

structures have been shown to be commensurate with simpler nitrogen-fluorine and carbon-fluorine species.

The tendency of first-row hexafluorides to form stable octahedral structures reflects the behavior of analogous second-row species such as PF_6^- and SiF_6^{2-} . The extremely large fluoride affinity of PF_5 , i.e. the large negative enthalpy of the reaction $\text{PF}_5 + \text{F}^- \rightarrow \text{PF}_6^-$, has been well studied experimentally. One study³⁸ has reported a value of -85 ± 10 kcal/mol while another³⁹ found -101 ± 8 kcal/mol. These may be compared with our computed result for the nitrogen species, -40 kcal/mol. The fluoride affinity of SiF_4 is apparently less well-known, although it is certainly much smaller than that of PF_5 . The double-fluoride affinity, i.e. the enthalpy of the reaction $\text{SiF}_4 + 2\text{F}^- \rightarrow \text{SiF}_6^{2-}$, has been reported as -33 kcal/mol from one experimental approach⁴⁰ and ranging between -1 and -33 kcal/mol depending on the way the data was interpreted according to another study.⁴¹ We computed the enthalpy of the analogous reaction involving carbon, $\text{CF}_4 + 2\text{F}^- \rightarrow \text{CF}_6^{2-}$, to be $+127$ kcal/mol. A comprehensive theoretical study of the fluoride affinities of a number of species, on the basis of SCF calculations, has been reported by O'Keeffe.⁴² His computed energy differences are in good agreement with the available experimental data and correspond to -97 kcal/mol for $\text{PF}_5 + \text{F}^- \rightarrow \text{PF}_6^-$ and -33 kcal/mol for $\text{SiF}_4 + 2\text{F}^- \rightarrow \text{SiF}_6^{2-}$.

The structure of "hypermatalated" species such as CLi_6 on the other hand appears to be more analogous to the octahedral environment often encountered in interstitial carbides.^{43,44} Such

solids frequently contain octahedral defects in their close-packed lattices in which a small atom such as hydrogen, boron, carbon, or nitrogen may reside if the spacing between the metal atoms is large enough.⁴³ A very similar situation occurs in metal-carbonyl clusters, compounds in which a carbon atom is frequently trapped in an octahedral or trigonal-prismatic arrangement of metal atoms.⁴⁵

Our previous results³ showed that increasing the number of fluorines attached to nitrogen increased the magnitude of stabilizing two-center energies of the resulting species and suggested the stability of NF_6^- . It is tempting to speculate that three-center, four-electron "hypervalent bonds"⁴⁶ account for the apparent stabilities of NF_6^- and CF_6^{2-} , which would be viewed as possessing three such linear three-center bonds at right angles to each other. However as shown by Tables VI and VII the multicenter analysis does not support this picture.

Clearly experimental tests (and/or computations employing much higher levels of approximation) will be required to establish conclusively whether these unique hexacoordinate anions are structurally unstable (or metastable) or whether they exhibit considerable structural stability, as the present study indicates. Our computed results for the thermodynamic properties, summarized in Figure 1, indicate that NF_6^- in particular might be readily prepared under experimental conditions favoring condensation into the larger species. These hexacoordinate ions should also present a useful test of current qualitative concepts of molecular electronic structures as applied to the first-row elements.

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The Syn Rotational Barrier in Butane

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Abstract: The syn barrier for rotation about the central bond in butane has been determined via ab initio theoretical techniques, with various basis sets up to and including triple- ζ with two sets of polarization functions of carbon, and with varying amounts of electron correlation up to and including the coupled cluster with single and double excitations (CCSD) level of theory. After including zero-point and thermal corrections, these studies give the best available ΔH^*_{298} value for this quantity at present as 4.89 kcal/mol. Previous theoretically determined syn-anti energy differences that disagreed with spectroscopically and molecular mechanics derived values are shown to be too large because of inadequate basis sets.

