smaller[20] than for the ethane case, it seems likely that the true partition function for this degree of freedom will be somewhat greater than the harmonic oscillator value used in the RRKM calculations. A larger partition function for the transition state would of course *increase* the activated complex theory rate constant. This in turn would result in poorer agreement with experiment, which is 65% of the standard (all vibrations treated as harmonic oscillators) activated complex theory result. Thus it appears unlikely that the harmonic oscillator treatment of the methyl rotation at the transition state is a source of the remaining disagreement between transition-state theory and experiment.

Concluding Remarks

The theoretical vibrational frequencies reported here for the $CH_3NC \rightarrow CH_3CN$ transition state are probably the most reliable obtained to date for a molecule of this size. This consistent reliability (~10%) makes ab initio calculations of activated complex and RRKM rate constants meaningful. At 500 K the experimental preexponential factor of Schneider and Rabinovitch[4] is 65% of that predicted from transition-state theory. Considering the limitations inherent in simple dynamical theories of the activated complex (transition state) or RRKM type, the agreement is encouraging. However, attempts to "invert" experimental rate constants (via the RRKM hypothesis) to infer transition state structural and vibrational parameters should probably be discouraged.

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Internal Rotations in Aliphatic Molecules: *n*-Butane and 2,2,3,3-Tetrafluorobutane

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Abstract: Rotational energy profiles for internal rotations about the central C–C bond of *n*-butane and 2,2,3,3-tetrafluorobutane (TFB) are calculated using ab initio and semiempirical quantum chemical methods. Extensive geometry optimizations are performed for each rotamer. The rigid rotor approximation is seen to provide an adequate representation in the trans-gauche transition region of *n*-butane but CCC bond angle optimizations are necessary in the vicinity of the syn conformer. Optimizations of several geometrical parameters are required for accurate results with the fluoro-substituted molecule. The approximate ab initio PRDDO method is in good agreement with minimal and extended basis set ab initio results for *n*-butane but furnishes poor energy differences and barriers for TFB. On the other hand, PRDDO does provide a cost-effective means of obtaining optimized geometries on which to perform ab initio calculations.

Internal rotations of molecules about covalent bonds play an important role in many branches of chemistry and biology. Much of the conformational freedom of proteins and nucleic acids arises from rotations about bonds involving C, N, O, and P atoms.[1,2] There is much evidence that the structural disorder and phase transitions observed in lipid bilayers[3] are a consequence of trans ↔ gauche rotational transitions about C–C bonds in saturated hydrocarbon domains.[3-5] Accurate po-

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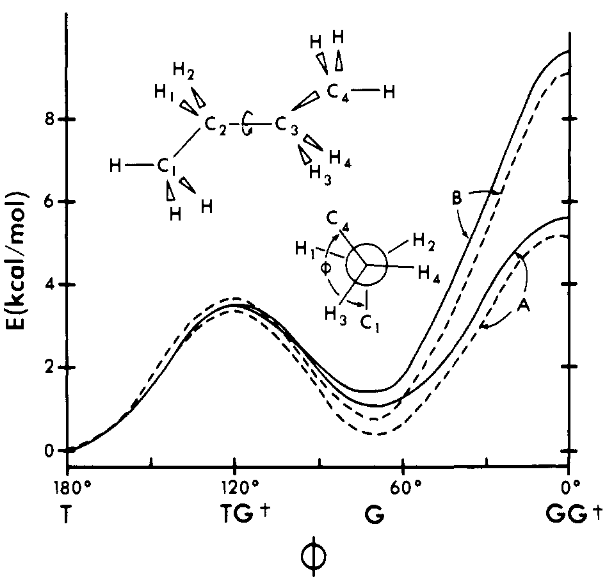

Figure 1. PRDDO (dashed curves) and STO-3G (solid curves) rotational energy profiles for n-butane. Also labeled on the horizontal axis are the trans (T) and gauche (G) conformations as well as the transition regions (TG† and GG†) separating them.

tential-energy profiles for such rotations are therefore necessary for theoretical modeling[4] as well as detailed understanding of the structure of biomembranes.

