Acknowledgment. We wish to acknowledge helpful discussions with Professor Edgar Heilbronner, and financial support of this research from the National Science Foundation.

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Analysis of the Topological Features of the Conformational Hypersurface of *n*-Butane†

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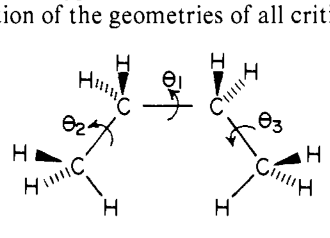
Abstract: An analytic conformational hypersurface was fitted to a total of 63 SCF energy points for *n*-butane. The location of the two minima and two maxima were determined by direct extremization while the positions of the four saddle and four super-saddle points were obtained by minimizing the Euclidean norm of the gradient vector. While the anti conformation was exactly at the point predicted by intuitive stereochemical arguments, the gauche conformation was very sensitive to CH_3 group torsional relaxations.

In recent years, much work has been done regarding conformational and reactive surfaces, but there have been few studied involving hypersurfaces (surfaces of more than two coordinates).[1] We wish to report the determination of the complete torsional hypersurface for *n*-butane (**1**), including the determination of the geometries of all critical points.



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(0, 0, 0)

This triple-rotor hypersurface is of interest for several reasons. First, it serves as an example of a conformational hypersurface of three coordinates. It also allows the accurate determination of the interaction effects of the nonbonded methyl groups, a crucial parameter (as a model for a "gauche interaction") in empirical force-field calculations such as molecular mechanics. Finally, it is a prelude to ab initio hypersurfaces of molecules containing heteroatoms which empirical methods may not be able to treat properly.

As *n*-butane is one of the simplest molecules capable of existing in two stable conformations, anti and gauche, it has been well studied experimentally (see Table I). Also summarized there are the previous empirical results and ab initio calculations. All previous ab initio studies and even some of the much less costly empirical calculations have fixed the methyl groups in the staggered conformation (that is, not allowed for methyl rotation) and have also assumed that the saddle point for the anti-to-gauche conversion occurs at the eclipsed conformer ($\theta_1 = 120°$). Some have even assumed that the gauche conformation has a torsional angle (θ_1) of 60°, despite accumulated experimental and theoretical data to the contrary.

Hendrickson, in the course of his molecular-mechanics calculations on the conformations of cycloalkanes, reported[2] that the gauche minimum occurred at (63°, 55°, 55°). The A(anti) → G(gauche) saddle point was found at the point predicted by simple stereochemical arguments about eclipsed and staggered bonds, namely (120°, 60°, 60°). The bond lengths were fixed at 1.533 and 1.09 Å for C–C and C–H, respectively, for all conformers studied. His barrier-height values (see Table I, ref 2), however, are lower than the experimental values.

Scheraga and co-workers determined[3] the critical points of the *n*-butane hypersurface, using rigid rotation. The gauche conformer was located at (65°, 52°, 52°), and the A → G saddle point at (121°, 60°, 60°). Note the large G → G barrier (see Table I, ref 3) of nearly 14 kcal/mol, compared to the experimental value of 6 kcal/mol.

Bartell calculated[4,5] the gauche minimum to be at (66.8°, 56.7°, 56.7°), optimizing all internal coordinates. All of these

† Presented in part at the "International Symposium on Stereochemistry", Kingston, Ontario, Canada, June 27–July 2, 1976.

0002-7863/78/1500-6911$01.00/0

Table I. Comparison of Experimental and Calculated Results for *n*-Butane

Experimental Results[a]

method	gauche–anti ΔE, kcal/mol	gauche angle (θ_1), deg	A–G[b] barrier, kcal/mol	G–G[b] barrier, kcal/mol	CH_3 rot. barrier[b] for A, kcal/mol	ref
IR spectrosc, entropy data	0.800		3.60		3.60[c]	14
heat capacity			3.60			15
raman spectrosc	0.770 (90)					16
raman spectrosc	0.76 (10)					17
heats of formn	0.7		3.72	5.30	3.40[c]	18
electron diffraction	0.630 (350)	63 (8)				19
electron diffraction		67.5 (11)				7
ultrasonic absorption			4.2 (4)	~6.7		20
temp-dependent NMR spectrosc	0.681 (35)	66 (1)				21
laser Raman spectrosc	0.966 (54)					22
electron diffraction	0.497 (220)	64.9 (60)				23