The butane molecule has long been regarded as the cornerstone of conformational analysis in organic chemistry.¹ Pitzer² in his classic work on the conformational properties of butane and alkanes in general, following his earlier work on the rotation barrier in ethane,³ concluded that the rotational profile for rotation about the central bond in butane was characterized by three minima, two of which are an enantiomeric pair of gauche conformations, and the other of which is the anti conformation. He concluded

from the thermodynamic and spectroscopic properties of butane and other alkanes that the gauche conformation was higher in energy than the anti by about 0.8 kcal/mol. He also concluded that there were rotational barriers separating these conformations, the lower of which separated the anti form from the gauche forms

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and had an approximate value of 3.3 kcal/mol, while the syn barrier (which resulted when the methyls went past each other) was somewhat higher. Reasonable estimates of this barrier height were made by Pitzer (4.4 kcal/mol)² from thermodynamic properties of alkanes, and by Ito (6.1 kcal/mol)⁴ from a consideration of the heat of formation of cyclopentane.

The early determinations of the gauche/anti energy difference and of the lower barrier in butane have proved to be quite durable, and the current values from both experiment and calculation are hardly changed from the early values as given above.⁵ On the other hand, the syn barrier has proved to be less susceptible to accurate measurement and/or calculation, and there are a large number of papers concerning the height of this barrier. Of these, we will explicitly consider four here. These four papers are respectively (1) an experimental paper by Compton et al.,⁶ (2) a molecular mechanics result from MM2,⁷ (3) ab initio calculations by Raghavachari,⁸ and (4) a recent ab initio paper by Wiberg and Murcko.⁵ These papers contain many references to still earlier work which will not be discussed here.

Taking first the paper on the vibrational spectrum of butane,⁶ transitions between the several lowest torsional levels for each of the conformations were determined in the far-infrared. Assuming a Fourier series description of the potential containing up to and including the sixth-order term, a potential was fit from these transitions. Including allowance for the other deformations of the molecule through the changing moment of inertia utilizing the so-called *f* number, this led to an experimental barrier height (ΔE) of 4.54 kcal/mol. This barrier height is, of course, sensitive to various other things which are known or assumed about the potential function, including the relative energy of the two conformations, and the dihedral angle at the energy minimum for the gauche form. It is difficult to know how reliable this value for the barrier height may be, but considering other similar cases, an error of several tenths of a kcal/mol would certainly be possible.

Next we may consider the molecular mechanics value.⁷ There are two points to consider here. One point is that the molecular mechanics value is assumed to be a transferable value, applicable to all four-carbon units of the type that occur in butane. Surely this is an approximation, but it is always assumed in molecular mechanics. The second point is the accuracy to which this transferable value can be determined experimentally. Concerning the first point, because we have heat of formation data on a great many cyclic compounds which have varying numbers of conformations at widely varying dihedral angles, and we also have structural information on some of these compounds, if the assumption of transferability is completely accurate, then a change of the transferable value which leads to the butane potential can hardly be >0.1 kcal/mol without noticeably and unfavorably impacting the heat of formation calculations. The potentials assumed in MM2 are then used to calculate the butane barrier, and this barrier was not itself used as part of the MM2 formulation. As originally published, the MM2 parameters give a butane barrier height of 4.73 kcal/mol. However, after this potential was fit, additional experimental data on the rotational barriers in a number of congested hydrocarbons became available,⁹ and these barriers are invariably higher than those calculated by MM2. We did not advocate changing the MM2 parameters to match these newer data for two reasons. One reason is that there are many published MM2 calculations available, and any changes in the basic parameters would render new calculations inconsistent with the previous ones. Unless the new values are very much superior to the old ones, it is better to retain values that are somewhat in error (in a known way and by a known amount).

