Quantum Chemistry Study of Conformational Energies and Rotational Energy Barriers in *n*-Alkanes

Grant D. Smith*

Department of Chemical Engineering, University of Missouri−Columbia, Columbia, Missouri 65211

Richard L. Jaffe

NASA Ames Research Center, Moffett Field, California 94035

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The gauche energy, the *t*–*g* barrier, and the cis barrier in *n*-butane and *n*-hexane have been investigated using high-level ab initio electronic structure calculations. CCSD(T)/cc-pVTZ//MP2/6-311G(2df,p) calculations yield a gauche energy in *n*-butane of 0.59 kcal/mol, which after correction for zero-point and thermal vibrational effects is within 0.05 kcal/mol of the values obtained from recent experiments. Calculations at the same level yield *t*–*g* and cis barrier energies in *n*-butane of 3.31 and 5.48 kcal/mol, respectively, supporting the traditional view that the cis barrier in *n*-butane is much higher than the *t*–*g* barrier. We found that torsional potential functions previously parametrized to reproduce the measured low-lying torsional vibrational transitions in the trans and gauche conformers of *n*-butane and which yield only a small energy difference between the barriers can be modified to reproduce both the spectroscopic data and the large quantum chemistry energy difference between barriers. For the central bond in *n*-hexane, the gauche energy is about 0.07 kcal/mol lower than the gauche energy in *n*-butane at the same level of theory. The chain length effect is greater on the barriers, with the *t*–*g* and cis barriers being about 0.5 and 0.3 kcal/mol lower, respectively, for the central bond in *n*-hexane compared to *n*-butane at the same level of theory.

Introduction

For alkanes and molecules containing alkane sequences, including many polymers, conformational properties are determined to a large extent by the energetics of rotation about the C−C bond. The conformational energy, as a function of the C−C−C−C torsional angle ϕ in *n*-butane or for a $t\phi t$ sequence in longer *n*-alkanes, is shown schematically in Figure 1. The lower energy trans (*t*) conformation is divided from the higher energy gauche (g^+ and g^-) conformations by the *t*–*g* barriers, while direct transition between the gauche states requires traversing the cis barrier. It has been known for more than 50 years[1] that the energy difference between the trans and gauche conformations is small (0.5−1.0 kcal/mol). However, the magnitudes of the energy barriers are less well established. In spite of the fact that many experimental and theoretical studies have been carried out for *n*-butane and other short chain *n*-alkanes, there exist a number of unsettled issues: (1) Are the gauche energy and barrier heights in *n*-butane representative of those in longer *n*-alkanes and polyethylene? (2) Are the *t*–*g* and cis barriers in *n*-butane comparable in energy, or is the cis barrier significantly higher? (3) Is the gauche energy different for *n*-butane in vapor, liquid, and solutions?

Thermodynamic,[2] spectroscopic,[3−12−14] and electron diffraction[15,16] measurements can provide much information about the conformational characteristics of *n*-alkanes. Ito[2] analyzed enthalpy data for a series of linear, branched, and cyclic alkanes and concluded that the gauche−trans energy difference is 0.7 kcal/mol, and the *t*–*g* and cis barriers are respectively 3.72 and 6.10 kcal/mol higher than the trans. This work supported older estimates of these quantities and stood unchallenged for many years. Better estimates of the gauche energy have been determined by analysis of the temperature dependence of IR and Raman vibrational spectra. Selected values so obtained for
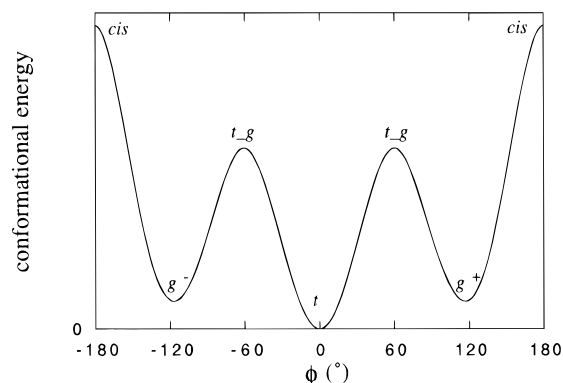

Figure 1. Schematic representation of the conformational energy of *n*-butane.

n-butane liquid are 0.57 ± 0.11[5] and 0.56 ± 0.01 kcal/mol.[6] The earlier gas phase determinations of 0.89 kcal/mol by Durig and Compton[3] and 1.1 kcal/mol by Durig, Wang, Beshir, and Little[13] led to the belief that a large condensed phase gauche stabilization exists for alkanes. However, more recent spectroscopically determined values for gas phase *n*-butane of 0.67 ± 0.10[14] and 0.69 ± 0.10[12] and the value of 0.71 ± 0.02 from analysis of electron diffraction data[11] clearly show that this condensed phase effect is only at most around 0.1 kcal/mol in magnitude. Values determined for *n*-pentane liquid, 0.50 ± 0.07 kcal/mol,[5] and vapor, 0.47 ± 0.03 kcal/mol,[9] and for *n*-$C_{11}H_{24}$ through *n*-$C_{14}H_{30}$ alkanes in the liquid phase, 0.51 ± 0.05 kcal/mol,[4] have shown that the gauche energy is higher in *n*-butane than in longer alkanes. Typically, a value of around 0.50 kcal/mol is used for modeling of long-chain alkanes and polyethylene which leads to a gauche fraction of approximately 0.38 at 298 K.[17]