Empirical Calculations

type of rotation	geometry	method	gauche–anti ΔE, kcal/mol	gauche angle (θ_1), deg	A–G[b] barrier, kcal/mol	G–G[b] barrier, kcal/mol	CH_3 rot. barrier[b] for A, kcal/mol	ref
relaxed	optimized[s]	molecular mechanics	0.6	63	3.2	3.7		2
relaxed[d]	optimized[d]	molecular mechanics	0.73[e]		2.94[f]	4.55[e]		24
relaxed	optimized	molecular mechanics	0.93[r]			4.9		25
relaxed	optimized	molecular mechanics	0.69	64				26
N/A[u]	N/A[u]	thermodynamic anal	0.76	62.3	3.50	4.44		27
rigid	expl	EPEN	1.02	65	4.38[f]		3.30[c]	28
relaxed	optimized[g]	molecular mechanics	0.92[e]		3.26[f]	4.49[e]		29
relaxed	optimized	molecular mechanics	0.675[h]	66.0				30
rigid	exptl	EPEN	0.68	65	3.94	13.74		3
relaxed	optimized	MUB-2	0.54[v]	66.8[w]	4.03	5.56		5

Ab Initio Calculations

type of rotation	geometry	basis set	total energy anti confn, hartrees	gauche–anti ΔE, kcal/mol	gauche angle (θ_1), deg	A–G[b] barrier, kcal/mol	G–G[b] barrier, kcal/mol	CH_3 rot. barrier[b] for A, kcal/mol	ref
rigid	exptl	*i*	−156.405 13	0.822	69.1	3.536[f]	6.821	2.92	31
rigid	exptl	*j*	−157.031 57	0.761	68.7	3.619[f]	6.834	2.94	31
rigid	std	*k*		1.76	77.2	4.00[f]	12.69	3.63[c]	12
rigid	exptl	*k*		1.22	72.3	3.50[f]	7.68	3.26[c]	12
relaxed[o]	std	*k*	−155.465 92	1.13	70.5	3.58[f]	5.72	3.40[c]	12
rigid	std	*l*	−133.024 9	1.47	68.	3.7[f]	10.1	5.5[c]	32
relaxed[o]	std	*m*	−157.070 44	1.09	68.5	3.58[f]	5.95	3.70	33
rigid	std	*n*	−156.535 0	1.8[e]		3.8[f]	10.2[e]	3.4[p]	34
rigid	exptl	*k*	−155.464 37	0.95	69.5	3.56	8.37	3.63[q]	35

[a] Estimated error in last figure enclosed in parentheses. [b] A is anti; G is gauche. [c] Value assumed to be for anti conformation. [d] Not stated explicitly. [e] Gauche conformation assumed to have $\theta_1 = 60°$. [f] Anti-guache barrier taken as $E(\theta_1 = 120°) - E(\theta_1 = 180°)$. [g] Except methyl-group torsional angles apparently. [h] This value is 0.730 kcal/mol when corrected for zero-point vibration. [i] (5s 2p/2s) → [2s 1p/1s]. [j] (7s 3p/3s) → [2s 1p/1s]. [k] STO-3G (Gaussian 70, ref 6). [l] FSGO. [m] 4-31G (Gaussian 70, ref 6). [n] (5s3p/2s) → [2s1p/1s]. [o] C–C–C angles only optimized at each point. [p] The value is 3.1 kcal/mol for the gauche conformation. [q] The value is 2.51 kcal/mol for the gauche conformation. [r] These values refer to ΔG and not ΔE. [s] Bond lengths fixed at 1.533 and 1.09 Å for C–C and C–H, respectively. Taken from ref 36 and used to calculate the G–G barrier. [u] Not applicable, as the authors based their results mainly on recalculations and averages of previous results. [v] This value is 0.63 when corrected for zero-point vibration. [w] Reference 4.

results indicate that there is appreciable methyl-group torsion as the methyl groups interact in the G conformer, but the A → G saddle point is very near the eclipsed conformation (120°, 60°, 60°) that many previous workers have assumed.

The purpose of this work is to investigate the torsional behavior of *n*-butane by ab initio methods, to compute the complete conformational hypersurface, and to determine all of the critical points of the hypersurface.