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rather than to change parameters. Second, in this particular case, the experimental data were not complete enough to really warrant such a change. The problem with the experimental data for the congested hydrocarbons is that they were values for ΔG^\ddagger , whereas the values which MM2 calculates are ΔH^\ddagger . Since it is anticipated that the values for ΔS^\ddagger will be nonzero, it cannot be assumed that the ΔH^\ddagger and the ΔG^\ddagger values are equal. Nonetheless, Osawa made this assumption¹⁰ and therefore devised another parameter set (in which other things were changed as well), which he called MM2', and the parameters which he advocated raised the syn barrier in butane to 5.2 kcal/mol. However, because of the faulty assumption regarding the equality of ΔG^\ddagger and ΔH^\ddagger , the value 5.2 is, in fact, quite a bit too high. If one properly compared the calculated value for ΔG^\ddagger with the experimental value of the same quantity for the rotational barrier data for the congested hydrocarbons, one could be led to a barrier (ΔH^\ddagger) in butane of approximately 5.0 kcal/mol. But this number disregards the other very extensive information on the structures and energies of ring and other compounds which have conformations that are removed from the energy minima. So 5.0 kcal/mol is really a maximum value that one can reach only by disregarding much of the data which lead to lower values. A more even-handed approach would be to utilize all of the earlier data, which gave the value 4.73 kcal/mol, plus the rotational barrier data as well, and all of these data together would yield a "best" MM2 value of approximately 4.85 kcal/mol. The data scatter around some, but one might conclude that the likely fitting error in this 4.85-kcal/mol value is not more than about 0.2 kcal/mol, if the assumption is correct that we are, in fact, dealing with a parameter here which is transferable with an error less than the random error (0.2 kcal/mol). It seems quite likely that this is the case, but there can, of course, be no guarantee that the butane molecule is not a particular case where the transferability breaks down (or breaks down worse than usual). We do not advocate changing the MM2 parameters now, however, for reasons discussed above, and prefer instead to acknowledge that the fitting error is greater than previously recognized. Thus, we now take the MM2 value for the syn butane barrier to be 4.73 (± 0.30) kcal/mol.

Since the butane barrier arrived at by papers 1⁶ and 2⁷ is the same to well within the error limits of the two methods (which we estimate at 0.6 and 0.3 kcal/mol, respectively), this would seem at first sight to solve the problem. However, the ab initio theoretical results available are not at all consistent with the previously discussed experimental results. Raghavachari carried out calculations about as extensive as could be done at the time,⁸ in which he optimized the geometry of the butane molecule at the SCF level with different basis sets, up to and including 6-31G*, and noted that the height of the barrier did not change very much with changing basis set size. In addition, reoptimization at the MP2/6-31G level of theory had no effect on the height of the barrier. He also determined the barrier height with varying degrees of electron correlation and noted that the results appeared to have been fairly well converged at the MP3 level. Raghavachari concluded that the "best" value that he could reach was 5.81 kcal/mol⁸ for ΔE^\ddagger . He projected a limit of 5.6–5.8 kcal/mol for this quantity from the trends in the calculations, and zero-point-corrected this would yield 5.8–6.0 kcal/mol for ΔH^\ddagger_0 . Raghavachari did not publish a value for ΔH^\ddagger_{298} , which is necessary to compare with molecular mechanics, but since the thermal corrections for different conformations of a molecule are typically smaller than and in the opposite direction from the zero-point corrections, we estimated¹¹ the value of ΔH^\ddagger_{298} as 5.7–5.9 kcal/mol from his data.

Recently, Wiberg and Murcko published another set of ab initio calculations on butane,⁵ in which they studied the gauche and anti forms at a fairly high level of theory, but for the syn form they stopped at about the same point that Raghavachari did. Their judgment was that the best value of ΔE^\ddagger for the syn barrier was

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6.14 kcal/mol and of ΔH^*_0 was 6.34 kcal/mol. They concluded that these values would not change very much if further and better calculations were carried out.

We have been concerned about this butane barrier problem for some years and were carrying out larger scale ab initio calculations prior to the appearance of the paper by Wiberg and Murcko.⁵ If we compare the barrier height of Raghavachari ($\Delta H^*_0 = 5.8$ – 6.0 kcal/mol) and that of Wiberg ($\Delta H^*_0 = 6.34$ kcal/mol) with the experimental value of ΔE 4.54 and the MM2 value of $\Delta H^*_{298} = 4.73$ kcal/mol as given earlier, painful discrepancies are evident. The possible updating of the MM2 value from 4.73 to 4.85 would not help much. The sources of these discrepancies are not immediately evident, and the problem could be in any or all of the values quoted.

