$E(\mathrm{RuB_3}^{3+/2+\cdot}) = -0.81$ V, $W_p - W_r = 0.01$ V, and eq 17 gives $E(0)(\mathrm{P}^{2+/+}) = -0.82$ V. Since $E(0)(\mathrm{P}^{2+/+})$ is the quencher potential where $\Delta G_{23} = 0$, at that potential on the plot in Figure 1, $RT \ln k_q' = RT \ln k_q'(0) = 0.41$ V.

(49) (a) M. J. Powers, D. J. Salmon, R. W. Callahan, and T. J. Meyer, *J. Am. Chem. Soc.*, **98**, 6731 (1976); (b) J. C. Curtis and T. J. Meyer, *ibid.*, **100**, 6284 (1978); (c) B. P. Sullivan and T. J. Meyer, submitted for publication.

Application of Force Field Calculations to Organic Chemistry. 8.[1] Internal Rotation in Simple to Congested Hydrocarbons Including 2,3-Dimethylbutane, 1,1,2,2-Tetra-*tert*-butylethane, 2,2,4,4,5,5,7,7-Octamethyloctane, and Cholestane

Eiji Ōsawa,* Haruhisa Shirahama, and Takeshi Matsumoto

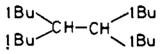
Contribution from the Department of Chemistry, Faculty of Science, Hokkaido University, Sapporo 060, Japan. *Received November 6, 1978*

Abstract: Allinger's new force field MM2 was tested for the calculation of barrier heights of internal rotation about the C–C bond in simple to congested acyclic hydrocarbons. This force field performs satisfactorily for simple hydrocarbons but systematically underestimates barrier heights for highly congested molecules. MM2 calculations were performed to investigate beyond experimental limits novel features of internal rotation in several molecules of current interest. Conformers having nonalternating Newman projections proposed recently by Mislow are confirmed to appear in the torsional itinerary of 2,3-dimethylbutane. 1,1,2,2-Tetra-*tert*-butylethane (**1**) is predicted to possess a distorted gauche ground-state conformation of $(\mathrm{FB})_3$, or essentially $\mathrm{FBE_2}$ rotamer type. Between this global energy minimum and gauche-anti barrier is a wide torsional range in which the novel $\mathrm{F_2BFB_2}$ rotamer type dominates. Internal compression effects were postulated in order to explain the unusually high rotational barrier of the central C–C bond of 2,2,4,4,5,5,7,7-octamethyloctane (**2**) and these were analyzed in some detail and given strong support. In addition, skeletal twisting and unique valence angle variations accompanying the internal rotation of **2** are also attributed to the compression effects. Steric energies of rotamers of cholestane (**3**) regarding the rotation about the $\mathrm{C_{17}}$–$\mathrm{C_{20}}$ bond have been calculated to clarify the controversy over their relative stabilities. They are separated by low barriers (at most 12 kcal/mol). Rotational barriers about the bond between $\mathrm{C_{17}}$ and various alkyl substituents are calculated for models of **3**, and the reason for the reported failure of freezing $\mathrm{C_{17}}$–*tert*-butyl bond rotation is rationalized.

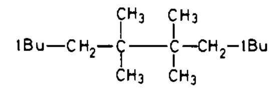
One of the most useful applications of empirical force field calculations[2] to organic chemistry is the analysis of dynamic molecular processes such as the pseudorotations of ring compounds[3] and the correlated rotations of bulky substituents.[4,5] The internal rotation about C–C bonds in alkanes[6] has, however, been treated by this theoretical method only sporadically.[7-12] Recent introduction of truncated Fourier series consisting of one- to threefold cosine functions as an improved expression for torsional potential for saturated molecules,[13,14] instead of the familiar $k(1 - \cos 3\omega)$ type,[2] prompted us to perform systematic survey calculations on the ability of the force field to reproduce experimental barrier heights of $\mathrm{C_{sp^3}}$–$\mathrm{C_{sp^3}}$ bond rotation in acyclic hydrocarbons.[15,16] A few reliable barrier values have recently been obtained for simple to congested alkanes by the dynamic NMR method.[18]

The improved torsional potential has been incorporated into two new force fields: Bartell's MUB-2[19] and Allinger's MM2.[20] The latter was used throughout this work.[21]

As described below, the MM2 force field performed well for simple hydrocarbons but was revealed to underestimate rotational barriers for congested molecules. However, the errors appear systematic and the correct barrier heights can be reasonably estimated based on the MM2-calculated barriers. On the basis of these results, we studied several current topics of internal rotation in some detail. They include the appearance of nonalternating rotamers during internal rotation, the possibility of internal rotations in the extremely crowded 1,1,2,2-tetra-*tert*-butylethane (**1**), the secondary effects of the high rotational barrier of 2,2,4,4,5,5,7,7-octamethyloctane (**2**), and the controversy over the restricted rotation about the $\mathrm{C_{17}}$–$\mathrm{C_{20}}$ bond in steroid systems like cholestane (**3**).

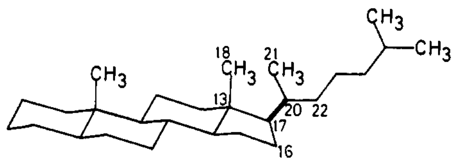


1



$$\mathrm{tBu{-}CH_2{-}\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{C}}{-}\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{C}}{-}CH_2{-}tBu}$$

2



3

Results and Discussion

Comparison between Calculated and Experimental Barriers. ***n*-Butane.** The torsional itinerary for the rotation about the central bond of *n*-butane was calculated by application of the Wiberg–Boyd bond drive technique.[22] Table I compares the characteristic features of the internal rotation obtained by MM2 with those obtained by partly geometry-optimized 4-31G ab initio molecular orbital calculations[23] and available experimental values. The MM2 anti → gauche barrier is in

0002-7863/79/1501-4824$01.00/0

Table I. Internal Rotation of *n*-Butane

	calcd		obsd
	MM2	ab initio	
$\Delta H_f°$, kcal/mol			
eclipse	−25.78		
gauche	−29.64		
anti	−30.50		
anti → gauche transition state	−27.15		
gauche CCCC dihedral angle, deg	65.2	68.5[a]	64.9 ± 6.0[b]
$\Delta\Delta H_f°$, kcal/mol			
gauche-anti	0.86	1.09[a]	0.97 ± 0.05[c]
anti → gauche barrier	3.4	3.58[a]	3.9 ± 0.4[d]
gauche → gauche barrier	3.9	5.95[a] (4.75 ± 1.0)[f]	(4.9)[e]

[a] 4-31G extended basis set with partial geometry optimization, ref 23. [b] W. F. Bradford, S. Fitzwater, and L. S. Bartell, *J. Mol. Struct.*, **38**, 185 (1977). [c] Reference 24. [d] Reference 25. [e] An estimation based on ultrasonic rotational barrier of 2-methylbutane from C_1 (anti) to C_s (gauche) conformation (4.7 kcal/mol, ref 26), the Raman conformational energy for these conformations (0.8 kcal/mol, ref 24), and RT correction (0.6 kcal/mol). [f] Estimate based on Pople's calculation. See text.

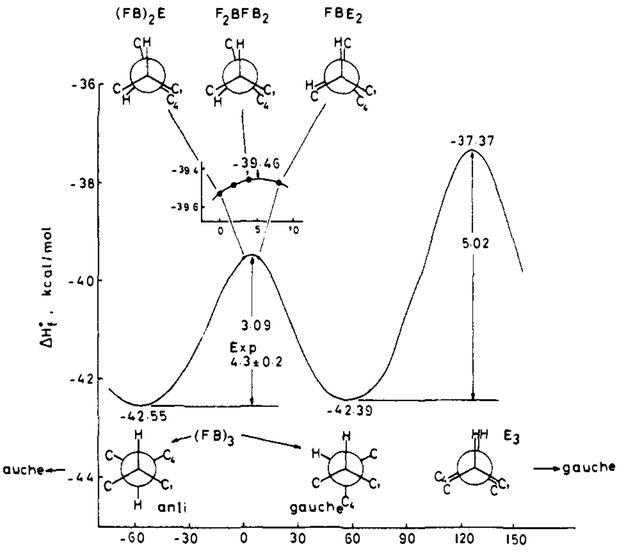


Figure 1. Dependence of calculated heat of formation ($\Delta H_f°$) on torsional angle C_1–C_2–C_3–C_4 of 2,3-dimethylbutane. Experimental value taken from ref 29.

good agreement with the recent experimental value, as is the gauche CCCC dihedral angle and anti vs. gauche conformational energy.