Many ab initio quantum chemistry studies of the gauche energy in *n*-alkanes have also been performed.[14,18−22] The

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calculated gauche energy in *n*-butane has been shown to depend on basis set, electron correlation treatment, and whether correlation effects are considered in the optimization of the molecular geometries. In the earlier studies (see, for example, refs 18 and 19) values of 0.7−0.9 kcal/mol were obtained after correction for zero-point vibrational energy contributions. However, the use of very large basis sets and electron correlation treatment (including geometry optimization) at the MP2 level or better appears to be necessary to obtain energies of experimental accuracy. In one of the better treatments to date, Frey et al.[22] calculated MP2 energies using a 6-311G** basis set at geometries determined with the same level of calculation (MP2/6-311G**//MP2/6-311G**). In their study, a gauche energy for *n*-butane of 0.50 kcal/mol was obtained.

The same level of effort which has been applied to the determination of the gauche energy in *n*-alkanes has not been applied to the determination of the rotational energy barrier heights. The rotational energy barriers cannot be determined directly from spectroscopic data. The usual approach is to represent the torsional potential in *n*-butane by a cosine series and adjust the coefficients so as to reproduce the observed gauche energy and several low-lying torsional transitions for both the trans and gauche conformers. The first estimates of the barrier heights by this approach were by Chen et al.[23] and Durig and Compton,[3] who both concluded that the *cis* barrier is only 0.8−1.0 kcal/mol higher in energy than the *t–g* barrier, leading to comparable barriers for $t \leftrightarrow g^{\pm}$ and $g^{+} \leftrightarrow g^{-}$ transitions. Later, Compton and co-workers[7] and Stidham and Durig[10] were able to detect more torsional transitions and repeated this analysis. Subsequently, Durig and co-workers[13,14] used the energy levels from ref 10 along with new determinations of the gauche energy and gauche torsional angle to deduce torsional potentials and barrier heights. In all these studies, however, the energies of the excited torsional states corresponding to the measured transitions all lie well below the barriers, and therefore considerable uncertainty may exist in the energy of the rotational energy barriers obtained in this manner. The newest estimates for the *t–g* and cis barriers[14] are 3.62 and 3.95 kcal/mol, respectively. The older spectroscopy-based studies[7,10] generally yielded similar values, with about 1 kcal/mol or less difference in energy between the barriers. As seen from refs 7, 10, 13, and 14, the resulting barrier energies are quite sensitive to the assumed values of the trans−gauche energy difference and the gauche torsion angle.

Ab initio calculations of the rotational energy barriers in *n*-butane indicate that the *cis* barrier is considerably higher in energy than the *t–g* barrier.[18,19,24] This is consistent with the early thermodynamic analysis[2] but is in contrast to values determined by spectroscopy in the manner described above, where similar values for the cis and *t–g* barriers have been estimated. The implications of the assignment of the cis barrier height on the conformational dynamics of the C−C−C−C torsion are considerable: if the cis barrier height is comparable to that of the *g–t* barrier, direct $g^{+}g^{-}$ transitions in *n*-alkanes will occur at a rate comparable to the rate of $t \leftrightarrow g^{\pm}$ transitions, while a high cis barrier would make these transitions unimportant compared to $t \leftrightarrow g^{\pm}$ transitions. The level of uncertainty in the barrier energies from these quantum chemistry studies is rather large, because the same level of theory applied in determining the gauche energy has not been applied in the case of the rotational energy barriers. In principle, it should not be much more difficult to obtain accurate values for the *t–g* barrier than the gauche energy, but one expects to obtain a larger dispersion energy contribution to the cis barrier. As a result, larger basis set (including multiple sets of polarization functions)

and more extensive electron correlation treatments should be used. Raghavachari[18] was the first to include the effect of electron correlation on both the geometry (at the 6-31G* MP2 level) and the energy (at the 6-311G** MP2 level). He obtained values of 3.3 and 6.0 kcal/mol for the *t–g* and cis barriers, respectively. To our knowledge, the only other reasonably high-level calculation of the *t–g* barrier to date is that of Wiberg and Murcko,[19] who performed MP3/6-31+G*//MP2/6-31G* calculations and obtained a *t–g* barrier of 3.40 kcal/mol and a cis barrier of 6.14 kcal/mol in *n*-butane. Allinger et al.,[24] using calculations at the MP2/TZ(2d,p)//CISD/DZ(d,p) level, determined a value of 5.37 kcal/mol for the cis barrier in *n*-butane.