Our current best estimate from MM3 gives us a value¹¹ for this barrier height of 4.81 kcal/mol (ΔH^*_{298}), as always with molecular mechanics, assuming a high degree of parameter transferability. We feel that this number is in good agreement with the MM2 value, and in satisfactory agreement with the value from the vibrational spectra, but most of the discrepancy between these experimental values and the ab initio values previously published remains. The present work will not be concerned with the experimental values, which are being examined separately. In this paper we will analyze the butane barrier from two aspects. First, we will discuss results of our ab initio study, which we have now pushed to the limits of our computational ability and quite a bit further than was achieved in previous theoretical efforts. Second, we will consider the thermochemical corrections which need to be made to the ab initio values for a proper comparison with experiment and molecular mechanics. This latter point is one that has not received enough attention in previous papers. When one is concerned about differences of less than a kcal/mol, it is important to distinguish carefully between ΔE , ΔH_0 , and ΔH_{298} .

Theoretical Methods

Ab initio molecular orbital studies were carried out with a variety of basis sets, each of which consisted of a flexible sp basis coupled with single or double sets of polarization functions. Three underlying sp sets were used. The first consisted of the standard Huzinaga–Dunning double- ζ basis set,^{12,13} labeled DZ and described as [4s2p/2s]. The second consisted of Dunning's¹⁴ triple- ζ contraction of Huzinaga's¹² (10s6p) set for carbon together with the DZ basis set for hydrogen. It is labeled TZ1 and may be described as [5s3p/2s]. The third sp set consisted of the TZ1 basis set for carbon but with Dunning's¹⁴ scaled triple- ζ contraction of Huzinaga's¹² (5s) basis for hydrogen. This is labeled TZ2 and may be designated [5s3p/3s]. To these basis sets were added single sets of polarization functions, $\alpha_d(\text{C}) = 0.75$ and $\alpha_p(\text{H}) = 0.75$. When two sets of d functions were added to carbon, we used the exponents $\alpha_d(\text{C}) = 1.5$ and 0.35.¹⁵ The notation TZ2(2d,p) has been employed to indicate use of the TZ2 basis set with the addition of two sets of d functions on carbon and one set of p functions on hydrogen. Using this style of notation, DZ(d,p) implies the basis set we usually refer to as DZP (or DZ + P or DZ + POL).

Electron correlation was included through use of the configuration interaction with single and double excitations (CISD),^{16,17} Moeller–Plesset (MP),^{18,19} and coupled cluster with single and double excitations (CCSD)^{20–22} formalisms. Geometry optimizations were carried out with

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(15) (a) These exponents are roughly twice and one-half the value of the single d exponent (0.75) and thus conform to the $2\alpha_{1/2}\alpha$ rule.^{15b} We were surprised, however, to find that the SCF energy with the DZ(2d) basis was actually higher than with the DZ(d) basis for both conformers (see Table II). Optimization at the SCF/DZ(2d) level of the d function exponents for the syn conformer led to $\alpha_d(\text{C}) = 1.39$, 0.60, and a significant drop in the SCF energy of 7 mhartrees. However, the CCSD (and MP2, MP3, etc.) total energies calculated with the two sets of exponents were very similar. (b) Frisch, M. J.; Pople, J. A.; Binkley, J. S. *J. Chem. Phys.* **1984**, *80*, 3265.

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Table I. Optimized Geometrical Parameters^a for the Anti and Syn Conformations of *n*-Butane

		geometrical parameter		
		$r(\text{C}_1\text{C}_2)$	$r(\text{C}_2\text{C}_3)$	$\theta(\text{C}_1\text{C}_2\text{C}_3)$
anti C_{2h}	SCF/6-31G(d) ^b	1.528	1.530	113.1
	MP2/6-31G(d) ^c	1.525	1.525	112.9
	SCF/6-31G(d,p) ^c	1.528	1.529	113.1
	SCF/DZ(d,p)	1.529	1.530	113.1
	CISD/DZ(d,p)	1.527	1.527	112.9
syn C_{2v}	SCF/6-31G(d) ^b	1.531	1.555	117.0
	MP2/6-31G(d) ^c	1.528	1.555	116.4
	SCF/6-31G(d,p) ^c	1.531	1.551	117.0
	SCF/DZ(d,p)	1.533	1.555	117.0
	CISD/DZ(d,p)	1.530	1.552	116.6