No experimental value is available for the gauche → gauche barrier, and Table I quotes the experimental C_1 (anti) → C_s (gauche) barrier of 2-methylbutane as an aid to its estimation.[25,27] However, the barrier of 2-methylbutane includes a HCCC eclipsing in addition to the CCCC eclipsing and hence 4.9 kcal is probably too high an estimate. Complete ab initio calculations would have been more useful than incomplete experiments. Unfortunately, Pople's value of 5.95 kcal[23] was obtained with partial geometry optimization and hence may be too high. It is suggested that full optimization with a larger basis set will give a substantially lower value (Table I).[28] Under such circumstances, the MM2 gauche → gauche barrier may be regarded as an adequate estimate.

2,3-Dimethylbutane. The structures and the relative populations of anti and gauche conformers of this moderately congested molecule are well studied.[8,29-31] The results of MM2 calculations of the torsional circuit are illustrated in Figure 1. The calculated anti → gauche barrier (enthalpy) is 1.2 kcal lower than the (free energy) NMR barrier, which was unfortunately not yet available when the MM2 parametrization was carried out. The difference is significant, since the entropy change accompanying the internal rotation is generally small[29,30] and the direct comparison between enthalpy and free energy should lead to errors of only a few tenths of a kcal/mol. The MM2 gauche → gauche barrier of 5 kcal may appear quite low compared to the result of STO-3G calculation (7.9 kcal) by Lunazzi,[29] but the ab initio value suffers from incomplete geometry minimization and the minimal basis set used. The best guess based on the STO-3G calculation[29] is 6.4 ± 1.5 kcal.[33] Hence the MM2 gauche → gauche barrier is somewhat low but may be acceptable.

Highly Congested Systems. Pentamethylethane, hexamethylethane, and 2,2,4,4,5,5,7,7-octamethyloctane (**2**) were subjected to MM2 calculations and their barrier heights to internal rotation about the central C-C bond are compared with DNMR values in Table II. The calculated barriers are 3-6 kcal lower than the observed values, and these errors are too high to be overlooked.

So far, the MM2-calculated barriers are always *lower* than experimental barriers for all five hydrocarbons examined. Even though the errors for *n*-butane and 2,3-dimethylbutane are of the order of the standard deviation of the ability of the MM2 force field to reproduce experimental heats of formation (0.42 kcal)[20] and can be overlooked, it is clear that the tendency of MM2 to underestimate the barrier accumulates as the congestion around the bond being rotated increases. As a general trend, the difference between the observed and calculated barrier increases with the number of eclipsing CCCC units at the rotational transition state and the difference per one eclipsing CCCC unit ranges from 1.2 kcal for the anti → gauche rotation of 2,3-dimethylbutane and 1.5 kcal for pentamethylethane and hexamethylethane to 1.8 kcal for gauche → eclipse' rotation (assumed to involve the lowest of the calculated barriers in Table II) of **2**. Since the observed barrier for **2** (13.8 kcal/mol) is the highest ever recorded for C_{sp^3}–C_{sp^3} bond rotation in acyclic hydrocarbons,[30] this molecule may be regarded to involve the highest degree of congestion at the rotational transition state. It then follows that the error in the MM2 calculations of C_{sp^3}–C_{sp^3} rotational barrier in congested molecules will be confined within a small range and this reasoning will be utilized below.

It may be useful to give here some thoughts on the origin of the underestimation of barriers by the MM2 force field. The apparent dependence of the error on the number of eclipsed CCCC units at the barrier may give an impression that either too low a C/C nonbonded repulsion or too small a V_1 constant in the onefold cosine term in the torsional potential is responsible. We do not adopt this argument because the MM2 force field has been parametrized for a large set of standard hydrocarbons which involve a number of cyclic molecules with CCCC eclipsings in the ground state, and it correctly reproduces the activation energy of inversion in cyclohexane.[20] Instead, we suggest that the slope of the repulsive region in H/H or C/H nonbonded interaction potential may be somewhat too low in MM2.[36] Nevertheless, we did not attempt any modification of MM2 but used the force field as it is and estimated in the subsequent discussion the best value for each barrier based on the corrections mentioned above.

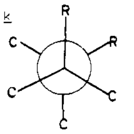
Occurrence of Nonalternating Rotamers. In his work on the extremely crowded 1,1,2,2-tetra-*tert*-butylethane (**1**), Rüchardt[37] commented on the unusual geometry, whose most striking aspect, as first noted by Mislow,[38] is a novel type of Newman projection in which the substituents on the central C-C bond show a nonalternating arrangement. Mislow[38] furthermore pointed out the generality of nonalternating ro-

Table II. Conformational Energies and Barrier Heights of Internal Rotation about the Central C-C Bond in Congested Hydrocarbons (kcal/mol)

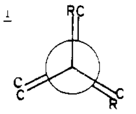
	$\Delta H_f°$ (calcd)[a]	barrier height	
		calcd[a]	obsd
pentamethylethane			
gauche	−48.78[b]	4.1	6.97,[c,d] 6.9[e]
eclipse	−44.72[b]		
hexamethylethane			
twist[f]	−53.99[g]	5.3	9.6–10.0[c,h]
gauche	−53.60		
eclipse	−48.72[b]		
2,2,4,4,5,5,7,7-octamethyloctane (**2**)			
anti	−87.99[i] (−82.83)[j]	a → e → 9.4	13.8[c,d]
gauche[k]	−86.93[i] (−84.25)[j]	g → e → g 8.3	
eclipse[l]	−78.62 (−77.63)[j]	g → e′ → g 7.8	
eclipse′[m]	−79.12 (−76.65)[j]		

[a] MM2 force field. [b] Energy minimization by pattern search procedure and careful adjustment of torsional angles "from both sides" (ref 35) give energy values 20–40 cal/mol lower than these values (K. Mislow. private communication). [c] Reference 30. [d] Free-energy term. [e] Free energy at −134 °C: C. H. Bushweller and W. G. Anderson. *Tetrahedron Lett.*, 1811 (1972). [f] Twist at the central bond of gauche conformation by 14° gives this global energy minimum: ref 31 and footnote 39 of ref 35. See footnote 34. [g] Based on final coordinates kindly provided by Professor K. Mislow. [h] Estimated enthalpy term. [i] DNMR experiments gave a free-energy difference between gauche and anti conformations of 44 cal/mol at −59 °C. ref 30. [j] Forced trans-periplanar conformation. See text. [k,l,m] See structures below.

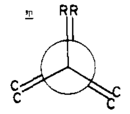
k



l



m

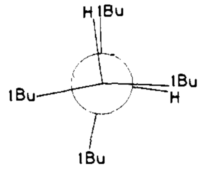


$R = CH_2C(CH_3)_3$, $C = CH_3$.

tamers in the torsional circuits of most simply substituted ethanes based on symmetry arguments. According to Mislow's theory, nonalternating rotamers usually appear near the torsional barriers and hence are difficult to detect by experiments. We checked the computer outputs of torsional circuit calculations for the molecules mentioned above and indeed found ample evidence supporting Mislow's proposal. We take here 2,3-dimethylbutane as an example (Figure 1). The computer drawing of the potential curve as a function of the C_1–C_2–C_3–C_4 dihedral angle initially had indicated the strange fact that the maximum of the gauche–anti interconversion barrier, the second highest point in Figure 1, corresponded neither to the C_1/C_4 eclipsed conformation ($(FB)_2E$ type according to Mislow's terminology[38] with the C_6/methine H dihedral angle of 8.4°) nor to the FBE_2 conformer in which C_6 and methine H are eclipsed. Closer examination revealed that the local maximum point had the nonalternating F_2BFB_2 conformation with dihedral angles of 4.0° for C_1–C_2–C_3–C_4 and −2.6° for H–C_2–C_3–C_6 (Figure 1). All the conformations near the maximum between the $(FB)_2E$ and FBE_2 rotamers are of F_2BFB_2 type, in agreement with Mislow's prediction. It should be noted here, however, that the F_2BFB_2 conformer occurs generally in a relatively small region of the torsional itinerary and gives only a small energy increase relative to the FBE_2 or $(FB)_2E$ conformers in the vicinity. The contribution of nonalternating conformers to the energetics of internal rotation can become significantly large in crowded molecules as discussed below.

Mislow[38] further presented molecular mechanics results indicating an F_2BFB_2 ground state conformation for **1**. Our results on this molecule are mentioned below, together with other computational aspects.