Because the C−C−C−C torsion in *n*-butane involves 1−4 interactions between the terminal methyl groups, the energetics for rotation about a single bond in longer *n*-alkanes, such as the central bond in *n*-hexane, may be quite different than in *n*-butane; i.e., "end" effects may result in different values for the gauche energy and rotational energy barriers for the *n*-butane torsion than in the central torsion *n*-hexane or longer *n*-alkanes. Variance in experimental values for the gauche energy as determined by various investigators for short-chain alkanes of different chain length makes it difficult to judge to what degree the gauche energy depends upon the length of the *n*-alkane chain, although it appears from experiment that the gauche energy is slightly lower in longer *n*-alkanes compared to *n*-butane. Wiberg and Murko[19] computed the gauche energy for the central bond in the series of C_4 to C_8 alkanes at the MP2/6-31g*//HF/6-31g* level and found to be 0.70 ± 0.02 kcal/mol, essentially independent of chain length. Tsuzuki et al.[20] calculated MP4(SDQ)/6-31G*//HF/6-31G* energies for all conformers of *n*-butane, *n*-pentane, and *n*-hexane and obtained an energy of 0.74 kcal/mol for the gauche conformer of *n*-butane and 0.73 kcal/mol for the *tgt* conformer of *n*-hexane. These energies indicate that the gauche−trans energy difference is independent of chain length. However, comparing the gauche energy for *n*-butane obtained by Frey et al.[22] using MP2 optimized geometries (0.50 kcal/mol) to their energy for the *n*-hexane *gtt* conformer (0.41 kcal/mol), some influence of chain length on the gauche energy is indicated. Unfortunately, no energy for the *n*-hexane *tgt* conformer is reported in ref 22. To the best of our knowledge, no studies of the effect of chain length on the rotational energy barriers have been performed.

Of the unsettled issues regarding conformational energies of *n*-alkanes raised above, the first two are particularly amenable to quantum chemistry studies. Specifically, quantum chemistry can address the effect of chain length on the gauche energy and barrier heights for single rotations in *n*-alkanes and the relative heights of the *t–g* and cis barriers. However, the accuracy of the conformational energies from quantum chemistry must first be firmly established. The most important issues which must be considered are the effects of electron correlation on optimized geometries and the resulting conformational energies and the effects of improved basis sets and higher levels of electron correlation treatment on the gauche energy and rotational energy barriers. For simple ethers where electrostatic interactions are important, we saw little change in relative conformer energies by performing geometry optimizations at the MP2 vs SCF level or by improving the treatment of electron correlation in single-point energy calculations over MP2.[25] As electrostatic effects are not likely to be important in *n*-alkanes, dispersion effects may be relatively more important. Therefore, the effects of including electron correlation in geometry optimizations should be investigated with large polarizable basis sets. It is well-known that MP2 level calculations tend to somewhat overestimate dispersion effects;[26] therefore, conformer

TABLE 1: Gauche Conformer Geometries and Energies in *n*-Butane and *n*-Hexane

conform.	geometry	torsional angle	basis set	energy (kcal/mol)[a]			
				SCF	MP2	CCSD	CCSD(T)
butane *g*	6-311G** SCF	114.5	6-311G**	0.95	0.60		
butane *g*	6-311G** MP2	117.8	6-311G**	1.05	0.51	0.59	0.54
hexane *tgt*	6-311G** SCF	113.5	6-311G**	1.03	0.54		
hexane *tgt*	6-311G** MP2	117.8	6-311G**	1.17	0.44		
butane *g*	6-311++G** SCF	114.5	6-311++G**	0.97	0.62		
hexane *tgt*	6-311++G** SCF	113.6	6-311++G**	1.04	0.52		
butane *g*	6-311G(2df,p) SCF	114.5	6-311G(2df,p)	0.99	0.62		
butane *g*	6-311G(2df,p) MP2	117.2	6-311G(2df,p)	1.09	0.53	0.62	
butane *g*	6-311G(2df,p) MP2	117.2	cc-pVTZ	1.13	0.56	0.65	0.59

[a] Absolute energies are available from the authors upon request.