^a Bond lengths in Å, angles in deg, with the carbon skeleton ordered C_1 – C_2 – C_3 – C_4 . All 11 geometrical parameters (under C_{2h} or C_{2v} symmetry) were fully optimized; only three of these parameters are shown here for clarity. ^b From ref 8. ^c From ref 5.

the use of analytic first derivatives at both the SCF²³ and CISD^{24,25} levels. Vibrational frequencies were determined through evaluation of analytic SCF second derivatives,²⁶ and thermal corrections to relative energies were obtained through the use of standard formulas.^{27,28} (The SCF/DZP frequencies were scaled by 0.9.)

Optimized geometrical parameters for the anti and syn conformations of butane are presented in Table I, total energies in Table II, and relative energies in Table III. Also included in Table III are improved CISD relative energies which include contributions from unlinked quadruple excitations as estimated by using the formula of Davidson.^{29,30} Results including this estimate are denoted by CISD(Q). Structures and relative energies of the gauche conformation of butane and the gauche \rightarrow anti transition structure were also determined in this work, and the results obtained³¹ are essentially in agreement with those of Raghavachari⁸ and Wiberg and Murcko.⁵

Ab Initio Results and Discussion

To assess the convergence of the syn–anti relative energies, the ab initio results should be analyzed from three distinct points of view: first, the effects of geometry optimization; second, the effects of including electron correlation; and third, the effects of enlarging the basis set.

The effects of geometry optimization as shown in Table I are seen to be negligible (in agreement with the results of previous theoretical work^{5,8}). The SCF/DZ(d,p) and CISD/DZ(d,p) structural parameters are very similar and the relative energies obtained with these two sets of geometries differ by 0.04 kcal/mol at most (Table III).

As noted by Raghavachari,⁸ the effects of including electron correlation energy appear to converge across the series MP2, MP3, MP4. Indeed, the MP4SDQ relative energies are very close to those obtained from the much more extensive CCSD treatment (Table III). Calculations at the CCSDT-1³² level with the DZ basis set have also been performed, and they indicate that the effect

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Table II. Total Energies (Hartrees) for the Anti (a) and Syn (s) Conformations of *n*-Butane^a

basis set ^b	structure	level of theory						
		SCF	CISD	CISD(Q)	MP2	MP3	MP4SDQ	CCSD
DZ(d)	a	-157.317 508			-157.833 083	-157.881 273	-157.889 965	-157.891 828
	s	-157.307 683			-157.823 653	-157.872 000	-157.880 761	-157.882 645
DZ(2d)	a	-157.311 815			-157.863 015	-157.910 113	-157.917 912	-157.919 391
	s	-157.302 136			-157.853 777	-157.901 002	-157.908 886	-157.910 369
DZ(d,p)	a	-157.332 663 ^c	-157.883 161 ^c	-157.962 889 ^c	-157.919 015 ^c	-157.974 178 ^c	-157.980 364 ^c	-157.981 124 ^c
		-157.332 538	-157.883 284	-157.963 189	-157.919 391	-157.974 536	-157.980 777	-157.981 553
	s	-157.322 805 ^c	-157.873 745 ^c	-157.953 706 ^c	-157.909 716 ^c	-157.965 058 ^c	-157.971 279 ^c	-157.972 055 ^c
		-157.322 649	-157.873 897	-157.954 049	-157.910 148	-157.965 461	-157.971 740	-157.972 531
DZ(2d,p)	a	-157.332 793			-157.944 080			
	s	-157.322 889			-157.935 156			
TZ1(d)	a	-157.327 639			-157.874 329	-157.918 563	-157.928 955	-157.930 252
	s	-157.317 872			-157.864 855	-157.909 217	-157.919 721	-157.921 026
TZ1(2d)	a	-157.324 701			-157.907 105	-157.950 377	-157.959 647	-157.960 584
	s	-157.314 855			-157.898 063	-157.941 406	-157.950 795	-157.951 726
TZ1(d,p)	a	-157.344 451			-157.960 570	-158.011 737	-158.018 883	-158.019 210
	s	-157.334 539			-157.951 069	-158.002 356	-158.009 589	-158.009 925
TZ2(d,p)	a	-157.347 586			-157.968 395			
	s	-157.338 100			-157.959 451			
TZ2(2d,p)	a	-157.349 351			-157.995 061			
	s	-157.339 748			-157.986 509			