The experimental results for n-butane,[6-19] the simplest hydrocarbon in which trans and gauche conformations are possible, have not succeeded in evaluating the crucial parameters to the required accuracy. For instance, experimental values of the gauche-trans energy difference range between 0.3[13] and 1.0[13a,16] kcal/mol. As a more dramatic example, the reported energy barriers for trans → gauche conversion vary from 2.2[18] to as high as 30[7] kcal/mol.

A number of theoretical calculations, ranging in methodology from empirical[20-25] to ab initio,[26-31] have been carried out on n-butane in an effort to narrow the ranges of uncertainty and provide detailed information concerning the underlying principles responsible for the potential profile. Whereas the empirical studies have made use of extensive geometry optimization, the ab initio computations have for the most part resorted to the rigid rotor approximation wherein all bond distances and angles are held fixed throughout the rotation of interest. Although this approximation may produce roughly accurate potentials in certain cases, one would not expect quantitatively reliable results without allowing some flexibility to the molecule. In fact, application of the rigid rotor approximation in some cases has resulted in potential-energy profiles with large quantitative errors.[31-36] Ab initio calculations of n-butane are reported here in which the geometry is extensively optimized for each value of ϕ, the dihedral angle about the central C-C bond.

In addition to lipid bilayers which involve saturated hydrocarbon chains, there has been recent interest in the perfluoro-substituted analogues.[37] However, information on relevant fluorine-containing molecules[38-55] is much less abundant than for the parent hydrocarbons. Experimental[45] and theoretical[52-55] evidence points to a slightly twisted helical structure as the most stable for the polymer $(CF_2)_n$, indicating a distortion of ~15° from the trans conformer. It is as yet unclear whether this twist is caused by factors inherent to the monomeric unit or is a result of polymerization. An empirical calculation[53] found a trans-gauche energy difference of 1.1-4.8 kcal/mol and an extremely high barrier of greater than 50 kcal/mol separating trans from gauche conformers of the polymer.

Early dipole measurements[39] of the perfluoro-substituted alkanes led to estimates of gauche-trans energy differences of 0.7-1.4 kcal/mol in contrast to the higher values of 1.1-4.8 kcal/mol obtained previously by IR data.[40] An empirical calculation[54] yielded values between 1.1 and 2.3 kcal/mol for the substituted butane. The only other pertinent data concerning the halogenated four-carbon monomeric unit comes from an NMR study[38] of $CH_3CX_2CX_2CH_3$ (X = Cl, Br).

This paper reports the first quantum-mechanical calculations involving the four-carbon molecule 2,2,3,3-tetrafluorobutane ($CH_3CF_2CF_2CH_3$). It is anticipated that the lack of fluoro substitution on the terminal carbon atoms (thereby maintaining a tractable number of basis orbitals) will not greatly affect the rotational profile about the central C-C bond. As in the case of n-butane, extensive geometry optimizations are carried out for each rotamer. Ab initio calculations are performed also on CHF_2CHF_2 to help gauge the methods used against available experimental data.

Methodology

For unsubstituted n-butane and 2,2,3,3-tetrafluorobutane (TFB), extensive geometry optimizations were performed for various values of the dihedral angle $\phi(C_1C_2C_3C_4)$. The rotamers were assumed to be of C_2 symmetry with the exception of the trans (ϕ = 180°) and syn (ϕ = 0°) structures, which were of C_{2h} and C_{2v} symmetries, respectively. The terminal methyl groups were assumed tetrahedral with r(CH) bond lengths of 1.09 Å but rotations of these groups about the corresponding C-C bonds were allowed. Unless otherwise indicated, the optimizations were carried out using the approximate ab initio method of partial retention of diatomic differential overlap (PRDDO),[56] which has been shown to give results in good agreement with comparable ab initio procedures.[56] A minimal basis set of 1s, 2s, and 2p Slater-type orbitals on C and F and a single 1s orbital on H were used.[57] For each PRDDO optimized geometry, a calculation was carried out using the ab initio GAUSSIAN-70 program[58] with a minimal STO-3G basis set.[59]

For purposes of comparison, in addition to the procedure outlined above and designated A, PRDDO and STO-3G calculations were performed also within the rigid rotor approximation. In this case (B), the geometry of each rotamer was obtained by a simple rotation about the central C-C bond of the PRDDO-optimized trans conformer with no additional geometry changes.