Method

A total of 63 unique (i.e., not symmetrically related) points on the hypersurface were chosen by independently varying θ_2 and θ_3 from 0 to 90° in 30° increments, for θ_1 values ranging from 0 to 180°, again in 30° steps. A point was also taken at (70°, 60°, 60°) near the anticipated gauche minimum. All calculations were performed using a minimal contracted Gaussian basis set,[6] for the rigid rotation (torsion) at the experimental geometry.[7] This geometry was used, with rigid rotation, for all previous ab initio studies on *n*-butane where a standard geometry was not used (see Table I). The geometries were not optimized for each point so that differences in the determination of the critical points from the hypersurface which permitted completely independent torsional freedom could be ascertained. Partial geometry optimization would probably improve the results but would obscure the comparison with previous ab initio work.

These points were then fitted[8] in a least-squares sense by the analytic equation

$$E(\theta_1,\theta_2,\theta_3) = \sum_{i=1}^{34} C_i f_{1i}(\theta_1,a_{1i},b_{1i}) \times f_{2i}(\theta_2,a_{2i},b_{2i}) f_{3i}(\theta_3,a_{3i},b_{3i}) \quad (1)$$

where θ_1, θ_2, and θ_3 are the torsional angles (measured in radians). The average error of the fit was 0.21 kcal/mol which

Table II. Terms and Coefficients of the Analytic Equation

	θ_1 term			θ_2 term			θ_3 term			
i	f_{1i}[a]	a_{1i}	b_{1i}	f_{2i}[a]	a_{2i}	b_{2i}	f_{3i}[a]	a_{3i}	b_{3i}	C_i
1	1			1			1			5.625 14
2	5	1.0	−2.00	1			1			14.063 08
3	4	0.0	−2.75	5	3.0	−2.50	5	3.0	−2.50	1.835 73
4	5	3.0	−2.00	5	3.0	−1.00	5	3.0	−1.00	0.553 19
5	3	0.0	1.00	1			1			−0.139 32
6	3	0.0	3.00	1			1			2.220 17
7	3	0.0	7.00	1			1			0.077 01
8	1			3	0.0	3.00	3	0.0	3.00	0.352 34
9	3	0.0	6.00	5	3.0	−1.50	5	3.0	−1.50	0.439 45
10	3	0.0	2.00	3	0.0	3.00	3	0.0	3.00	−1.215 11
11	3	0.0	3.00	3	0.0	3.00	3	0.0	3.00	−1.127 71
12	3	0.0	4.00	3	0.0	3.00	3	0.0	3.00	0.447 15
13	3	0.0	5.00	3	0.0	3.00	3	0.0	3.00	1.693 13
14	3	0.0	6.00	3	0.0	3.00	3	0.0	3.00	0.870 57
15	1			3	0.0	3.00	1			1.451 55
16	1			1			3	0.0	3.00	1.451 55
17	3	0.0	1.00	3	0.0	3.00	1			−0.707 75
18	3	0.0	1.00	1			3	0.0	3.00	−0.707 75
19	3	0.0	3.00	3	0.0	3.00	1			0.781 00
20	3	0.0	3.00	1			3	0.0	3.00	0.781 00
21	3	0.0	4.00	3	0.0	3.00	1			0.871 38
22	3	0.0	4.00	1			3	0.0	3.00	0.871 38
23	3	0.0	5.00	3	0.0	3.00	1			0.869 22
24	3	0.0	5.00	1			3	0.0	3.00	0.869 22
25	3	0.0	6.00	3	0.0	3.00	1			0.320 84
26	3	0.0	6.00	1			3	0.0	3.00	0.320 84
27	4	1.0	−4.00	2	0.4	3.00	2	0.4	3.00	−11.089 79
28	4	−1.0	−4.00	2	−0.4	−3.00	2	−0.4	−3.00	−11.089 79
29	4	0.8	−2.25	3	0.87	3.00	3	0.87	3.00	8.768 77
30	4	−0.8	−2.25	3	−0.87	3.00	3	−0.87	3.00	8.768 77
31	4	0.4	−4.00	3	0.82	3.00	1			−5.592 75
32	4	0.4	−4.00	1			3	0.82	3.00	−5.592 75
33	4	−0.4	−4.00	3	−0.82	3.00	1			−5.592 75
34	4	−0.4	−4.00	1			3	−0.82	3.00	−5.592 75

[a] Function codes: 1, 1.0; 2, $\sin(b(\theta - a))$; 3, $\cos(b(\theta - a))$; 4, $\exp(b(\theta - a))^2)$, where $-\pi \le \theta - a \le \pi$; 5, $\exp(b(a\theta)^2)$, where $-\pi \le a\theta \le \pi$.

represents a relative error of 0.47% since the calculated SCF energy difference between the global minimum and global maximum was 45.00 kcal/mol.