^a Obtained with the use of CISD/DZ(d,p) optimized geometries unless otherwise noted. ^b TZ1 is the [5s3p/2s] basis set, and TZ2 is the [5s3p/3s] basis set. See text for details. ^c Obtained with the use of SCF/DZ(d,p) optimized geometries.

Table III. Calculated Syn–Anti Relative Energies (kcal/mol)^a

basis set ^b	no. of bfn ^c	level of theory						
		SCF	CISD	CISD(Q)	MP2	MP3	MP4SDQ	CCSD
DZ(d)	84	6.17			5.92	5.82	5.78	5.76
DZ(2d)	108	6.07			5.80	5.72	5.66	5.66
DZ(d,p)	114	6.19 ^d	5.91 ^d	5.76 ^d	5.84 ^d	5.72 ^d	5.70 ^d	5.69 ^d
		6.20	5.89	5.74	5.80	5.70	5.67	5.66
DZ(2d,p)	138	6.21			5.60			
TZ1(d)	100	6.13			5.95	5.86	5.79	5.79
TZ1(2d)	124	6.18			5.67	5.63	5.55	5.56
TZ1(d,p)	130	6.22			5.96	5.89	5.83	5.83
TZ2(d,p)	140	5.95			5.61			
TZ2(2d,p)	164	6.03			5.37			(5.25) ^e

^a Obtained with the use of CISD/DZ(d,p) optimized geometries unless otherwise noted. ^b See footnote *b* of Table II. ^c Number of basis functions. ^d Obtained with the use of SCF/DZ(d,p) optimized geometries. ^e Estimated value (see text).

of including triple excitations with large basis sets would be to lower the syn–anti barrier by only another 0.02 kcal/mol. Thus, the rightmost column of Table III represents the limit to within 0.1 kcal/mol of the syn–anti relative energy for a given basis set. From Table III it may be seen that the syn–anti relative energy is consistently lowered by just over 0.1 kcal/mol on going from the MP2 to the CCSD level with a variety of basis sets. We have used this observation to estimate the correlation energy limits for our largest basis set calculations (see below).

Enhancing the flexibility of the underlying basis set appears to have considerable effects of the syn–anti barrier (Table III). The inclusion of p functions on hydrogen and multiple sets of d functions on carbon is clearly important. The expansion of the sp part of the basis set also makes a significant contribution to the change in relative energies. However, the trends are not obvious, and the use of additivity schemes for estimating basis set effects is not practical in this case where we are concerned with getting relative energies to within a few tenths of a kcal/mol. It would be premature to speculate on the effects of enlarging the sp basis set still further, or of adding diffuse functions or f functions. Nevertheless, it should be emphasized that the basis sets employed here are considerably larger than those used by Raghavachari⁸ and by Wiberg and Murcko.⁵ Our largest basis set is [5s3p2d/3s1p]. With this basis set the syn–anti barrier in butane is calculated to be 5.37 kcal/mol at the MP2 level.³³ With the use of the MM2-CCSD energy difference (taken to be 0.12

kcal/mol) discussed previously, the CCSD value for the barrier is estimated to be 5.37 – 0.12 = 5.25 kcal/mol with this basis set. This represents the best ab initio prediction of ΔE^\ddagger currently available and is 0.5–1.0 kcal/mol below the previous best ab initio results.^{5,8}

Thermodynamic Corrections

Comparisons between rotational barriers determined by ab initio, molecular mechanics, and spectroscopic methods require special care. Each method, in its simplest form, measures something entirely different. The total energies and harmonic vibrational frequencies determined by ab initio quantum mechanical methods are perhaps the most fundamental, as these may be combined with the full machinery of statistical mechanics and kinetic rate theories to bridge the gap between the spectroscopic and molecular mechanics based barriers. In this section we describe the appropriate way to make these comparisons.