TABLE 2: Rotational Barrier Geometries and Energies in *n*-Butane and *n*-Hexane

conform.	geometry	torsional angle	basis set	energy (kcal/mol)[a]			
				SCF	MP2	CCSD	CCSD(T)
		t–g Energies					
butane *t–g*	6-311G** SCF	60.7	6-311G**	3.65	3.43		
butane *t–g*	6-311G** MP2	60.7	6-311G**	3.68	3.40	3.33	3.28
hexane *t–g*	6-311G** SCF	60.7	6-311G**	3.32	2.92		
hexane *t–g*	6-311G** MP2	60.5	6-311G**	3.36	2.89		
butane *t–g*	6-311G(2df,p) SCF	60.8	6-311G(2df,p)	3.66	3.47		
butane *t–g*	6-311G(2df,p) MP2	60.5	6-311G(2df,p)	3.69	3.45	3.36	
butane *t–g*	6-311G(2df,p) MP2	60.5	cc-pVTZ	3.67	3.44	3.36	3.31
		cis Energies					
butane cis	6-311G** SCF	180.0	6-311G**	6.31	5.96		
butane cis	6-311G** MP2	180.0	6-311G**	6.36	5.92	5.79	5.74
hexane cis	6-311G** SCF	180.0	6-311G**	6.43	5.69		
hexane cis	6-311G** MP2	180.0	6-311G**	6.48	5.63		
butane cis	6-311G(2df,p) SCF	180.0	6-311G(2df,p)	6.31	5.82		
butane cis	6-311G(2df,p) MP2	180.0	6-311G(2df,p)	6.37	5.76	5.67	
butane cis	6-311G(2df,p) MP2	180.0	cc-pVTZ	6.39	5.67	5.58	5.48

[a] Absolute energies are available from the authors upon request.

energies and rotational energy barriers in *n*-butane should be determined with large basis sets and improved electron correlation treatment in order to establish the accuracy of the quantum chemistry energies. This is especially important for the rotational energies barriers, where high levels of theory have not been applied and energies, particularly for the cis barrier, are apparently inconsistent with experiment.

Quantum Chemistry Calculations

We have carried out ab initio electronic structure studies of the conformer energies and rotational energy barriers for *n*-butane and *n*-hexane. These calculations were conducted using the quantum chemistry codes GAUSSIAN92[27] and MULLIKEN[28] on IBM RS6000 workstations at the NASA Ames Research Center and the University of Missouri—Columbia. In our study, SCF and MP2 geometry optimizations of the trans and gauche conformers, the *t–g* barrier, and the cis barriers in *n*-butane were performed using 6-311G** and 6-311G(2df,p) basis sets. For *n*-hexane, SCF and MP2 geometry optimizations were performed for the *ttt* and *tgt* conformers, the *tt–gt* (*t–g*) barrier, and the *tcist* (cis) barrier using a 6-311G** basis set. The well-documented second-order effect which stabilizes *gg* sequences[20–22] in *n*-alkanes is not discussed in this paper. The SCF geometries for the *n*-butane gauche and *n*-hexane *tgt* conformers were also calculated using a 6-311++G** basis set. For *n*-butane, energies were determined at the SCF and MP2 level for the SCF optimized geometries and at the SCF, MP2, CCSD, and CCSD(T) levels for the MP2 geometries. CCSD[29] and CCSD(T)[30] (coupled-cluster with single and double excitations with an approximate treatment of triple excitations)

represent improved treatment of electron correlation over MP2. In fact, the infinite-order CCSD calculations represent a better treatment of electron correlation effects than MP4SDQ[31,32] and the perturbational treatment of triple excitations is comparable in CCSD(T) and MP4SDTQ. Energies were calculated for the various geometries with the same basis set used in the geometry optimization, except for cc-pVTZ[33] single-point energy calculations, where the 6-311G(2df,p) MP2 geometries were used. The cc-pVTZ basis set is a valence triple-zeta basis set with two sets of d polarization functions and a set of f polarization functions on the carbon atoms and a set of p polarization functions on the hydrogen atoms. The basis set parameters were optimized to provide a balanced description of electron contributions from the s, p, d, and f shells which is not the case for the similar-sized 6-311G(2df,p) basis set. The latter is less accurate (but requires less computer time) owing to the added constraint of using the same primitive Gaussian exponents for the valance s and p orbitals. For *n*-hexane, SCF and MP2 energies were determined for all optimized geometries at the SCF and MP2 levels using the same basis set used in the geometry optimizations. The calculated C—C—C—C torsional angles and gauche energies for *n*-butane and *n*-hexane are summarized in Table 1, while the rotational energy barriers are summarized in Table 2.

Gauche Energy in *n*-Butane. The largest basis set and best electron correlation treatment used in our study, CCSD(T)/cc-pVTZ//MP2/6-311G(2df,p), yields a gauche energy for *n*-butane of 0.59 kcal/mol. As described below, using the computed thermodynamic data in Table 3 to adjust for zero-point energy and thermal vibrational effects, gauche—trans enthalpy differ-

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TABLE 3: Thermal Vibrational and Zero-Point Energy Effects for *n*-Butane Conformers and Barriers at 298 K

conf	temp, K	$H_{thermal}$,[a] kcal/mol	$S_{thermal}$,[a] kcal/(mol K)	$A_{thermal}$,[a] kcal/mol	H_{zp},[b] kcal/mol	ΔH_{zp},[c] kcal/mol	ΔH,[d] kcal/mol	ΔA,[e] kcal/mol
t	298	1.927	0.0110	−1.365	80.65	0.00	0.00	0.00
g	298	1.865	0.0106	−1.290	80.77	0.12	0.05	0.19
t	220	0.998	0.0075	−0.643	80.65	0.00	0.00	0.00
g	220	0.949	0.0071	−0.604	80.77	0.12	0.07	0.15
t–g	298	1.374	0.0067	−0.704	80.69	0.04	−0.51	0.70
cis	298	1.394	0.0071	−0.730	80.75	0.10	−0.43	0.74