The form of the analytic equation (1), detailed in Table II, is deserving of some comment. Each of the 34 terms is a product $f_{1i}(\theta_1)f_{2i}(\theta_2)f_{3i}(\theta_3)$ of three functions, one for each hypersurface coordinate θ_1, θ_2, and θ_3. The actual functions used in each term (f_{1i}, f_{2i}, f_{3i}) and the associated constants (a_{1i}, b_{1i}; a_{2i}, b_{2i}; a_{3i}, b_{3i}) are listed in Table II, along with the terms linear coefficient (C_i) in the sum (1). For example, the first term is $-1.21511 \cos 2\theta_1 \cos 3\theta_2 \cos 3\theta_3$. The function consists of terms for independent rotation about each of the bonds (terms 2, 5-7, 15, and 16) and terms which account for the correlation among the various torsions (terms 3, 4, 8-14, 17-34). The function may also be broken down into terms which are symmetric with respect to rotation (that is θ_i and $-\theta_i$ are not distinguished) and those that are antisymmetric. The first 26 terms fall into the former category, while the last 8 terms (27-34) contribute the hypersurface asymmetry.

There are several restrictions placed on the form of the equation by the symmetry of *n*-butane:

(1) The conformations (θ_1, θ_2, θ_3) and (θ_1, θ_3, θ_2) are enantiomeric, so the equation must be invariant to interchange of θ_2 and θ_3. In other words, for all values of θ_1, the hypersurface must have a diagonal mirror plane cutting the (θ_2, θ_3) subspace.

(2) The conformations (θ_1, θ_2, θ_3) and ($-\theta_1$, $-\theta_2$, $-\theta_3$) are equivalent, forcing inversion symmetry about the origin (0°, 0°, 0°). The point (180°, 0°, 0°) is therefore also a center of inversion.

(3) The equation must be periodic in θ_1, θ_2, and θ_3 with periods of 360, 120, and 120°, respectively.

This last requirement was readily met by using a Fourier expansion, but due to the sharp maxima and large energies calculated for syn conformers (θ_1 near 0°), Gaussian functions proved to give a more compact description of the hypersurface. To obtain a "repeating Gaussian" in accordance with (3), the arguments were reduced to lie between $-\pi$ and π by addition or subtraction of multiples of 2π. These functions (codes 4 and 5 of Table II) are used in terms 2, 3, 4, 9, and 27-34.

Property 1, the equivalence of θ_2 and θ_3, was realized in two ways, the simplest of which is to use a product $f_{2i}f_{3i}$ where the functions f_{2i} and f_{3i} are identical. This may be seen in Table II for functions 1-14 and 27-30. Alternatively, two terms could be added as in $C_if_{1i}f_{2i} + C_if_{1i}f_{3i}$ where f_{2i} is identical with f_{3i}. This form of (1) may be seen for the pairs of terms 15,16 through 25,26, 31,32, and 33,34.

The centers of inversion, property 2, were already incorporated into terms 1-26 since $\cos\theta = \cos(-\theta)$ and all the "repeating Gaussians" were centered at $\theta = 0°$. While deviation of θ_1 from the ideal staggered and gauche angles has been accounted for by the Fourier terms 5-7, 9-14, and 17-26, no such allowance has been made for the methyl rotors. In fact, terms 1-25 will not distinguish between (θ_1, θ_2, θ_3) and (θ_1, $-\theta_2$, θ_3) for any value of θ_1 [there must be no difference for the syn (θ_1 = 0°) or anti (θ_1 = 180°) conformations]. Thus all θ_2 and θ_3 minima will occur at 60° for all values of θ_1.