1,1,2,2-Tetra-*tert*-butylethane (1). This remarkably congested hydrocarbon was extensively studied in recent years by Ingold[39] (DNMR), by Rüchardt[37,40] (thermolysis, combustion, and molecular mechanics), and most recently by Mislow.[38] Despite its apparent similarity to 1,1,2,2-tetraphenylethane,[41] which exists preferentially in the anti form, NMR spectra of **1** indicate that it exists exclusively in the gauche form.[37,39] Some ambiguity exists, however, regarding the preferred conformation of the gauche form. Molecular mechanics calculations[37,38,42] with the Engler–Schleyer[43] and Allinger 1971[44] and 1973[2,45] force fields indicate a nonalternating F_2BFB_2 rotamer type[38] (**1A**), whereas calculations with



1A

MUB[38] and White–Bovill[46] force fields lead to an $(FB)_3$ rotamer type. In our hands, relaxation with MM2 force field of an initial coordinate set for the gauche conformer without imposing any symmetry constraint resulted in an $(FB)_3$ rotamer type **1B** (Figure 2).[47] Among the unusual structural features of **1** predicted by the MM2 calculations are a very long C_t–C_t bond (1.604 Å)[48] and a number of abnormal valence angles.

No experimental technique is available to distinguish between **1A** and **1B**; the only information, $^3J_{HH}$ (less than 2 Hz),[39] applies to both. It is thus at the moment impossible to decide which is really preferred. However, the diverse computational results for **1** have one thing in common: the C_q–C_t–C_q angle is widely opened, owing to strong repulsion between geminal *tert*-butyl groups, and consequently the "outer" *tert*-butyl group is almost eclipsed with methine hydrogen at the vicinal carbon atom giving structures which may be regarded as essentially FBE_2 type. We suggest that the apparently diverse results from various force fields arise from the shallow global energy minimum of **1** as shown below.

Bond drive calculations were performed on **1** in order to gain information on its energy hypersurface. At first, the usual "one-bond drive" calculations[22] were attempted by driving only one dihedral angle around the C_t–C_t bond as was done for smaller molecules like *n*-butane and 2,3-dimethylbutane. However, the conventional technique led only to extraordinarily strained, unsymmetrical structures with enormous steric energies, and we could never achieve passing of two *tert*-butyl

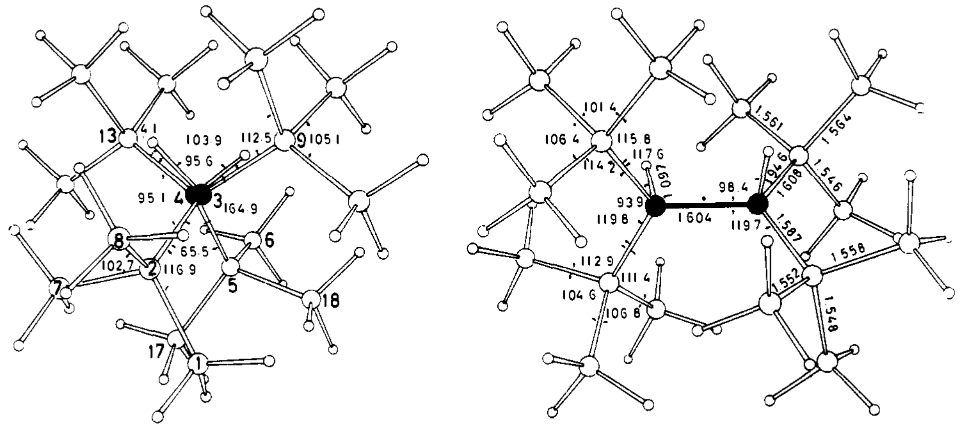


Figure 2. ORTEP drawings of the most stable gauche conformation of 1,1,2,2-tetra-*tert*-butylethane (**1B**). Lengths in ångstroms and angles in degrees.

Table III. Calculated Heats of Formation of Various Conformers and Barrier Heights of Internal Rotation in 1,1,2,2-Tetra-*tert*-butylethane (**1**) by MM2 Force Field (kcal/mol)

$\Delta H_f°$	gauche **1B**	−68.34 (−64.4[a])
	anti **1C**	−27.4[b]
	eclipse **1D**[c]	−38.32[d]
	eclipse **1E**[c]	−17.3[b,d]
	gauche **1F**	−65.41
	gauche **1F'**	−66.66
	gauche **1F''**	−66.19
barrier	gauche → anti (**1B** → **1D**)	43[d]
	gauche → gauche (**1B** → **1E**)	51[d]
	1B → **1F**	8.5 (7[e])

[a] Based on heat of combustion, ref 37. [b] Energy minimization not completed. See text and footnote 51. [c] Energy maximum. [d] These values could be higher by as much as 1.8 kcal/mol per eclipsing CCCC unit because of the tendency of the MM2 force field to underestimate rotational barriers of congested molecules. See text. [e] Experimental free energy observed at −123 °C, ref 39.

groups. It was then realized that simultaneous driving of two, equivalent four-atom units, C_2-C_3-C_4-C_{13} and C_9-C_3-C_4-C_5 (see Figure 2 for numbering), would smoothly rotate the C_t-C_t bond.[49] The potential curves given in Figure 3 were all obtained by the "two-bond drive" calculations.

The solid line corresponds to the C_t-C_t rotation and indicates that both gauche → anti (from **1B** to the left) and gauche → gauche (to the right) interconversions would demand extremely high barriers. As it turned out, the anti form **1C** is not an energy minimum but a maximum. Energy minimization of **1C** could not be completed within an economical run time, but it is probably about 40 kcal/mol more strained than **1B**.[51] The barrier **1D** appearing between **1B** and **1C** is hardly outstanding because of very rapid increase in strain beyond the barrier. Another barrier **1E**, expected to appear in the gauche → gauche process, is so strained that the MM2 force field failed to accomplish energy minimization.[52]

Ingold[39] has suggested a low-temperature gauche conformation **1F** based on the observed splitting of one of the *tert*-butyl signals at −123 °C. We could reach **1F**, an apparent local energy minimum, by rotating the C_q-C_t bonds of **1B** by "two-bond drive" involving C_1-C_2-C_3-C_4 and C_3-C_4-C_5-C_6 after passing through an energy barrier of 8.5 kcal (dashed line, Figure 3), which agrees well with the observed value of 7 kcal.[39] Why did not this barrier come out much lower as the MM2 barrier of the crowded molecules generally did? The rotation **1B** → **1F** does not involve the passing of bulky groups across the rotating axis but can be regarded as an example of a "gear" effect wherein nonbonded H/H distances need not be very short to tide over the barrier. Close examination of the structure of **1F** revealed that C_1-C_2-C_3-C_4 and C_3-C_4-C_5-C_{17} are both eclipsed, and hence there should be lower energy conformations in its vicinity. **1F** was thereupon subjected to the two-bond drive around the C_t-C_t bond. The second drive (dotted line, Figure 3) successfully invoked correlated libration of *tert*-butyl groups[53] at C_2 and C_5, and revealed two new energy minima, **1F'** (C_2 point group, C_8-C_2-C_3-C_4 17.8°) and **1F''** (C_2, C_8-C_2-C_3-C_4 −7.3°) (Table III), which we believe correspond to Ingold's low-temperature gauche conformers of **1**.[54] Thus, the observed splitting of the *tert*-butyl NMR signal at low temperature[39] can be best interpreted in terms of an equilibrium between **1B**, **1F'**, and **1F''** via low barriers by a series of bond rotations.[55]

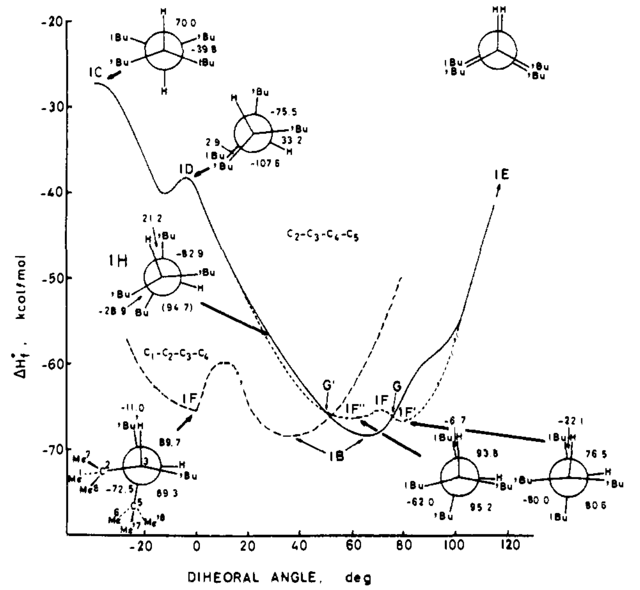


Figure 3. Dependence of calculated heat of formation ($\Delta H_f°$) on torsional angle C_q-C_t-C_t-C_q (C_2-C_3-C_4-C_5, solid and dotted line) and CH_3-C_q-C_t-C_t (C_1-C_2-C_3-C_4, dashed line) in 1,1,2,2-tetra-*tert*-butylethane (**1**). Figures on Newman projections are dihedral angles. Parenthesized figure refers to valence angle. G and G' are crossing points between solid and dotted lines. See text for detail.