[a] Thermal vibrational contributions to enthalpy, entropy, and free energy. [b] H_{zp} = zero-point vibrational contribution to enthalpy. [c] Δ indicates value relative to the *t* conformer. [d] $\Delta H = \Delta H_{thermal} + \Delta H_{zp}$. [e] $\Delta A = \Delta A_{thermal} + \Delta H_{zp}$.

TABLE 4: Calculated Structural Parameters for Butane Backbone as a Function of Torsion Angle[a]

dihedral $C_1-C_2-C_3-C_4$	bonds		angle $C_1-C_2-C_4$
	$R(C_1-C_2)$	$R(C_2-C_3)$	
0 (trans)	1.522	1.523	112.64
	$(1.526)^b$	$(1.528)^b$	$(112.9)^b$
22.5	1.522	1.527	112.74
60.5 (*t–g* barrier)	1.523	1.540	112.77
90	1.524	1.532	112.49
105	1.524	1.527	113.03
117.2 (gauche)	1.524	1.526	113.47
$(116.2)^b$	$(1.526)^b$	$(1.528)^b$	$(113.8)^b$
$(117.2)^c$	$(1.531)^c$	$(1.531)^c$	$(113.3)^c$
$(117.6)^d$	$(1.530)^d$	$(1.534)^d$	$(114.3)^d$
135	1.524	1.530	114.21
150	1.530	1.543	114.21
180 (cis barrier)	1.526	1.550	112.20

[a] Calculated at the MP2/6-311G(2df,p) level. Bond lengths in angstroms and angles in degrees. The complete butane Cartesian coordinates are available from the authors on request. [b] MP2/6-31G* as given in ref 13. [c] From electron diffraction data (ref 15) as given in ref 14. [d] From microwave spectroscopy data (ref 35), reanalyzed and given in ref 14.

ences of 0.70 kcal/mol at 0 K, 0.66 kcal/mol at 220 K, and 0.64 kcal/mol at 298 K are obtained, in excellent agreement with the value of 0.67 kcal/mol obtained in the recent IR study of *n*-butane vapor discussed above.[14] The experimental value was obtained from measurements of the gauche fraction over the temperature range 220−298 K. In the analysis it was assumed that the enthalpy and entropy differences between the gauche and trans conformers are nearly independent of temperature. As can be seen from Table 3, this assumption appears to be valid and probably represents a smaller source of uncertainty in the reported experimental gauche−trans enthalpy difference than scatter in the experimental data (see Figure 2 of ref 14).

For all basis sets and geometry optimizations utilized, the MP2 gauche energies are about 0.5 kcal/mol lower than the corresponding SCF values, indicating the presence of important attractive dispersion interactions which favor the gauche conformation. The CCSD and CCSD(T) gauche energies are slightly higher than the MP2 energies, consistent with the fact that MP2 treatment of electron correlation tends to overestimate dispersion effects. The differences between MP2 and CCSD-(T) gauche energies are only a few hundredths of a kcal/mol, however, indicating that MP2 treatment of electron correlation is adequate for calculating the gauche energy in *n*-butane. Small increases (<0.05 kcal/mol) in the gauche energy are seen when diffuse functions (6-311++G**) or additional polarization functions (6-311G(2df,p) or cc-pVTZ) are included in the atomic basis set description.

Geometric parameters involving the carbon backbone are given in Table 4. For a given basis set, the MP2 optimized geometries yield a torsional angle for the gauche conformation about 3° nearer to cis than is found with SCF optimized geometries. The MP2 gauche energies calculated at the MP2 optimized geometries are about 0.1 kcal/mol lower than the MP2 gauche energies calculated at SCF optimized geometries, indicating that for calculation of the gauche energy in *n*-butane optimization of geometries at the MP2 level is more important than using basis sets larger than 6-311G** or electron correlation treatments better than MP2. It is worth noting that our best value for the torsional angle of the gauche conformer of *n*-butane (117.2°, MP2/6-311G(2df,p)) is the same as that obtained from gas phase electron diffraction studies.[15,16] However, the skeletal C−C−C angle is about 0.5−1.0° smaller than the values deduced in ref 14 from the experimental rotational constants.[35] Finally, the calculated dipole moment for gauche *n*-butane (0.08 D) is in excellent agreement with the experimentally determined value (0.09 D).[11]

Given the small differences in the gauche energy in *n*-butane resulting from geometry optimization at the MP2 level vs SCF level (0.1 kcal/mol), from improved correlation treatment over MP2 (<0.05 kcal/mol), and from improvements in the basis set over 6-311G** (<0.05 kcal/mol), we are confident that our best energy of 0.59 kcal/mol from CCSD(T)/cc-pVTZ//MP2/6-311G(2df,p) is accurate to within ±0.10 kcal/mol.