Additional procedures followed for TFB included geometry optimizations via the ab initio STO-3G[59] and semiempirical MNDO[60] methods. Finally, in order to assess the effects of basis-set size on the rotational energy profile of TFB, methods ranging from minimal basis set PRDDO and STO-3G to more extended split valence-shell 4-31G[61] were applied to the smaller 1,1,2,2-tetrafluoroethane (TFE) molecule and the calculated results compared to available experimental data.

Results and Discussion

***n*-Butane.** The potential-energy profiles calculated for n-butane by the above procedures are illustrated for positive values of ϕ in Figure 1. The curves for negative ϕ are mirror images of those shown. The entire range of ϕ thus encompasses three stable rotamers: trans (ϕ = 180°), gauche ($\phi \sim 70°$), and the enantiomer of the latter ($\phi \sim -70°$). The PRDDO and STO-3G profiles, shown as dashed and solid curves, respectively, may be seen to share similar characteristics in either the geometry optimized (A) or rigid rotor (B) cases. Of particular import is the near coincidence of all four curves in the transition region separating trans (T) and gauche (G) conformers. Calculated values of the T → G energy barrier (TG†) which occurs at ϕ = 118° all agree to within 0.2 kcal/mol. The largest deviation between optimized and rigid rotor results occurs in the

Table I. PRDDO Optimized Geometries of *n*-Butane

conformer	dihedral angles, deg[a]		bond angles, deg		bond lengths, Å		
	$C_1C_2C_3C_4(\phi)$	$C_1C_2C_3H_1$[b]	$C_1C_2C_3$	$H_1C_2C_3$[b]	C_1C_2	C_2C_3	C_2H_1[b]
T	180	122	111	110	1.54	1.56	1.10
TG† [c]	118	122	112	110	1.54	1.55	1.10
G	69	122	112	109	1.54	1.55	1.10
GG†	0	123	117	109	1.55	1.57	1.10

[a] Terminal methyl groups remain in staggered conformation with respect to adjacent CH_2 groups for all rotamers studied with exceptions at $\phi(C_1C_2C_3C_4) = 69$ and 30°, where small rotations (~5°) are noted. [b] H_2 may be substituted for H_1 as optimized values are identical. [c] The energy of the TG† conformer is minimized with respect to all geometrical parameters except the dihedral angle ϕ, for which it is maximized.

Table II. Energies[a] and Dihedral Angles for *n*-Butane[f]

	PRDDO		STO-3G					4-31G[b]	
	A	B	A	B	C[d]	D[d]	E[d]	C	exptl[c]
G-T	0.5	0.9	1.08	1.37	1.13	1.22	1.76	1.09	0.3-1.0
TG† [e]	3.4	3.6	3.41	3.51	3.58	3.50	4.00	3.58	2.2-4.6
GG†	4.7	8.2	4.6	8.3	5.72	7.77	12.69	5.96	2.1-6.3
ϕ_G, deg	69	69	69	69	70.5	72.3	77.2	68.5	55-71

[a] All energies are in kcal/mol. [b] Reference 30. [c] Ranges of values from ref 6-19. [d] Reference 31. [e] ϕ = 118° for A, B; ϕ = 120° for C, D, E. [f] A, PRDDO geometry optimization (this work); B, rigid rotation of PRDDO-optimized trans structure (this work); C, rigid rotation (including θ (CCC) optimization) of standard geometry (denoted "C" in ref 31); D, rigid rotation of experimentally determined trans geometry (denoted "D" in ref 31); E, rigid rotation of standard trans geometry (denoted "A" in ref 31).

transition region separating the two enantiomeric gauche conformers. Geometry optimization reduces the rigid rotor energy barrier at ϕ = 0° (GG†) by 45 (STO-3G) and 43% (PRDDO).

Analysis of Table I, where the PRDDO optimized geometries are presented, reveals that the only parameter undergoing a large change during rotation is the CCC bond angle. This angle remains approximately constant throughout the trans → gauche transition but widens by 5° in the syn rotamer separating the two gauche enantiomers. In contrast, the relative invariance of the other geometrical parameters indicates that CCC angle optimization may serve as an effective substitute for the more costly full optimization in the case of *n*-butane. It is perhaps interesting to note that the small rotations of the terminal methyl groups predicted by PRDDO for the gauche conformer (footnote *a*, Table I) have also been observed by Peterson and Csizmadia[26] via ab initio optimizations.