Upon continuing the two-bond drive of the C_t-C_t bond of **1F** in both directions, the potential curve (dotted line) merges into that from **1B** (solid line). Namely, the correlated rotation among *tert*-butyl groups works effectively as the groups approach each other and leads to the comfortable disposition of methyl groups in the solid line conformers. Hence, there is no by-pass in the gauche → gauche or gauche → anti intercon-

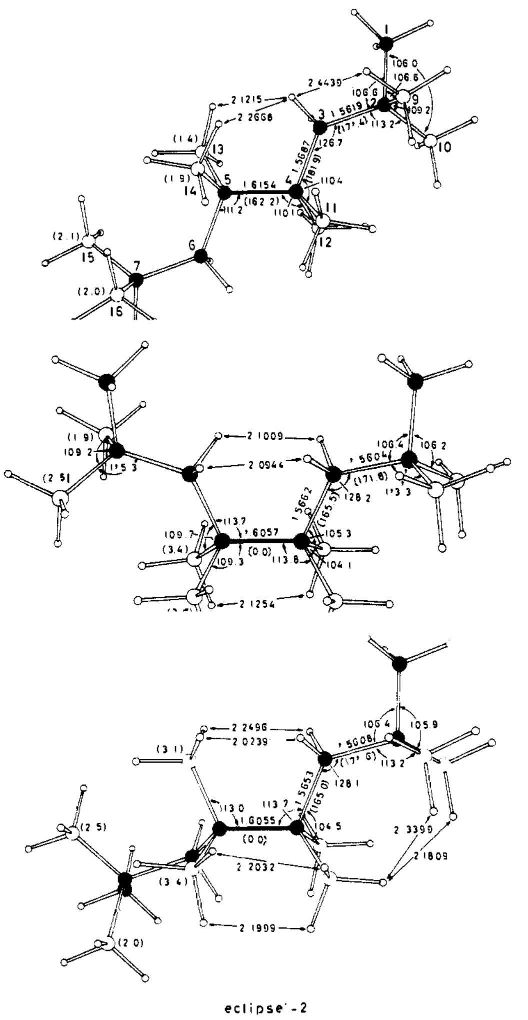


Figure 4. ORTEP drawings of anti, C_{2v} eclipse, and C_2 eclipse conformations of 2,2,4,4,5,5,7,7-octamethyloctane (**2**). Lengths in Ångstroms and angles in degrees. Brackets: dihedral angle along trans C–C–C–C chain involving colored carbon atoms. Parentheses: tilt angle of methyl group from C_{3v} local symmetry.

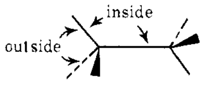
versions of **1** that starts from **1F′** or **1F″**. This conclusion agrees with the experimental observation that **1** decomposes upon heating;[37,39] the estimated lower limits of the rotational barriers to either direction (Table III) are higher than the observed[37] free energy of activation of thermolysis of **1** (31.5 kcal).

While the NMR spectra of **1** do not change at all during heating,[39] our calculations indicate an interesting feature behind the scene. Distinct F_2BFB_2 rotamer type appears near the ground-state conformation **1B**. Suppose the front half of **1B** (or **1F**) is fixed while the back half is rotated clockwise toward **1D**. As the dihedral angle C_2–C_3–C_4–C_5 starts to decrease, the initially small dihedral angles H–C_3–C_4–C_{13} and H–C_4–C_3–C_9 are soon zeroed in and the methine hydrogens quickly pass over eclipsing *tert*-butyl groups, whereas the two "inner" *tert*-butyl groups approach only slowly toward each other to give rise to the F_2BFB_2 type. According to our calculations, this rotamer type already appears when the C_2–C_3–C_4–C_5 dihedral angle decreased from 65.5° in **1B** to 55° with an enthalpy change from −68 to −67 kcal, and persists until immediately before **1D**, or more practically until thermal decomposition sets in. A typical F_2BFB_2 conformer **1H** encountered in the course of rotation is illustrated in Figure 3. In contrast to less congested molecules like 2,3-dimethylbutane, the F_2BFB_2 rotamer type populates heavily near the rotational ground state of **1**.[56]

Table IV. Structural Parameters near Central C–C Bond of Acyclic Alkanes in Various Conformations as Calculated by MM2 Force Field

	length of central bond, Å	angles, deg inside[a]	angles, deg outside[a]	$\sum\Delta$ outside/ $\sum\Delta$ inside[h]
		n-Butane		
anti	1.538	112.200	109.097	
gauche	1.539	113.745	108.918[c]	
eclipse	1.544	116.695	107.935	0.25
		Hexamethylethane		
twist[d,e]	1.572[f]	112.063	106.751[f]	1.07
gauche	1.578[g]	112.261	106.550	1.08
eclipse	1.592[g]	113.198	105.534	
		2,2,4,4,5,5,7,7-Octamethyloctane (**2**)		
anti	1.615	110.426[c]	108.481[c]	
gauche	1.594	110.828[c]	108.055[c]	
eclipse	1.605	111.716[c]	106.429[c]	1.59
eclipse′[h]	1.606	112.272[c]	106.414[c]	1.12

[a] See illustration below. [b] Outside = $\theta_e - (\theta_g, \theta_t, \theta_a)$, inside = $(\theta_g, \theta_t, \theta_a) - \theta_e$. [c] Average value. [d] See footnote *f*, Table II. [e] Based on coordinates supplied from Professor K. Mislow. [f] Electron diffraction values: length of central bond 1.581 ± 0.01 Å, C_m–C_q–C_m (outside) angle 111.0 ± 0.3°, ref 31. [g] Minimum energy structures attained by the pattern search method give slightly shorter lengths for the central C–C bond: 1.574 Å for gauche and 1.586 Å for eclipsed conformer (Professor K. Mislow, private communication). [h] See Figure 4.



Secondary Effect to Rotational Barrier in 2. A startling observation was recently reported, that the rotational barrier around the central bond of hexamethylethane increased as much as 30% as the result of attaching *tert*-butyl groups to methyl groups two bonds away from the rotating bond as in **2** (Table II).[30] Actually, the observed barrier of **2** is the highest recorded for the rotation about a C_{sp^3}–C_{sp^3} bond in an acyclic alkane.[57,58] This observation was interpreted by Anderson[30] on the basis of a compression effect resembling B strain. No evidence for such an effect was, however, presented. We objectively evaluate here the effect by means of force field calculations, and the results strongly support Anderson's theory.

The most straightforward indications for the existence of internal compression that can be extracted from the calculated structures of the various conformers of **2** (Figure 4) are the abnormally large C_2–C_3–C_4 (and C_5–C_6–C_7) angles. They are 126.7, 126.9, 128.1, and 128.2° for the anti, gauche, eclipse (anti → gauche barrier), and eclipse′ (gauche → gauche barrier) conformers, respectively. Such large angles are clearly the result of internal compression operating between the *tert*-butyl and the methyl groups attached at C_4.