The last 8 terms in Table II allow for deviations in the (θ_2, θ_3) surface. Note that the effects of these terms are highly localized in θ_1 coordinate space by the large negative exponents

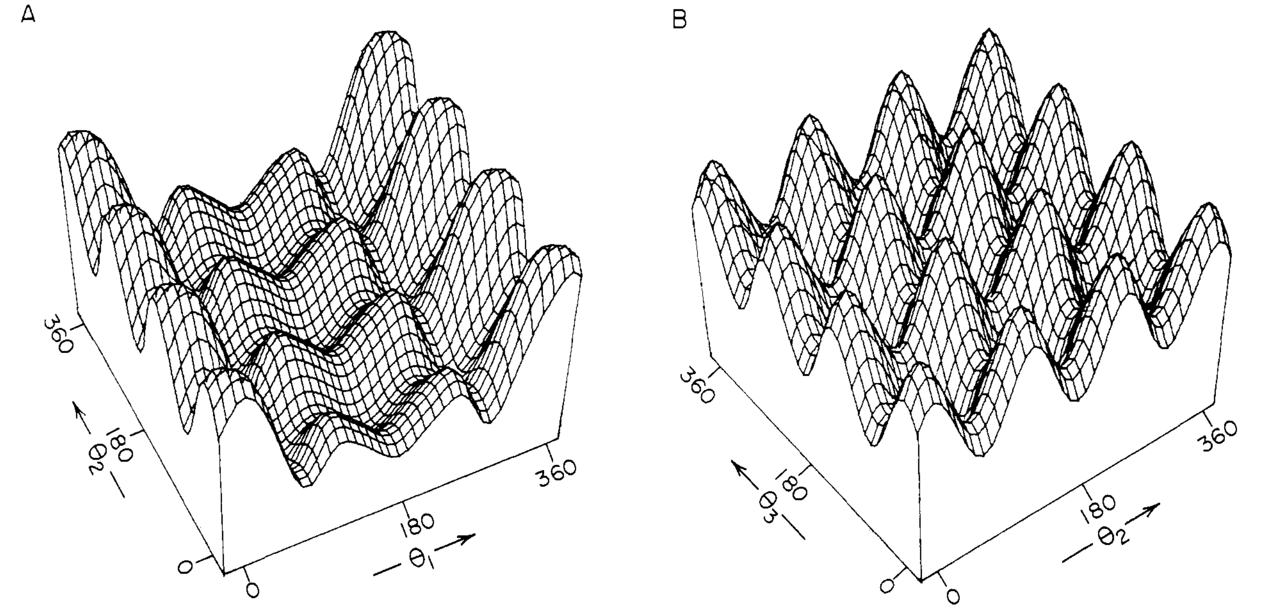

Figure 1. Two cross-sections of the n-butane hypersurface: (A) $E(\theta_1,\theta_2)$ with θ_3 held staggered (60°); (B) $E(\theta_2,\theta_3)$ for the anti conformer (θ_1 = 180°).

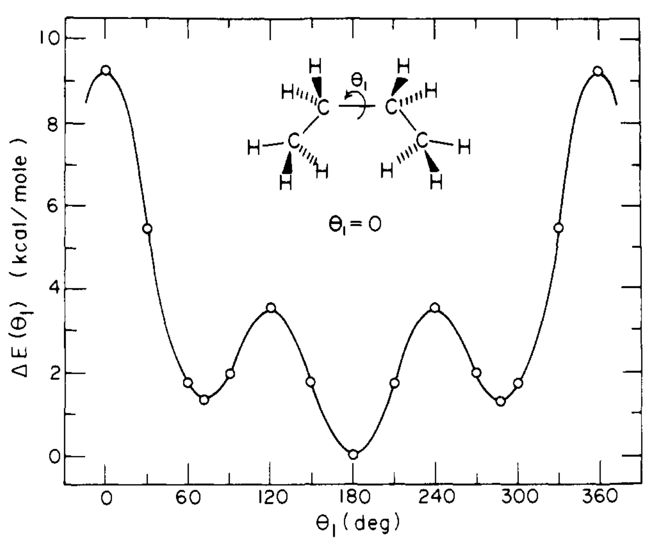

Figure 2. Potential energy of central C-C bond rotation, with both methyl groups held staggered ($\theta_2 = \theta_3$ = 60°).

of the θ_1 "repeating Gaussian" functions. Pairs of terms 27,28 and 29,30 are required to maintain the inversion centers, and the phase of the sine function in term 28 must be reversed to that of 27 when the direction of rotation is inverted. The pair of terms 31,32 is required by property 1 and the pair 33,34 by property 2, resulting in four terms with the same linear coefficient being generated by using term 31.

