. A.; Raghavachari, K.; Trucks, G. W.; Pople, J. A. *J. Chem. Phys.* **1991**, *94*, 7221.

(5) Nicolaides, A.; Rauk, A.; Glukhovtsev, M. N.; Radom, L. *J. Phys. Chem.* **1996**, *100*, 17460−4.

(6) Curtiss, L. A.; Raghavachari, K. In *Computational Thermochemistry*, ACS Symposium Series 677 ed.; Irikura, K. K., Frurip, D. J., Eds.; American Chemical Society: Washington, D.C., 1997.

(7) Rogers, D. W.; McLafferty, F. J.; Podosenin, A. V. *J. Phys. Chem. A* **1998**, *102*, 1209−13.

(8) Feller, D.; Dixon, D. A. *J. Phys. Chem. A* **2000**, *104*, 3048−56.

(9) Dixon, D. A.; Feller, D.; Sandrone, G. *J. Phys. Chem. A* **1999**, *103*, 3744.

(10) Li, Z.; Rogers, D. W.; McLafferty, F. J.; Mandziuk, M.; Podosenin, A. V. *J. Phys. Chem. A* **1998**, *103*, 426−30.

(11) Yamada, T.; Bozzelli, J. W. *J. Phys. Chem. A* **1999**, *103*, 3733.

(12) Rogers, D. W.; McLafferty, F. J. *J. Phys. Chem. A* **1999**, *103*, 8733.

(13) Petersson, G. A. In *Computational Thermochemistry*, ACS Symposium Series 677 ed.; Irikura, K. K., Frurip, D. J., Eds.; American Chemical Sociery: Washington, D.C., 1997.

(14) Martin, J. M. L.; de Oliveira, G. *J. Chem. Phys.* **1999**, *111*, 1843−56.

(15) Montgomery, J. A., Jr.; Frisch, M. J.; Ochterski, J. W.; Petersson, G. A. *J. Chem. Phys.* **2000**.

(16) Petersson, G. A.; Frisch, M. *J. Phys. Chem. A* **2000**, *104*, 2183−90.

(17) Martin, J. M. L. In *Computational Thermochemistry*, ACS Symposium Series 677 ed.; Irikura, K. K., Frurip, D. J., Eds.; American Chemical Society: Washington, D.C., 1997.

(18) Cioslowski, J.; Liu, G.; Piskorz, P. *J. Phys. Chem. A* **1998**, *102*, 9890−900.

(19) Kafafi, S. A. *J. Phys. Chem. A* **1998**, *102*, 10404−13.

(20) Ibrahim, M. R.; Schleyer, P. v. R. *J. Comput. Chem.* **1985**, *6*, 157−67.

(21) Zachariah, M. R.; Melius, C. F. In *Computational Thermochemistry*, ACS Symposium Series 677 ed.; Irikura, K. K., Frurip, D. J., Eds.; American Chemical Society: Washington, D.C., 1997.

(22) Cioslowski, J.; Liu, G.; Moncrieff, D. *J. Phys. Chem. A* **1999**, *103*, 11465−8.

(23) Marshall, P. *J. Phys. Chem. A* **1999**, *103*, 4650.

(24) Cohen, N.; Benson, S. W. *Chem. Rev.* **1993**, *93*, 2419.

(25) Benson, S. W.; Cohen, N. In *Computational Thermochemistry*, ACS Symposium Series 677 ed.; Irikura, K. K., Frurip, D. J., Eds.; American Chemical Society: Washington, D.C., 1997.

(26) Benson, S. W. *J. Phys. Chem. A* **1999**, *103*, 11481.

(27) Domalski, E. S.; Hearing, E. D. *J. Phys. Chem. Ref. Data Suppl.* **1988**, *17*, 1637.

(28) Domalski, E. S.; Hearing, E. D. *J. Phys. Chem. Ref. Data* **1993**, *22*, 805.

(29) Cohen, N. *J. Phys. Chem. Ref. Data* **1996**, *25*, 1411.

(30) Dorofeeva, O. V. *Thermochim. Acta* **1992**, *194*, 9−46.

(31) Wiberg, K. B. *J. Comput. Chem.* **1984**, *5*, 197.

(32) Wiberg, K. B. *J. Org. Chem.* **1985**, *50*, 5285−91.