The salient features of the calculations described above are reported in columns A and B of Table II, where they are compared with previous ab initio and experimental data. Columns C, D, and E contain the STO-3G and 4-31G results of Radom et al.[30,31] using several variations of the rigid rotor approximation. Case C includes optimization (via STO-3G) of the CCC bond angle while D and E refer to true rigid rotations.

The largest amount of available experimental information concerns the gauche-trans energy difference (G-T), which has been obtained by calorimetric,[6-10] ultrasonic relaxation,[11] electron diffraction,[12,13] and spectroscopic[14-16] measurements. The most reliable theoretical value obtained in this study by STO-3G calculations of the optimized geometries (1.08 kcal/mol), nearly identical with that found by Radom et al.[30] using the larger 4-31G basis set, is very close to the upper limit of experimental values. The trans → gauche barrier (TG†) calculated here is 3.4 kcal/mol, within the range of experimentally determined data, as are the gauche → gauche barrier of 4.6 kcal/mol and the optimized dihedral angle ϕ = 69° for the gauche conformer.

The near agreement between STO-3G entries in columns A and C support the contention that CCC bond angle optimization is a good approximation to full optimization in *n*-butane. In contrast, rigid rotations of various geometries (B, D, E) lead to substantially larger values of the gauche → gauche transition barrier. For example, the barrier obtained by rigid rotation of a "standard" geometry (case E) is more than double that obtained via either full (A) or partial (C) geometry optimization.

Of further interest is the comparison between energetics calculated by various quantum-mechanical techniques. It may be noted that there is excellent agreement between PRDDO and STO-3G for either case A or case B with the exception of the gauche-trans energy difference, where PRDDO values are smaller by ~0.5 kcal/mol. Further refinement of technique by use of 4-31G leads to very little change in STO-3G results as may be seen by a comparison of the respective values in columns C.

In summary, the geometry optimizations of *n*-butane described above lead to results which are in good agreement with available experimental and previous ab initio data.

2,2,3,3-Tetrafluorobutane. Rotational energy profiles for the fluoro-substituted analogue of *n*-butane are depicted in Figure 2. The qualitative features of the PRDDO and STO-3G profiles in either the optimized (A) or rigid rotor (B) cases are similar with an important exception. For rigid rotation, the PRDDO curve shows a much smaller barrier to gauche → trans conversion (0.2 kcal/mol) than does STO-3G (0.9). Upon PRDDO geometry optimization (A), the STO-3G barrier is reduced to 0.5 kcal/mol, while it has completely disappeared in the PRDDO profile. In order to eliminate the PRDDO parametrization as a source of error, geometries of several rotamers were optimized also using the ab initio STO-3G and the semiempirical MNDO[60] methods. The geometries obtained by all three techniques are described in Table III and the energetics listed in Table IV. STO-3G optimization (denoted A′) produced no change in the magnitude of the gauche → trans barrier but increased both the trans → gauche barrier and the gauche-trans energy difference by 0.5 kcal/mol. The MNDO results indicate a considerably smaller value of the gauche-trans energy difference (0.3 kcal/mol) and a larger trans → gauche barrier (3.7 kcal/mol) than the other methods.

The various optimized bond lengths in Table III are all rather longer than might otherwise be expected. Whereas aliphatic CF and CC bond lengths are typically in the neighborhood of 1.36 and 1.54 Å, respectively,[62] the lengths in Table III range to as high as 1.39 and 1.68 Å. Electron-diffraction studies of various fluoro-substituted ethanes[41-44] yield CC bond lengths between 1.49 and 1.56 Å and CF lengths of