In total there are 23 different terms, the remaining 11 terms being required to give the hypersurface the correct symmetry properties. There are 15 nonlinear parameters (the a's and b's in eq 1 and Table II) that were partially optimized manually. The 23 linear coefficients were determined by least-squares regression.

Results and Discussion

In Figure 1 are shown two cross sections of the hypersurface. One (Figure 1A) gives $E(\theta_1,\theta_2)$ with θ_3 held staggered, while the other (Figure 1B) displays the dependence of the potential energy on the methyl-group torsional angles for the anti conformer. Figure 2 shows the cross section for central C-C bond rotation with both methyl groups held staggered.

A critical point is defined by a null energy gradient vector

$$\text{grad } E = \mathbf{0} \tag{2}$$

with components

$$\left(\frac{\partial E}{\partial q_1}, \frac{\partial E}{\partial q_2}, \ldots, \frac{\partial E}{\partial q_n}\right) = (0, 0, \ldots, 0) \tag{3}$$

where q_i is some coordinate, often an internal coordinate, and n is the number of coordinates included in the study. A hypersurface of three coordinates may possess four types of critical points: minima (order 0), saddle points (order 1), super-saddle points (order 2), and maxima (order 3). The order refers to the number of negative eigenvalues (imaginary "frequencies")[9] of the Hessian ("force constant") matrix **H**, which has elements

$$H_{ij} = \partial^2 E/\partial q_i \partial q_j \tag{4}$$

Stereochemical intuition may be used to predict the approximate structure of the various critical points since, for hydrocarbons, staggered conformers are usually more stable than eclipsed ones. The critical structures derived from this intuitive consideration are shown in Figure 3. These geometries were used as initial guesses for the critical-point searches on the fitted hypersurface.

The two minima and two maxima were found by direct extremization of the energy, using a variable-metric optimization technique.[10] The eight saddle points were located by the minimization of S_g, the squared length of the gradient vector,[11] where

$$S_g = \sum_{i=1}^{3} [\partial E/\partial \theta_i]^2 \tag{5}$$

Figure 4 shows the positions of the various critical points in a unit cell of the coordinate space. Note especially that there is a saddle point between each pair of adjacent minima and a super-saddle point between each pair of adjacent maxima. Saddle points may be interconnected either through minima or super-saddle points, while in going from one super-saddle point to another, one must pass through either a saddle point or a maximum.

In Table I our results are presented with the experimental values and also with the other theoretical results. Those of

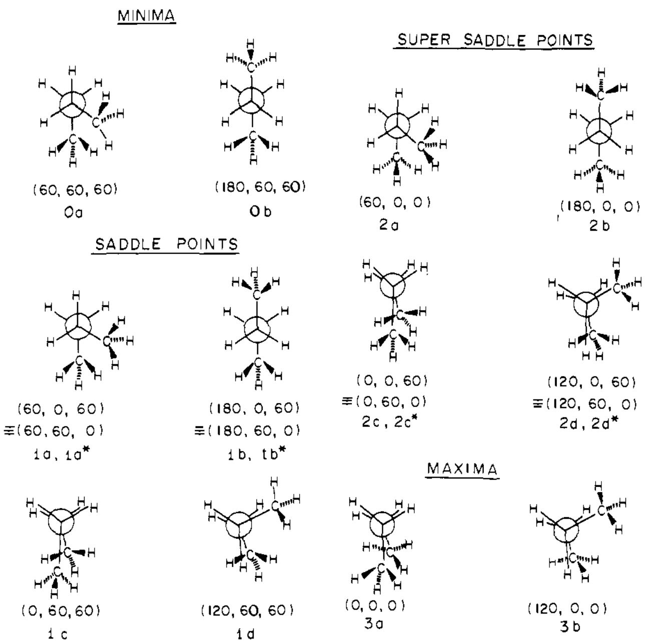

Figure 3. Intuitive structures of the critical points of the n-butane hypersurface.