Now, molecular mechanics is parameterized to reproduce both experimental *equilibrium* ΔH_{298} values and ΔH^\ddagger values (at various temperatures), which are indistinguishable in that method at a practical level. In a sense, even at a transition state, the potential has been partially determined as though all $3N - 6$ vibrational frequencies are real and thus is not strictly comparable to ΔH^\ddagger_{298} . Nonetheless it is probably best to compare the molecular mechanics value for the syn–anti barrier to an ab initio ΔH^\ddagger_{298} . The ab initio quantum mechanical ΔH^\ddagger_{298} corresponds to that which would be obtained from a measured reaction rate via conventional rate theory:

$$\text{rate} = (k_B T/h) e^{-(\Delta H^\ddagger_{298} - T\Delta S^\ddagger_{298})/RT}$$

provided we include all $3N - 6$ vibrational degrees of freedom in

(33) As the basis set gets larger and larger we would expect the changes from one basis set to the next to get smaller. From the results in Table III, this might lead us to conclude that the basis set limits will be within 0.5 kcal/mol of the results obtained with the largest basis set used here.

Table IV. Summary of Best Available Values for the Syn Rotational Barrier in Butane (kcal/mol)

method	ΔE^*	ΔH^*_0 ^a	ΔH^*_{298} ^b
vibrational spectroscopy		4.37 ^c	
MM2			4.73
MM3			4.81
ab initio ^d	5.81	6.0	
ab initio ^e	6.14	6.34	
ab initio (current study)	5.25	5.43 ^f	4.89 ^g

^a ΔE^* + difference in ZPVE for the anti and syn conformers. ^b ΔH^*_0 + difference in $H_{298} - H_0$. ^cDerived from the spectroscopically determined ground-state vibrationally adiabatic potential barrier ΔV^{AG} by subtracting the zero-point vibrational energy for the torsional mode (see text). ^dFrom ref 8. ^eFrom ref 5. ^fWith the use of unscaled frequencies. $\Delta H^*_0 = 5.45$ kcal/mol. ^gWith the use of unscaled frequencies. $\Delta H^*_{298} = 4.92$ kcal/mol.

the equilibrium structures but only $3N - 7$ degrees of freedom in the transition structure (the remaining degree of freedom being the reaction coordinate, which appears in the $k_B T/h$ term).³⁴ Thus, in calculating the thermodynamic corrections to the ab initio ΔE^* value for the butane barrier, it is appropriate to include all the vibrational frequencies for the anti conformation and to omit the imaginary frequency for the syn conformation. With this strategy, we find that the difference in the zero-point vibrational energies (syn minus anti) is 0.18 kcal/mol, and the difference in the $(H_{298} - H_0)$ values is -0.54 kcal/mol.³⁵ Combined with our ab initio ΔE^* value of 5.25 kcal/mol, this leads to our theoretical prediction for ΔH^*_{298} of 4.89 kcal/mol (Table IV).

In the Introduction, we referred to the value for the barrier derived from spectroscopy as ΔE . Literally, this is not so. It is an effective potential barrier which is probably best modeled by a ground-state vibrationally adiabatic potential barrier³⁶ ΔV^{AG} , since it was obtained by fitting a one-dimensional potential $V(\tau)$ for the motion along the C-C-C-C torsional coordinate τ in the presence of all the other modes. The resulting ground-state vibrationally adiabatic potential barrier, $\Delta V^{AG} = V(0^\circ) - V(180^\circ) = 4.54$ kcal/mol, neglects the effect of ZPVE for the torsional mode, but the ZPVE's in all the orthogonal modes are included. Experimentally, the torsional frequency is measured⁶ as 121 cm^{-1} , which gives a ZPVE for that mode of 0.17 kcal/mol. Taking this value into account, we derive an experimental ΔH^*_0 of $4.54 - 0.17 = 4.37$ kcal/mol (Table IV).