Rotational Energy Barriers in *n*-Butane. Our best treatment of the rotational energy barriers, CCSD(T)/cc-pVTZ//MP2/6-311G(2df,p), yields *t–g* and cis barrier energies of 3.31 and 5.48 kcal/mol, respectively, indicating that the cis barrier in *n*-butane is considerably higher than the *t–g* barrier. A consistent lowering of the barriers is seen with improved treatment of electron correlation; however, the differences between MP2 and CCSD(T) energies are small compared to the height of the barriers or the difference between the *t–g* and cis barriers. Little difference is seen between barrier energies calculated using SCF and MP2 geometries, reflecting the fact that at the barriers the torsional angles are the same for the SCF and MP2 geometries. As was found for the gauche energy, only minor changes in the energy of the *t–g* barrier occur when the basis set is improved over 6-311G**. Some lowering of the cis barrier is seen with the improved basis sets. A complete torsional potential curve computed at the MP2/6-311G(2df,p) level of theory is shown in Figure 2. For the nonstationary points on that curve, the backbone torsional angle was fixed and the remaining degrees of freedom were optimized.

Given the magnitudes of changes in the *t–g* and cis barriers in *n*-butane resulting from optimization at the MP2 level vs SCF level (both <0.05 kcal/mol), from improved correlation treatment over MP2 (<0.05 and <0.3 kcal/mol, respectively), and from improvements in the basis set over 6-311G** (<0.05 and <0.3 kcal/mol, respectively), we are confident that our CCSD-(T)/cc-pVTZ//MP2/6-311G(2df,p) energy of 3.31 kcal/mol for the *t–g* barrier is accurate to within 0.1 kcal/mol and estimate that a value no more than 0.5 kcal/mol lower than our best value of 5.48 kcal/mol for the cis barrier could be expected for the infinite basis set/full configuration interaction limit. *There is no evidence to indicate that higher levels of theory will bring the cis barrier to within about 1 kcal/mol or less of the t–g barrier.*
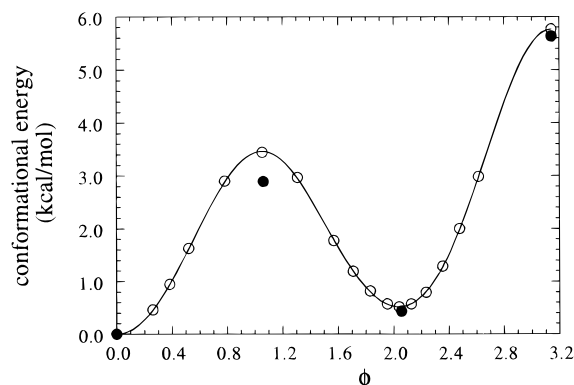
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Figure 2. Computed conformational energies for *n*-butane from MP2/6-311G(2df,p) quantum chemistry calculations. The open circles are the computed energies; the solid curve is an eight-term cosine expansion fit to these data. The solid circles are the *tgt* conformer and barrier energies computed for *n*-hexane at the MP2/G-311G** level.

n-Hexane. Conformational energies for the central torsion in *n*-hexane were also investigated. We believe that MP2/6-311G**//MP2/6-311G** values are sufficiently accurate for comparison of the energies with *n*-butane in order to investigate the effect of chain length. The *tgt* energy in *n*-hexane is slightly lower than the gauche energy in *n*-butane determined at this level of theory (0.44 vs 0.51 kcal/mol). The largest difference between *n*-butane and *n*-hexane is in the t_{-g} barrier, which is about 0.5 kcal/mol lower in *n*-hexane than in *n*-butane (2.89 vs 3.40 kcal/mol). A smaller decrease in the cis barrier is seen (5.63 vs 5.92 kcal/mol). It can be seen in Figure 2 that the energetics for rotation about the central torsion in hexane are similar to those in butane. Considering chain length effects $(5.63 - 5.92 = -0.31$ kcal/mol) along with basis set and electron correlation limitations for *n*-butane discussed above (on the order of −0.5 kcal/mol), our estimated lower bound for the cis energy in *n*-alkanes is $(5.48 - 0.31 - 0.5) = 4.7$ kcal/mol. Even for this limit, the cis barrier is much higher in energy than the t_{-g} barrier. Therefore, for *n*-alkanes of any chain length, the rate of $g^+ \leftrightarrow g^-$ transitions should be negligible compared to the $t \leftrightarrow g^{\pm}$ transitions at reasonable temperatures.