(33) Allinger, N. L.; Schmitz, L. R.; Motoc, I.; Bender, C.; Labanowski, J. K. *J. Am. Chem. Soc.* **1992**, *114*, 2880−3.

(34) Allinger, N. L.; Schmitz, L. R.; Motoc, I.; Bender, C.; Labanowski, J. K. *J. Phys. Org. Chem.* **1990**, *3*, 732−6.

(35) Kneisler, J. R.; Allinger, N. L. *J. Comput. Chem.* **1996**, *17*, 757−66.

(36) DeTar, DeL. F. *J. Org. Chem.* **1992**, *57*, 902−10.

(37) DeTar, DeL. F. *J. Org. Chem.* **1995**, *60*, 7125−33.

(38) DeTar, DeL. F. *J. Org. Chem.* **1991**, *56*, 1463−70.

(39) DeTar, DeL. F. *J. Org. Chem.* **1991**, *56*, 1470−4.

(40) DeTar, DeL. F. *J. Org. Chem.* **1991**, *56*, 1474−8.

(41) DeTar, DeL. F. *J. Org. Chem.* **1991**, *56*, 1478−81.

(42) DeTar, DeL. F. *J. Org. Chem.* **1987**, *52*, 1851−7.

(43) Pedley, J. B.; Naylor, R. D.; Kirby, S. P. *Thermochemical Data of Organic Compounds*, 2nd ed.; Chapman and Hall: Cambridge, England, 1986.

(44) Knauth, P.; Sabbah, R. *Struct. Chem.* **1990**, *1*, 43−6.

(45) Knauth, P.; Sabbah, R. *Thermochim. Acta* **1990**, *164*, 145−52.

(46) Benson, S. W. *Thermochemical Kinetics*, 2nd ed.; John Wiley & Sons: New York, 1976.

(47) Marsi, I.; Viscolcz, R.; Seres, L. *J. Phys. Chem. A* **2000**, *104*, 4497−504.

(48) Grev, R. S.; Janssen, C. L.; Schaefer, H. F., III. *J. Chem. Phys.* **1991**, *95*, 5128.

(49) DeTar, DeL. F.; Binzet, S.; Darba, P. *J. Org. Chem.* **1985**, *50*, 5298−303.

(50) Montgomery, J. A., Jr.; Ochterski, J. W.; Petersson, G. A. *J. Chem. Phys.* **1994**, *101*, 5900.

(51) Petersson, G. A.; Tensfeldt, T. G. *J. Chem. Phys.* **1991**, *94*, 6091.

(52) Ochterski, J. W.; Petersson, G. A.; Montgomery, J. A., Jr. *J. Chem. Phys.* **1996**, *104*, 2598.

(53) Truax, D. R.; Wieser, H. *Chem. Soc. Rev.* **1976**, *5*, 411−29.

(54) Teppen, B. J.; Cao, M.; Frey, R. F.; van Alsenoy, C.; Miller, D. M.; Schaefer, L. *J. Mol. Struct. (THEOCHEM)* **1994**, *314*, 169−90.

(55) Csonka, G. I.; Csizmadia, I. G. *Chem. Phys. Lett.* **1995**, *243*, 419−28.

(56) Cramer, C. J.; Truhlar, D. G. *J. Am. Chem. Soc.* **1994**, *116*, 3892−900.

(57) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. J.; Robb, M. A.; Cheesman, J. R.; Keith, T.; Petersson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Laham, M. A.; Zakrzewski, V. J.; Ortiz, J. V.; Foresman, J. B.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andres, J. L.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, D. J.; Defrees, D. J.; Baker, J.; Stewart, J. P.; Head-Gordon, M.; Gonzalz, C.; Pople, J. A. *Gaussian* **1995**, *94*.

(58) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G.; Robb, M. A.; Cheesman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi. M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Froesman, J. B.; Cioslowski, J.; Ortiz, J. V.; Baboul, A. G.; Stefanov, R. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Andres, J. L.; Head-Gordon, M.; Pople, J. A. Gaussian Inc.: 1998, Pittsburgh, PA.

(59) Wagman, D. D.; Evans, W. H.; Parker, V. B.; Schumm, R. H.; Halow, I.; Bailey, S. M.; Churney, K. L.; Nuttall, R. L. *J. Phys. Chem. Ref. Data Suppl.* **1982**, *11, Suppl. 2*, 37−114.