Concluding Remarks

We agree with Raghavachari that the effect of geometry optimization at higher levels of theory on the syn-anti energy difference in butane is minimal, and that correlation effects beyond MP3 (or MP2) are small and predictable. On the other hand, enlarging the one-particle basis set beyond DZP quality has a significant effect on the syn-anti energy difference, especially at correlated levels of theory. Our final best number (ΔE^*) for the energy difference between the syn and anti structures is 5.25 kcal/mol, significantly lower than previous estimates by Raghavachari⁸ or by Wiberg and Murcko.⁵ For comparison with the

molecular mechanics value, the vibrational correction needs to be added to the equilibrium value, and we calculate this to be -0.36 kcal/mol ($+0.18$ kcal/mol for the zero-point correction, and -0.54 kcal/mol for the thermal correction at 298 K). This gives us a ΔH^*_{298} value of 4.89 kcal/mol, to compare with the MM2 value of 4.73 ± 0.3 kcal/mol, and the current MM3 value of 4.81 ± 0.2 , with the caveats previously discussed. Comparison between the ab initio and spectroscopically derived values of ΔH^*_0 , 5.43 versus 4.37 kcal/mol (Table IV), is less satisfactory than the now excellent agreement between ab initio and molecular mechanics derived values of ΔH^*_{298} , but is nonetheless much better than indicated by previous theoretical studies.

On the negative side, if we compare Raghavachari's and Wiberg's and our ab initio ΔE^* values, we have 5.8, 6.1, and 5.3 kcal/mol. The first two values result from what are currently considered as big basis set calculations with a large amount of electron correlation, and when these are compared with the last number, the conclusion seems to be clear. While 1–2 kcal/mol accuracy now seems attainable by ab initio theoretical techniques for many conformational problems, to get the error down to less than 0.5 kcal/mol, even for an apparently simple problem, takes a very large calculation indeed.^{37,38}

Finally, for completeness, we include a proper comparison between the ab initio, molecular mechanics, and spectroscopically derived values for the lower anti-gauche barrier. The spectroscopically derived⁶ ΔV^{AG} of 3.63 kcal/mol, when corrected for the torsional zero-point vibrational energy of 0.17 kcal/mol as above, yields an experimental anti-gauche ΔH^*_0 of 3.46 kcal/mol. This is in excellent agreement with the value found here, $\Delta H^*_0 = 3.36$ kcal/mol, and by others.^{5,8} Frankly, we expect the spectroscopic value for this barrier to be more accurate than that for the syn-anti, as numerous vibrational transitions in the anti and gauche wells have been observed, and these, together with the low anti-gauche barrier height, place major constraints on the potential in this region. By contrast, the syn barrier is more of an extrapolated value. The MM3 value for the anti-gauche barrier is $\Delta H^*_{298} = 3.29$ kcal/mol. Thermal corrections to the ab initio ΔE^* of 3.33 kcal/mol include $+0.03$ kcal/mol for ZPVE and -0.53 kcal/mol for $H_{298} - H_0$, yielding a final ab initio $\Delta H^*_{298} = 2.83$ kcal/mol. All things considered, one can hardly expect better agreement.

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Registry No. Butane, 106-97-8.

(34) Kreevoy, M. M.; Truhlar, D. G. *Investigation of Rates and Mechanisms of Reactions*, 4th ed.; Bernasconi, C. F., Ed.; Wiley: New York, 1986; Part 1, p 13.

(35) With the use of unscaled vibrational frequencies, the zero-point correction is $+0.20$ kcal/mol and the thermal correction is -0.53 kcal/mol.

(36) Garrett, B. C.; Truhlar, D. G.; Grev, R. S.; Magnuson, A. W. *J. Phys. Chem.* **1980**, *84*, 1730.

(37) A similar conclusion might be drawn from the related work on the relative energies of the gauche and anti conformations of 1,2-difluoroethane. See: Wiberg, K. B.; Murcko, M. A. *J. Phys. Chem.* **1987**, *91*, 3616. Miyajima, T.; Kurita, Y.; Hirano, T. *J. Phys. Chem.* **1987**, *91*, 3954. Dixon, D. A.; Smart, B. E. *J. Phys. Chem.* **1988**, *92*, 2729, and references therein.

(38) The single point calculation of the MP2 energy with our largest basis set (164 basis functions) required 80 min. of CPU time on an IBM 3090-400/E, for each conformation.