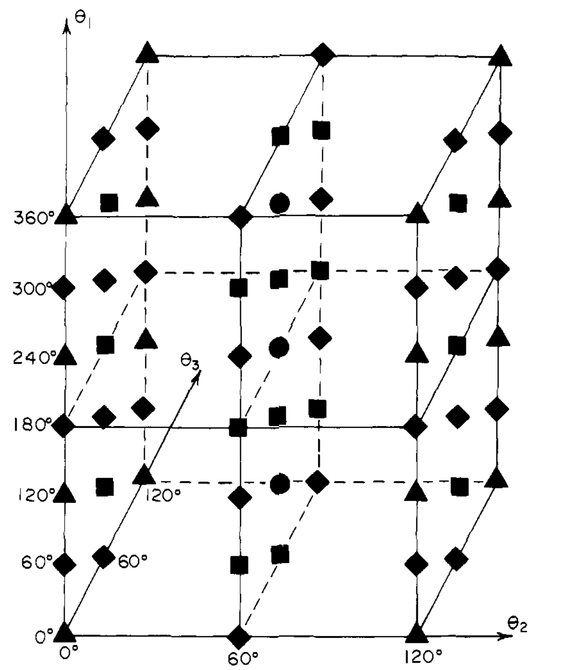

Figure 4. Unit cell of the (θ_1, θ_2, θ_3) coordinate space showing the positions and types of critical points: (●) minima, (■) saddle points, (♦) supersaddle points, (▲) maxima of the hypersurface.

Radom and Pople (ref 12, fourth row of the ab initio part of Table I), who have also calculated ab initio the relevant parameters for rigid rotation of n-butane at the same experimental geometry[7] (curve D of their paper), using the same basis set, are the most comparable. As expected for rigid rotation, the energies of conformers where nonbonded atoms (here, the methyl-group hydrogens) come into close proximity (as in the syn conformers **1c, 2c, 3a**) are overestimated, as the molecular geometry was not relaxed to reduce the interaction. This leads to the overestimation of the gauche–syn–gauche barrier, as may be seen in Figure 2, which corresponds to curve D of Radom and Pople.

In the gauche conformation (**0a**) the methyl groups are rotated away from the "ideal" staggered angle (60°) to reduce the nonbonded hydrogen–hydrogen interaction. This lowers the gauche–anti energy difference by 0.27 kcal/mol and reduces the gauche dihedral angle compared with that of Radom and Pople,[12] who did not allow methyl-group rotation, but has little effect on the anti–gauche barrier since the saddle point still occurs very near the "ideal" (120°, 60°, 60°) conformation (**1d**, see Table III). Our results, however, are in very close agreement with the empricial studies[2-4] mentioned earlier, where the methyl groups were allowed to relax during the searches for the critical points.

The same effect is noticed for methyl-group rotation in the gauche conformation; however, in this case both the minima (**0a**) and the saddle-point (**1a**) structures are significantly shifted from the idealized values (see Table III). The central C–C angle (θ_1) is predicted to increase by about 5° as the saddle point is approached.

Although it might be desirable to compare the hypersurface equation (1) with a simple sum of cosine terms[37]

$$E(\theta_1,\theta_2,\theta_3) = C_1 + C_2 \cos\theta_1 + C_3 \cos 2\theta_1 + C_4 \cos 3\theta_1 + C_5 (\cos\theta_2 + \cos\theta_3) \quad (6)$$

for which a physical interpretation could be assigned to the various terms, there are several difficulties. Primarily, cosine terms alone do not allow for differing energies (the asymmetry discussed earlier) depending on the direction of rotation for θ_2 or θ_3 when θ_1 is not 0 or 180° (note that the energy must be the same for both directions of rotation for O_2 and O_3 when O_1 is 0 or 180°). This is a nonphysical constraint on the equation and would not be lifted by the addition of products of cosine terms for the interaction of θ_1, θ_2, and θ_3 rotations.

Another major difficulty is the average error of 3.26 kcal/mol found for eq 6. This error is larger than most of the barriers and energy differences that are to be determined. The inclusion of cosine terms for the interaction of the three torsions reduced the average error to 2.01 kcal/mol, still unacceptably large. However, as is well-known in statistical analysis,[38] the inclusion of any interaction terms negates the possibility of discussion of the coefficients for the simple (or "main effects") cos $n\theta_i$ terms. This applies not only to this specific case but also to any surface or hypersurface equation with two or more coordinates, where terms which depend on more than one of the coordinates (the interaction terms) are present.