The compression seems large enough to cause several further structural deformations. The calculated central bond lengths in various conformers of **2** are considerably longer than those of hexamethylethane (Table IV). In view of the large force constant of C–C stretching,[2,43] the long bond in **2** indicates the existence of very large repulsions across this bond.[59] In *anti*-**2** (Figure 4), for example, 11- and 12-methyl groups must have been pushed strongly by terminal 9- and 10-methyl groups toward the 6-methylene group. Since the 6-methylene is buttressed by a terminal methyl (C_8), which is in turn buttressed by geminal methyl groups (C_{15} and C_{16}), elongation of the C_4–C_5 bond is apparently the only alternative to reduce the crowding. This interpretation is similar to that given by Bar-

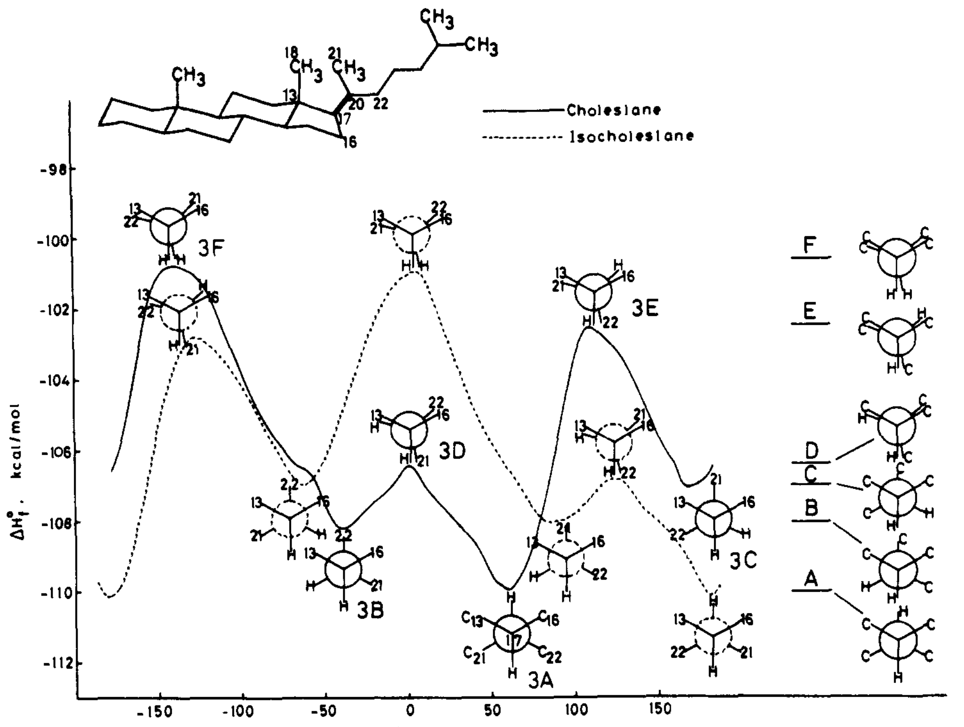


Figure 5. Dependence of calculated heat of formation ($\Delta H_f°$) on torsional angle C_{16}–C_{17}–C_{20}–C_{22} of cholestane (3) and isocholestane (4).

tell[60] to explain the observed elongation of internal relative to external C–C bonds in large *n*-alkanes.[61]

Close analysis of calculated structures of conformers of **2** revealed one more mechanism operating to relieve the internal strain. The trans zigzag arrangement of carbon atoms in the *n*-octane chain of *anti*-**2** is not exactly periplanar as in *n*-octane itself, but is twisted as much as 18° (given in brackets in Figure 4). Such torsional displacements are most pronounced at the center of the molecule, and obviously reduce some of the internal strain due to "1,3-eclipse" type of nonbonded interactions between substituents along the carbon chain of **2** at the small expense of angle strain increase.[62] Eclipsed conformers (Figure 4) may also be regarded as being composed of two twisted *n*-butane units. The amounts of energy gained by the skeletal twists can be estimated by comparing with the energy of an artificial conformer having perfectly trans periplanar skeletal configuration. Results of such calculations, performed utilizing a modification[50] of the Wiberg–Boyd bond drive technique,[22] are included in Table II. The stabilization amounts to 1–5 kcal and significantly affects relative stability of eclipse vs. eclipse′ conformers.

Still another manifestation of unusually strong B strain in **2** is the large deviation from a C_{3v} symmetry in some of the methyl groups. Figure 4 includes the "tilt" angles of methyl groups, which differ among geminal methyl groups because of the skeletal twists mentioned above. The tilt angles appear to increase in going from anti or gauche to eclipse conformers.

Among the structural deformations of **2** examined above, valence angle variations are most pronounced and can be best utilized to demonstrate the effect of B strain on the rotational barrier. Table IV summarizes the valence angles around the central carbon atoms in the main conformers of **2** and related molecules. Angles involving the central, rotating bond are termed here "inside" angles and others at the central atoms "outside angles". The last column of Table IV gives $\sum\Delta$out/$\sum\Delta$in where Δ means angle change between ground state (anti or gauche) and barrier while $\sum$ means taking summations for the anti-eclipse and gauche-eclipse changes. In *n*-butane (and other lightly substituted molecules), for example, the eclipsing bonds bend away from each other, namely, the "inside" angle increases and "outside" angle decreases at the rotational barrier with a consequence that $\sum\Delta$out/$\sum\Delta$in for *n*-butane is considerably smaller than 1. In hexamethylethane, this value is almost equal to 1, since the repulsion among eclipsing methyl groups across the rotating central bond at the barrier is counterbalanced by repulsion among geminal methyl groups. In **2**, this value is considerably greater than 1, indicating that the eclipsing bonds are pushed toward each other compared to its anti conformation. Clearly, the large internal compression present originally in the anti form *increases* in the rotational transition state.

It is very likely that the high rotational barrier in **2** is the result of high B strain in the ground-state conformations which cannot be relieved in the rigid transition state. This mechanism contrasts with unexpectedly low barriers in such crowded molecules as 1,2-di-*tert*-butylcyclohexane[63] and 1,2-di-*tert*-butylbenzene[64] wherein the strain in the rotational transition state can be readily dissipated by structural deformations.[6a,65]

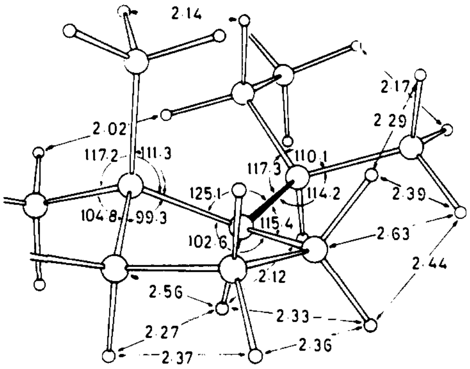
Rotation of the C_{17}–C_{20} Bond of Cholestane. Severe steric congestion between the C_{18} methyl and the side chain attached at C_{17} of steroids was suggested long ago.[66] While the first claim of isolation of a C_{17}–C_{20} rotamer by Kohen[67] was denied by X-ray product analysis by Osawa,[68] controversy on the possibility of uneven rotamer populations continues between two American research groups.[69,70] Nes[69] proposes that some conformational preference manifests itself in the unique product distributions in Grignard additions to some pregnones and in the catalyzed hydrogenation of C_{17}–C_{20} unsaturated derivatives. Trachtenberg[70] opposes this idea by demonstrating that the corresponding rotation in a C_{17} *tert*-butylpregnane cannot be frozen out, even at −110 °C. In view of the ability of the MM2 force field to predict energies and structures of internally rotating systems as demonstrated above, we performed full relaxation calculations of a number of C_{17}–C_{20} rotamers of cholestane (**3**) and 20-isocholestane (**4**).

Starting from the anti H_{17}–H_{20} conformer (**3A**, Figure 5), for which the X-ray coordinates of 2,3-dichlorocholestane[71] served as starting input, the C_{17}–N_{20} bond was rotated through

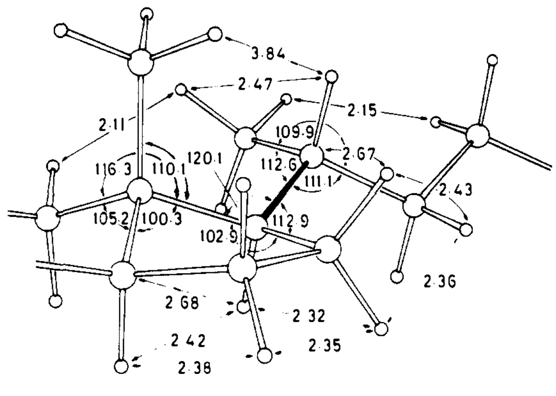
Table V. Relative Steric Energies of C_{17}-C_{20} Rotamers of Cholestane (3) and C_5-C_{10} Rotamers of 1,1,2-Trimethyl-5-*sec*-butylcyclopentane (5) by MM2 Force Field

	3			5		
rotamer[a]	ϕ (16-17-20-22), deg	$\Delta H_f°$, kcal/mol	$\Delta\Delta H_f°$,[b] kcal/mol	ϕ (4-5-10-11), deg	$\Delta H_f°$, kcal/mol	$\Delta\Delta H_f°$,[b] kcal/mol
A	58.315	−109.93	0	57.484	−59.43	0
B	−37.709	−108.21	1.72	−39.594	−58.81	0.62
C	167.556	−107.09	2.84	166.635	−57.02	2.41
D	0.190	−106.44	3.49	0.019	−57.36	2.07
E	104.346	−102.75	7.18	102.465	−52.44	6.99
F	−135.305	−100.87	9.05	−126.349	−50.39	9.04

[a] See Figure 5 for rotamer types. [b] These barriers could be underestimated by as much as 1.8 kcal/mol per eclipsing CCCC unit. See text.