Thermal Vibrational and Zero-Point Energy Effects

In the above discussion, zero-point energy and thermal vibration contributions to the conformer energy differences and rotational energy barriers have not been considered. We calculated these contributions for *n*-butane at 298 K using the harmonic normal-mode frequencies for all real modes. These frequencies were determined at the MP2/6-311G**//MP2/6-311G** level and were scaled by 0.96 to account for the effects of anharmonicity.[34] For the trans and gauche conformers there are 36 real vibrational modes, while for the barriers there are 35 real vibrational modes and one imaginary mode. The thermal vibrational contributions to the enthalpy, entropy, and free energy, along with zero-point energies, are shown in Table 3. The zero-point energy differences between the conformations are small. The loss of a mode in the barrier conformations results in a significant decrease in the thermal vibrational energy relative to the trans and gauche conformers.[36] The loss of this mode also results in a decrease in the thermal vibrational contribution to the entropy, with a net increase in the free energy of the barrier conformations relative to the trans and gauche conformers due to thermal vibrational effects.

The thermodynamic data given in Table 3 were obtained assuming that all modes behave harmonically, so the accuracy of these values needs to be investigated. The scaling factor of 0.96 has been shown to account well for anharmonic effects for modes involving bending and stretching motions.[34] For the torsional modes, however, a uniform scaling of the harmonic frequencies is not as well grounded. The amplitudes of the torsional motions are larger and anharmonic effects tend to be greater than for other modes. A better assignment of torsional energy levels and assessment of the thermal vibrational effects requires solving the Schrödinger equation for a hindered rotor. However, the torsional potential energy function as determined from our quantum chemistry calculations is probably not sufficiently accurate for this purpose. The relative energies of conformations near the trans and gauche minima would have to be accurate to within ±0.02 kcal/mol for 2% accuracy in the energy levels. While we have shown that CCSD(T)/cc-pVTZ//MP2/6-311G(2df,p) level calculations give the gauche−trans energy difference to within experimental error (±0.05 kcal/mol), our calculation of the harmonic vibrational frequencies at the MP2/6-311G**//MP2/6-311G** level yields 114.1 and 116.0 cm^{-1} for the backbone torsional mode for the trans and gauche conformers, respectively. Harmonic vibrational frequencies based upon the experimental observed transitions are 122.9 and 118.5 cm^{-1}, respectively.

We have calculated the contribution of the backbone torsional mode to the zero-point energy and thermal vibrational energy and entropy differences between the trans and gauche conformers using the energy levels and harmonic frequencies determined from the experimental observed transitions.[10] The resulting contributions differ little from those determined using the harmonic frequencies from quantum chemistry. Therefore, the enthalpy and free energy difference between the trans and gauche conformers given in Table 3 are likely to be accurate to within about ±0.05 kcal/mol. The barriers do not involve this mode, and therefore the corresponding energy differences are at least as accurate for the cis and t_{-g} barriers. While it is unclear (at least to the authors) how thermal vibrational and zero-point effects given in Table 3 should best be considered in comparing ab initio energies for rotational energy barriers with either potentials derived to reproduce experimentally observed torsional transitions or values from potential functions used in classical molecular mechanics calculations, it is evident that these effects are very similar for the t_{-g} and cis barriers and that improved treatment of the torsional modes is unlikely to significantly alter the difference in energy between the t_{-g} and cis barriers determined from our quantum chemistry studies. The conclusion is that the quantum chemistry calculations unambiguously support an energy difference of approximately 2 kcal/mol between the heights of the cis and t_{-g} barriers.

Torsional Potential Function for *n*-Butane

Our quantum chemistry studies indicate unequivocally that the cis barrier in *n*-alkanes is significantly higher than the t_{-g} barrier, as discussed above. Previous efforts at deriving torsional potential functions for *n*-butane which reproduce the observed low-lying torsional transitions for the trans and gauche conformers have indicated that the cis and t_{-g} barriers are similar in energy.[3,7,10,14,23] However, we believe that the large energy difference between the cis and t_{-g} barriers in *n*-butane predicted by our quantum chemistry calculations is consistent with the observed torsional transitions. The most recent torsional potential function for *n*-butane based upon observed torsional transitions is that of Herrebout et al.[14] They used a gauche energy of 0.67 kcal/mol at a torsional angle of 117.2°, in good agreement with our quantum chemistry predictions, in determining their potential. In that work, the conformational energy of *n*-butane $V(\phi)$ as a function of the backbone torsional angle ϕ
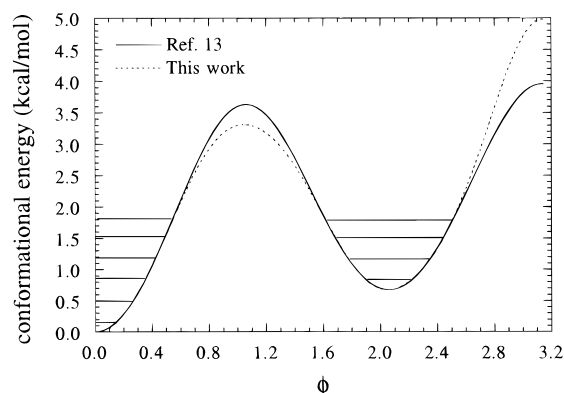
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Figure 3. Torsional potential function for *n*-butane. The solid line is from ref 13. The dashed line is given by eq 1 for $j = 8$ and $M_1 = 1.1942$, $M_2 = -0.3579$, $M_3 = 3.4117$, $M_4 = -0.2102$, $M_5 = 0.2664$, $M_6 = -0.142\,26$, $M_7 = 0.107\,82$, and $M_8 = -0.087\,48$, all in kcal/mol. The horizontal lines are the torsional energy levels corresponding to the observed transitions.