Despite the lack of physical utility of eq 6, the critical points and relative energies determined from it are given in Table IV. The largest energy differences occur for the crucial conformers **0a** and **0b**, the G → G saddle point **1c**, and the global maximum **3a**. The anti–gauche energy difference is 0.95 kcal/mol,

Table III. Critical-Point Torsional Angles for the n-Butane Hypersurface

point[a]	θ_1, deg	θ_2, deg	θ_3, deg	order	energy,[b] kcal mol^{-1}
0a	69.5	52.3	52.3	0	0.90
0b	180.0	60.0	60.0	0[c]	−0.05
1a	74.8	−9.7	60.7	1	3.41
1b	180.0	0.0	60.0	1[c]	3.58
1c	0.0	60.0	60.0	1[c]	9.27
1d	121.5	60.4	60.4	1	3.51
2a	58.1	−6.5	−6.5	2	8.01
2b	180.0	0.0	0.0	2[c]	7.20
2c	0.0	0.0	60.0	2[c]	18.09
2d	112.2	0.7	58.5	2	8.47
3a	0.0	0.0	0.0	3[c]	44.76
3b	125.5	−0.2	−0.2	3	12.93

[a] The structures are shown in Figure 3. [b] The energy was calculated from the fitted equation (1) relative to the total ab initio energy of structure **0b**. [c] This point can also be predicted exactly from stereochemical intuition.

Table IV. Critical Points of the *n*-Butane Hypersurface as Determined from a Simple Sum of Cosines Equation

point[a]	θ_1, deg	θ_2, deg	θ_3, deg	order	energy,[b] kcal mol^{-1}
0a	74.5	60.0	60.0	0	−1.92
0b	180.0	60.0	60.0	0[c]	−2.87
1a	74.5	0.0	60.0	1	3.95
1b	180.0	0.0	60.0	1[c]	3.01
1c	0.0	60.0	60.0	1[c]	15.51
1d	123.6	60.0	60.0	1	2.66
2a	74.5	0.0	0.0	2	9.83
2b	180.0	0.0	0.0	2[c]	8.88
2c	0.0	0.0	60.0	2[c]	21.39
2d	123.6	0.0	60.0	2	8.54
3a	0.0	0.0	0.0	3[c]	27.26
3b	123.6	0.0	0.0	3	14.41

[a] The structures correspond to those of Table III and are shown in Figure 3. [b] The energy was calculated from eq 6, relative to the total ab initio energy of **0b**. [c] This point can also be predicted exactly from stereochemical intuition.

identical with the full hypersurface value, but the barrier heights are not fitted well by (6). For example, the A → G barrier is predicted to be 5.53 kcal/mol (3.56 kcal/mol from (1), and the barrier to methyl rotation in the anti conformation is now 5.88 kcal/mol (3.63 kcal/mol from (1)). Note also that all gauche and eclipsed conformers occur with θ_1 at 74.5 and 123.6°, respectively, and that the values of θ_2 and θ_3 are always 0 to 60° since there are no asymmetric terms for these coordinates.

Although many geometrical quantities are adequately predicted by single-determinant minimal basis set calculations, these results indicate that much care must be taken in the optimization of the minimum and saddle-point geometries for reliable relative energies and barrier heights. Although it would be desirable to generate a complete hypersurface involving more variables (the central C-C bond length and C-C-C angles in particular), the three-coordinate hypersurface for rigid rotation, reported in this work, is already quite complex. The empirical force field results of Bartell,[13] however, indicated that 82% of the stabilization energy on going from a rigid gauche ($\theta_1 = 60°$) structure to the fully relaxed one came from the torsional modes and only 18% from bond-length and bond-angle adjustments. In view of the small potential improvement, the inclusion of more hypersurface coordinates was regarded to be prohibitively complicated.

Acknowledgments. The authors are grateful to Professor L. S. Bartell for helpful suggestions and discussion. We are indebted to the National Research Council of Canada for continuous financial support. M.R.P. thanks the National Research Council of Canada for the award of a postgraduate scholarship.

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