HIGHEST BARRIER



LOWEST POINT

Figure 6. ORTEP drawings of D ring portion of cholestane (3) in its lowest (3A) and highest (3F) energy rotamer around C_{17}-C_{20} bond. Calculated nonbonded distance in ångstroms and valence angle in degrees.

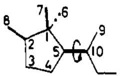
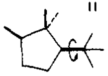
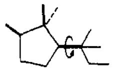
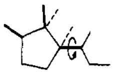
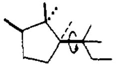
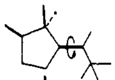
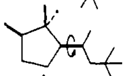
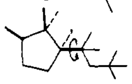
360° at about 10° intervals. Similar calculations were repeated for **4**. In the course of rotation, the D ring showed considerable fluctuation but maintained essentially the C_2 conformation found in crystals.[71] Changes in the calculated heats of formation with C_{16}-C_{17}-C_{20}-C_{22} dihedral angle are plotted in Figure 5. The irregular contour of the potential curve must be the result of five different substituents at C_{17} and C_{20}. Inspection of these curves reveals that the relative heights among the energy maxima and minima depend simply on the pattern in the Newman projection (see the right end of Figure 5). The natural conformer **3A** differs from the other two gauche conformers (**3B** and **3C**) in which one of the two alkyl groups on C_{20} has a 1,3-diaxial relationship with the C_{18}-methyl. **3C** is less stable than **3B** because the large isohexyl group is on the congested C_{13} side. Among the eclipsed conformers (**3D, 3E,** and **3F**), the one involving two eclipsed CCCC pairs (**3F**) is least stable. The relative stability of **3D** vs. **3E** again depends on whether or not the CCCC eclipsing takes place on the C_{13} side. The calculated energies and C_{16}-C_{17}-C_{20}-C_{22} dihedral angles of the cholestane conformers **3A-F** are given in Table V. Isocholestane (**4**) gave essentially the same results as **3**.

Nes[69a,b] states that an eclipsed conformer **3F** can be as stable as the natural gauche form **3A**. According to our calculations, however, **3F** corresponds to the highest rotational barrier. Figure 6 compares the calculated geometry of **3F** near the D ring with that of **3A**. Note, for example, the large C_{13}-C_{17}-C_{20} angle and short H_{12}/H_{21} nonbonded distance in **3F**. We predict that **3F** is about 12 kcal higher in steric energy (after appropriate correction according to footnote *d* of Table VI) than **3A**. This rotational barrier for **3** (and also for **4**) is of a magnitude comparable to that of **2** and hence temperatures close to −40 °C should be necessary to freeze the C_{17}-C_{20} rotation of **3**. Since the rotation of this bond should be practically free at ambient temperature, Nes' proposal[69] of the presence of rotational isomers under the reaction conditions appears unrealistic.

On the other hand, Trachtenberg[70] cooled a 17-*tert*-butylpregnane derivative to −110 °C and still could not observe any sign of line broadening in the NMR signal. However, as discussed above in connection with **2**, attachment of three methyl groups at one end of a bond does not necessarily guarantee a maximum steric hindrance to the internal rotation of the bond. In order to further investigate Trachtenberg's observation, we studied the effect of various substituents at C_{17} and C_{20} on the barrier of rotation about the C_{17}-C_{20} bond by means of model calculations. 1,1,2-Trimethyl-5-*sec*-butylcyclopentane (**5**, Table VI) was chosen as a model and first the computed barriers of C_5-C_{10} bond rotations were compared with those of cholestane **3** (Table V). The relative energies and structures of the important rotamers of **5** agree quite well with those of **3**, and thus we presume that our model is correct. The rotational barriers at C_5-C_{sub} bond of a number of 5-substituted 1,1,2-trimethylcyclopentanes were thereupon calculated and are summarized in Table VI.

It is rather surprising to find that 1,1,2-trimethyl-5-*tert*-butylcyclopentane (**6**), the model for Trachtenberg's compound, is predicted to have the lowest barrier among all the molecules examined! Comparison of **6** with **5** reveals that the *tert*-butyl group raises the energy of the gauche form more effectively than the *sec*-butyl group does, but is not as effective to destabilize the rotational transition state as the *sec*-butyl group. The secondary effect (B strain) appears to operate in **5** to raise the barrier. The same argument applies to the low

Table VI. Steric Energies of Important Rotamers and Barrier Heights of Rotation about C_5–C_{sub} Bond of 5-Substituted 1,1,2-Trimethylcyclopentanes (**5**–**12**) by MM2 Force Field (kcal/mol)

		Most stable rotamer (A)[a]		Most unstable rotamer (F)[a]		Rotational barrier of C_5-C_{sub} bond	
		ΔH_f°	S.E.[b]	ΔH_f°	S.E.[b]	$\Delta H(A)-\Delta H(F)$[c]	corr[d]
5		-59.43	16.47	-50.39	25.50	9.1	12.3
6		-58.88	19.64	-54.08	24.44	4.8	8.5
7		-61.55	22.62	-55.40	28.87	6.2	10.0
8		-61.69	22.58	-52.74	31.54	9.0	12.8
9		-59.94	32.71	-51.45	41.18	8.5	12.3
10		-67.05	24.64	-50.49	41.19	16.5	19.9
11		-76.04	21.40	-67.05	30.39	9.0	12.8
12		-72.01	42.19	-65.19	49.00	4.8	8.9

[a] See Figure 5 for the rotamer type. [b] Strain energy. For definition, see ref 44. [c] Probably too low owing to the tendency of the MM2 force field to underestimate rotational barriers of congested molecules. See text. [d] Corrected barrier estimate based on comparison with test molecules. Corrections per one CCCC eclipsing follow: 1.2 kcal/mol for 1,1,2,2-tetraalkylethane type, 1.5 kcal/mol for 1,1,1,2,2-pentaalkyl- and 1,1,1,2,2,2-hexaalkylethane type, and 0.1 kcal/mol as the secondary effect for each β or γ branch at the rotating bond.

barrier calculated for **7**. Likewise, full substitution at C_5 (**8**) is not effective in raising the barrier of **5**. Full substitution at both ends of the rotating bond (**9**, **12**) works more to raise the energy of the gauche form than to destabilize the eclipsed conformation. Finally, compare **10** and **11**, where hydrogen atoms of an isopropyl methyl of 1,1,2-trimethyl-5-isopropylcyclopentane are replaced by three methyl groups or one *tert*-butyl group. In the case of the C_{sec}–C_{sec} bond rotation, the former replacement is more effective in raising the barrier height. Thus, the cholestane model **5** may be regarded as having efficient structural elements to produce a moderate barrier to C_5–C_{10} bond rotation. It is now clear that Trachtenberg chose a wrong model.

Despite some tendency of the force field employed in this work to underestimate strain at the rotational barriers of heavily congested molecules, the molecular mechanics approach proved powerful in explaining various dynamic conformational phenomena involving the internal rotation of C_{sp^3}–C_{sp^3} bond of several hydrocarbons. Efforts are being continued to apply this computational technique to other areas of interest.

Acknowledgments. We are especially grateful to Professors N. L. Allinger and Kurt Mislow for reading the manuscript. We thank a referee for bringing Professor Bartell's work to our attention, Professor C. Rüchardt for coordinates of **1**, Mr. M. Nojima for generous donation of computer time at the Hokkaido Takushoku Bank, Ltd., Dr. V. V. Kane for a gift of steroid literature collection, and Mr. K. Aigami of Kao Soap Co. for technical assistance. A part of the computer time at the Hokkaido University Computing Center was defrayed by a Grant-in-Aid for Scientific Research from the Ministry of Education, Science and Culture, Japan.