TABLE 5: Observed and Calculated Torsional Transition Energies in *n*-Butane

| | | transition energy (cm^{-1}) | | |
| | | observed | calculated | |
conformer	transition	ref 10	ref 14	this work
trans	$1 \leftarrow 0$	121.28	121.48	121.15
	$2 \leftarrow 1$	118.82	118.99	119.20
	$3 \leftarrow 2$	116.08	116.26	116.61
	$4 \leftarrow 3$	113.00	113.25	113.40
	$5 \leftarrow 4$	109.84	109.93	109.54
gauche	$\mp1 \leftarrow \pm0$	116.60	116.62	116.51
	$\mp2 \leftarrow \pm1$	114.10	114.16	113.78
	$\mp3 \leftarrow \pm2$	111.30	111.37	111.00

was fit to a cosine series of the form

$$V(\phi) = \sum_{n=1}^{j} 0.5 M_n (1 - \cos(n\phi)) \qquad (1)$$

where $j = 6$. The torsional potential function, along with the energy levels corresponding to the observed transitions, is shown in Figure 3. The resulting cis and t–g barriers are 3.95 and 3.62 kcal/mol, respectively. The observed transitions involve only torsional energy levels that lie well below the barriers.

An alternative torsional potential function of the form of eq 1 with $j = 8$ is also shown in Figure 3. This function was chosen so as to accurately reproduce the conformational energy of *n*-butane as predicted by the potential function of ref 14 (which accurately reproduces the observed transitions) for energies below those of the highest torsional energy levels shown in Figure 3. The torsional potential function also reproduces our best estimates for the cis and t–g barriers in *n*-butane based upon quantum chemistry. We have calculated torsional energy levels for both torsional potential functions illustrated in Figure 3 using the internal rotation constant as a function of ϕ for *n*-butane given by Herrebout et al.[14] and the basis set expansion technique described in ref 37. The torsional transition energies are given in Table 5. Using the torsional potential parameters given in ref 14, our calculated transition energies are 0.1–0.25 cm^{-1} higher than the experimentally observed values for *trans*-butane and are within 0.1 cm^{-1} for *gauche*-butane. Herrebout et al.[14] claim better agreement with experimental data, but they do not provide the torsional potential parameters to sufficient precision to allow us to reproduce their results. The transition energies resulting from our modified

torsional potential (which has not been optimized with respect to the observed transitions) are also in good agreement with experiment.

The agreement between the energy levels calculated for these two torsional potentials demonstrates that the actual barrier heights cannot be determined unambiguously from the observed torsional transitions between low-lying trans and gauche energy levels. We have demonstrated that quantum chemistry calculations can be used to reliably determine the gauche energy, conformer geometries, and barrier heights. We therefore believe the most accurate torsional potential can be obtained by using this information in conjunction with observed transition energies.

Conclusions

High-level quantum chemistry studies yield energies for the gauche conformer and the t–g and cis barrier of 0.59 ± 0.1, 3.31 ± 0.1, and 5.48 kcal/mol, respectively, in *n*-butane. Our estimated lower bound for the cis energy is 5.0 kcal/mol, indicating that the cis barrier in *n*-butane is much higher than the t–g barrier. For the central bond in *n*-hexane, the gauche energy is about 0.07 kcal/mol lower than the gauche energy in *n*-butane at the same level of theory. The chain length effect is greater on the barriers, with the t–g and cis barriers being about 0.5 and 0.3 kcal/mol lower, respectively, for the central bond in *n*-hexane compared to *n*-butane. Incorporation of thermal vibrational and zero-point contributions results in an enthalpy difference at 298 K between *gauche*- and *trans*-butane of 0.64 kcal/mol, in excellent agreement with the recent determination of this quantity by Herrebout et al.[14]

Even at the very high level of theory used in this study, the difference between the cis and t–g barriers obtained from quantum chemistry remains in disagreement with values obtained by parametrizing the torsional potential in *n*-butane to reproduce observed torsional transitions. We have demonstrated that a torsional potential function which reproduces the large energy difference between the cis and t–g barriers as determined from quantum chemistry can give the same low-lying torsional transition energies as potentials which maintain little difference between the cis and t–g barriers. A torsional potential can perhaps be best obtained using a combination of observed torsional transitions and high-level quantum chemistry conformer and barrier energies and geometries.

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