References and Notes

(1) Parts 6 and 7 of this series: E. Ōsawa, K. Aigami, and Y. Inamoto, *J. Chem. Soc., Perkin Trans. 2*, 172, 181 (1979).
(2) (a) N. L. Allinger, *Adv. Phys. Org. Chem.*, **13**, 1 (1976); (b) O. Ermer, *Struct. Bonding (Berlin)*, **27**, 161 (1976); (c) S. R. Miketic and K. Rasmussen, "The Consistent Force Field", Springer-Verlag, West Berlin, 1977.
(3) (a) F. A. L. Anet and T. N. Rawdah, *J. Am. Chem. Soc.*, **100**, 5003, 7166, 7810 (1978); (b) F. A. L. Anet and I. Yavari, *ibid.*, **99**, 6496, 6986, 7640 (1977); **100**, 7814 (1978).
(4) (a) K. Mislow, *Acc. Chem. Res.*, 9, 26 (1976); (b) K. Mislow, D. A. Dougherty, and W. D. Hounshell, *Bull. Soc. Chim. Belg.*, **87**, 555 (1978).
(5) E. Ōsawa, *J. Am. Chem. Soc.*, in press.
(6) Reviews: (a) M. Ōki, *Angew. Chem.*, **88**, 67 (1976); (b) H. Kessler, *ibid.*, **82**, 237 (1970); (c) G. J. Karabatsos and D. J. Fenoglio, *Top. Stereochem.*, **5**, 167 (1970); (d) M. Charton and B. Charton, *J. Am. Chem. Soc.*, **97**, 6472 (1975); (e) R. J. Williams, *Angew. Chem., Int. Ed. Engl.*, **16**, 766 (1977).
(7) Butadiene, vinylcyclopropane, and bicyclopropyl by modified Boyd force field: H. Braun and W. Lüttke, *J. Mol. Struct.*, **31**, 97 (1976). Cf. F. Heinrich and W. Lüttke, *Chem. Ber.*, **110**, 1246 (1977).
(8) *n*-Butane by Engler force field: E. Ōsawa, J. B. Collins, and P. v. R. Schleyer, *Tetrahedron*, **33**, 2667 (1977).
(9) *n*-Butane by the first version of Allinger force field: N. L. Allinger, M. A. Miller, F. A. van Catledge, and J. A. Hirsch, *J. Am. Chem. Soc.*, **89**, 4345 (1967).
(10) Benzenedicarbaldehyde by MMI—MMPI: J.-M. Bernassau, T. Drakenberg, and T. Liljefors, *Acta Chem. Scand., Ser. B*, **31**, 836 (1977).
(11) Haloethanes by special force field: R. J. Abraham and K. Parry, *J. Chem. Soc. B*, 539 (1970); R. J. Abraham and P. Loftus, *J. Chem. Soc., Chem. Commun.*, 180 (1974).
(12) Haloethanes by special force field: (a) G. Heublein, R. Kühmstedt, P. Kadura, and H. Dawczynski, *Tetrahedron*, **26**, 81 (1970); (b) G. Heublein, R. Kühmstedt, H. Dawczynski, and P. Kadura, *ibid.*, **26**, 91 (1970); (c) A. Goursot-Leray and H. Bodot, *ibid.*, **27**, 2133 (1971).
(13) L. S. Bartell, *J. Am. Chem. Soc.*, 99, 3279 (1977).
(14) N. L. Allinger, D. Hindman, and H. Hönig, *J. Am. Chem. Soc.*, **99**, 3282 (1977).
(15) There are two reasons for excluding the C_{sp^3}–C_{sp^3} bond in cyclic hydrocarbons from the test. First, the incorporation of rigid cyclic groups such as phenyl or triptycyl drastically increases rotational barriers for apparent mechanical reasons (ref 6a). Second, the rotation of the endocyclic bond (pseudorotation of ring) has been adequately tested (ref 3).
(16) Ab initio molecular orbital calculations on a sufficiently large basis set with complete geometry optimization (ref 17) are applicable only to small molecules and the force field method provides a practical and general technique for studying complex processes of relatively large molecules with high accuracy and speed.
(17) (a) R. F. Nalewajski, *J. Mol. Struct.*, **40**, 247 (1977); *J. Am. Chem. Soc.*, **100**, 41 (1978); (b) D. Poppinger, *Chem. Phys. Lett.*, **34**, 332 (1975); (c) A. Komornicki, K. Ishida, K. Morokuma, R. Ditchfield, and M. Conrad, *ibid.*, **45**, 595 (1977).
(18) L. M. Jackman and F. A. Cotton, Eds., "Dynamic Nuclear Magnetic Resonance Spectroscopy", Academic Press, New York, 1975.
(19) S. Fitzwater, and L. S. Bartell, *J. Am. Chem. Soc.*, **98**, 5107 (1976).
(20) N. L. Allinger, *J. Am. Chem. Soc.*, 99, 8127 (1977).
(21) MM2 was chosen for this study because of the availability of its previous version MMI/MMPI through the Quantum Chemistry Program Exchange (N. L. Allinger and Y. H. Yuh, QCPE, No. 318). We adapted almost all the features of MMI to construct the MM2 program. The work of adaption requires considerable skill and time. The complete program of MM2 will be released in due time (N. L. Allinger, private communication).
(22) K. B. Wiberg and R. H. Boyd, *J. Am. Chem. Soc.*, **94**, 8426 (1972).
(23) L. Radom, W. A. Lathan, W. J. Hehre, and J. A. Pople, *J. Am. Chem. Soc.*, **95**, 693 (1973).
(24) A. L. Verma, W. F. Murphy, and H. J. Bernstein, *J. Chem. Phys.*, **60**, 1540 (1974).
(25) J. E. Piercy and M. G. S. Rao, *J. Chem. Phys.*, **46**, 3951 (1967).
(26) J. M. Young and A. A. Petrauskas, *J. Chem. Phys.*, **25**, 1943 (1956).
(27) Pople's paper (Table III, ref 23) implies that the gauche-gauche barrier of *n*-butane could be as high as 6.7 kcal/mol (which should read 6.5 kcal/mol), quoting Piercy and Rao's work (ref 25). This value is based not on *n*-butane but on the ultrasonic barrier from C_1 (anti) to C_s (gauche) conformer of 2-methylbutane, and is no longer correct since the conformational energy of 1.8 kcal/mol for these two rotamers used by Piercy now turned out to be too high by a recent Raman experiment (ref 24).
(28) Full geometry optimization will lower the barrier by about 1.2 ± 0.5 kcal/mol and the basis set used leads to a probable error of about 0.5 kcal/mol (N. L. Allinger, private communication).
(29) L. Lunazzi, D. Macciantelli, F. Bernardi, and K. U. Ingold, *J. Am. Chem. Soc.*, **99**, 4573 (1977).
(30) J. E. Anderson and H. Pearson, *J. Am. Chem. Soc.*, 97, 764 (1975).
(31) L. S. Bartell and T. L. Boates, *J. Mol. Struct.*, **32**, 379 (1976).
(32) R. H. Boyd, *J. Am. Chem. Soc.*, **97**, 5353 (1975).
(33) Complete geometry optimization and exact location of the transition state would decrease the barrier (ref 29) by 1.5 ± 0.5 kcal/mol and the error due to the STO-3G basis set will be as high as 1.0 kcal (N. L. Allinger, private communication).
(34) The calculated structure is in good agreement with that obtained by gas electron diffraction analysis, ref 31.
(35) L. D. Iroff and K. Mislow, *J. Am. Chem. Soc.*, **100**, 2121 (1978).
(36) Like in other force fields, the standard set of molecules used to parametrize MM2 force field contains only a few highly congested molecules (hexamethylethane and di-*tert*-butylmethane) at their most stable conformations.
(37) H.-D. Beckhaus, G. Hellmann, and C. Rüchardt, *Chem. Ber.*, **111**, 72 (1978).

(38) W. D. Hounshell, D. A. Dougherty, and K. Mislow, *J. Am. Chem. Soc.*, **100**, 3149 (1978).

(39) S. Brownstein, J. Dunogues, D. Lindsay, and K. U. Ingold, *J. Am. Chem. Soc.*, **99**, 2073 (1977).

(40) C. Rüchardt, H.-D. Beckhaus, G. Hellmann, S. Weiner, and R. Winiker, *Angew. Chem., Int. Ed. Engl.*, **16**, 875 (1977).

(41) D. A. Dougherty, K. Mislow, J. F. Blount, J. B. Wooten, and J. Jacobus, *J. Am. Chem. Soc.*, **99**, 6150 (1977).

(42) Private communication from Professor C. Rüchardt.

(43) (a) E. M. Engler, J. D. Andose, and P. v. R. Schleyer, *J. Am. Chem. Soc.*, **95**, 8005 (1973); (b) J. D. Andose et al., QCPE, No. 348.

(44) N. L. Allinger, M. T. Tribble, M. A. Miller, and D. H. Wertz, *J. Am. Chem. Soc.*, **92**, 2377 (1970).

(45) D. H. Wertz and N. L. Allinger, *Tetrahedron*, **30**, 1597 (1974).

(46) D. N. J. White and M. Bovill, *J. Chem. Soc., Perkin Trans. 2*, 1610 (1977).

(47) We subjected all the final coordinates from previous calculations of **1** by other force fields, provided by courtesy of Professors K. Mislow and C. Rüchardt, as inputs to MM2 calculations and invariably ended up with the same structure **1B**.

(48) For a list of long C–C bonds, both calculated and experimental, see: W. D. Hounshell, D. A. Dougherty, J. P. Hummel, and K. Mislow, *J. Am. Chem. Soc.*, **99**, 1916 (1977).

(49) For a software of the multiple-bond drive technique, see ref 50. The success of two-bond drive and failure of one-bond drive do not necessarily mean that actual molecular movements of **1** involve simultaneous rotation of the two bonds. Failure of the Wiberg–Boyd bond drive technique (ref 22) to rotate large groups of atoms such as phenyl has been previously noticed: J. D. Andose and K. Mislow, *J. Am. Chem. Soc.*, **96**, 2168 (1974).

(50) E. Ōsawa, K. Aigami, and Y. Inamoto, *J. Chem. Soc., Perkin Trans. 2*, 172 (1979).

(51) Rüchardt (ref 37) also indicated unusually high calculated steric energy of **1C**. Complete energy minimization of **1C** was achieved with BIGSTRAN at Princeton and **1C** was indeed shown to be 40 kcal/mol above the ground state (private communication from Professor K. Mislow). However, the final coordinates, kindly supplied by Professor Mislow, failed to converge to an energy minimum with MM2.

(52) The enthalpies in Figure 1 are not corrected for the tendency of MM2 to underestimate the steric energy of congested rotational barriers, in order to keep continuity of the potential curve.

(53) The rotation of *tert*-butyl groups from **1B** to **1F**′ and **1F**″ is the result of forced, concerted, two-bond drive, and hence must be distinguished from "correlated rotation" of *tert*-butyl groups in tri-*tert*-butylsilane (W. D. Hounshell, L. D. Iroff, R. J. Wroczynski, and K. Mislow, *J. Am. Chem. Soc.*, **100**, 5212 (1978)), wherein the passage from one energy minimum to another leads to a permutational exchange in the ligands of both rotors when one is driven and the other follows.

(54) That both **1F**′ and **1F**″ are true energy minima was confirmed by freely relaxing several conformations near **1F**′ and **1F**″ obtained in the course of the second drive calculations. Relaxation of **1F** without any constraint led to **1F**′.

(55) The lowest energy path from **1B** to **1F**′ (or **1F**″) will probably involve concerted three-bond rotation wherein two C_t–C_q bonds and the central C_t–C_t bond rotate more or less simultaneously. It is approximately correct to think that the transformation involves crossing over at the apparent cross point G (or G′) between the solid and dotted lines (Figure 3). At this point and between the solid and dotted lines lie a barrier similar to that depicted between **1B** and 1F with dashed line.

(56) After the present work was completed, a paper appeared in which the occurrence of F_2BFB_2 rotamer type along the torsional circuit of 1,1,2,2-tetra-*tert*-butyldisilane has been demonstrated by empirical force field calculations: S. G. Baxter, D. A. Dougherty, J. P. Hummel, J. F. Blount, and K. Mislow, *J. Am. Chem. Soc.*, **100**, 7795 (1978).

(57) Much higher rotational barriers have been reported for the C_{sp^3}–C_{sp^3} bond connecting rigid, cage substructures: L. H. Schwartz, C. Koukotas, and C.-S. Yu, *J. Am. Chem. Soc.*, **99**, 7710 (1977); H. Iwamura, *J. Chem. Soc., Chem. Commun.*, 232 (1973); M. H. P. Ardebili, D. A. Dougherty, K. Mislow, L. H. Schwartz, and J. G. White, *J. Am. Chem. Soc.*, **100**, 7994 (1978).

(58) For an extensive compilation of experimental data, see S. Sternhell in "Dynamic Nuclear Magnetic Resonance Spectroscopy", L. M. Jackman and F. A. Cotton, Eds., Academic Press, New York, 1975, Chapter 6, p 163.

(59) Such a reasoning is limited to cases where only the nonbonded repulsion is responsible for the elongation of bonds. Other interpretations are available for the experimentally observed bond lengthening of other types: ref 48 and D. A. Dougherty, H. B. Schlegel, and K. Mislow, *Tetrahedron*, **34**, 1441 (1978).

(60) S. Fitzwater and L. S. Bartell, *J. Am. Chem. Soc.*, **98**, 8338 (1976).

(61) In Bartell's case of long *n*-alkanes, it is the 1,3-methylene/methylene nonbonded repulsion which affects the C–C bond length, whereas in the present case it is 1,3-methyl/methylene interactions that count.

(62) Torsional deformations and tilts similar to what is discussed here have been observed in di-*tert*-butylmethane: L. S. Bartell et al., *J. Mol. Struct.*, **37**, 113 (1977).

(63) H. Kessler, V. Husowski, and M. Hanack, *Tetrahedron Lett.*, 4665 (1968).

(64) W. A. Gibbons and V. M. S. Gil, *Mol. Phys.*, 9, 163 (1965).

(65) For this reason, the *P* values proposed by J. E. Anderson and H. Pearson, *J. Chem. Soc. D*, 871 (1971); *J. Chem. Soc., Chem. Commun.*, 908 (1972), do not appear to provide a general basis for estimating van der Waals interactions, unless the difference in the extent of relaxation at the ground state and high-energy state is taken into account for each compound.

(66) C. Altona and H. Hirschmann, *Tetrahedron*, **26**, 2173 (1970), and references cited therein.

(67) F. Kohen, R. A. Mallory, and I. Sheer, *J. Chem. Soc. D*, 580 (1969).

(68) Y. Osawa, T. Makino, and C. M. Weeks, *J. Chem. Soc., Chem. Commun.*, 990 (1976).

(69) (a) W. R. Nes and T. E. Verkey, *J. Org. Chem.*, **41**, 1652 (1976); (b) W. R. Nes, T. E. Verkey, and K. Krevitz, *J. Am. Chem. Soc.*, **99**, 260 (1977); (c) W. R. Nes, *ibid.*, **100**, 999 (1978).

(70) E. N. Trachtenberg, C. Byon, and M. Gut, *J. Am. Chem. Soc.*, **99**, 6145 (1977).

(71) H. J. Geise, C. Romers, and E. W. M. Rutten, *Acta Crystallogr.*, **20**, 249 (1966).

Direct Calculation of Resonance Energies of Conjugated Hydrocarbons with ab Initio MO Methods

Herbert Kollmar

Contribution from the Lehrstuhl für Theoretische Chemie, Ruhr-Universität, 463 Bochum, West Germany. *Received September 21, 1978*

Abstract: Resonance energies of conjugated hydrocarbons were calculated as the energy difference between the ab initio SCF energy and the energy expectation value with respect to a model wave function in which the SCF π orbitals were replaced by appropriate nonresonating localized π MOs (reference state). The contributions of electron correlation and of relaxation of σ orbitals on resonance energies were also computed and found to be rather small in most cases. Since all electrons were included in the calculations, vertical and adiabatic resonance energies could be obtained. The adiabatic resonance energy of butadiene, which was computed to be about 9 kcal/mol, has partly to compensate for the unfavorable repulsion of the two nonresonating π MOs in the reference state. The resonance energies of other hydrocarbons were normalized with respect to butadiene and could thus be compared with thermochemical resonance energies. The largest molecules studied were naphthalene and azulene. The SCF calculations on the latter system gave evidence that azulene probably has a structure with bonds of alternate lengths.

I. Introduction

Originally, the resonance energy of a conjugated hydrocarbon was conceived as the enthalpy difference between the conjugated system and its reference state containing localized nonresonating double bonds.[1-5] The heat of formation of the latter model compound is not a measurable quantity but was deduced from additivity relationships with bond increments taken from compounds without conjugated double bonds.[2-5] However, there is no unique method for the determination of

0002-7863/79/1501-4832$01.00/0