Table III. Optimized Geometries of 2,2,3,3-Tetrafluorobutane

		bond lengths, Å			bond angles, deg		dihedral angles, deg[a]	
conformer	method	C_2C_3	C_1C_2	C_2F_1[b]	$C_1C_2C_3$	$F_1C_2C_3$[b]	$C_1C_2C_3C_4(\phi)$	$C_1C_2C_3F_1$[b]
T (C_{2h})	PRDDO	1.60	1.56	1.39	108	110	180	122
	STO-3G	1.60	1.56	1.38	111	109	180	122
	MNDO	1.67	1.59	1.36	114	108	180	123
TG† [c] (C_2)	PRDDO	1.65	1.57	1.38	111	109	120	122
	STO-3G	1.61	1.56	1.38	112	109	120	122
	MNDO	1.68	1.59	1.36	114	109	120	123
G (C_2)	PRDDO	1.63	1.57	1.39	111	109	87	122
	STO-3G	1.61	1.56	1.38	112	109	82	122
	MNDO	1.67	1.59	1.36	114	108	62	123
GG† (C_{2v})	PRDDO	1.65	1.58	1.39	115	108	0	123
	MNDO	1.68	1.59	1.36	115	108	0	123

[a] Terminal methyl groups are staggered relative to adjacent CF_2 group for all conformers. [b] Values for F_2 are identical with those for F_1. [c] See footnote c, Table I.

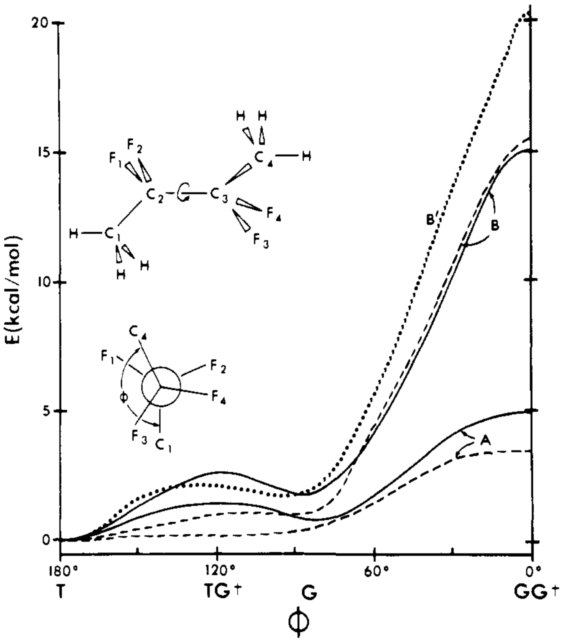

Figure 2. Calculated rotational energy profiles for TFB. Solid curves represent STO-3G and broken curves PRDDO results. The dotted curve (labeled B′) represents rigid rotation with $r(C_2C_3)$ = 1.54 Å as described in the text.

1.32-1.39 Å. It is therefore only the central C_2C_3 bond of TFB for which the calculated lengths deviate significantly from experimental data. (It may be noted that the MNDO procedure yields considerably longer CC bond lengths than the other methods.) It was considered likely that the long C_2C_3 bond was a result of inadequate treatment of the highly electronegative F atoms by the minimal basis sets used.[63]

In order to check whether this long bond was producing artifacts in the calculated profiles, the C_2C_3 bond length of the PRDDO optimized trans geometry of TFB was shrunk to the standard[62] value of 1.54 Å and a rigid rotation than repeated. The curve obtained using this prescription (designated B′) is shown in Figure 2, where it may be compared to PRDDO curve B, obtained using $r(C_2C_3)$ = 1.60 Å. The bond shortening has increased the gauche → trans energy barrier slightly from 0.2 to 0.4 kcal/mol. Other changes include an increase of the gauche-trans energy difference and a 25% increase in the gauche → gauche barrier. However, the lack of qualitative changes indicates that central bond shortening will not drastically affect the calculated results.

There is no pertinent experimental data currently available for TFB. However, some estimates of the gauche-trans energy difference obtained for similar molecules are presented in Table V. Of particular note is the fact that the most reliable G-T energy difference calculated here (1.4 kcal/mol) lies within the ranges found both by dipole-moment measurements of the oligomers $H(CF_2)_nH$ by Bates and Stockmayer[39] and by use of empirical potential energy functions for $F(CF_2)_4F$ by Bates.[54]

The consistency of experimental values of the gauche-trans energy difference of CHF_2CHF_2 provides a valuable means of gauging the accuracy of the results reported here. This molecule may be expected to contain F-F interactions similar to those in TFB, although the terminal methyl groups are absent. However, the experimental and calculated data for un-

Table IV. Relative Energies[a] of Rotamers of 2,2,3,3-Tetrafluorobutane[b]

	PRDDO			STO-3G			MNDO
	A	B	B′	A	B	A′	A″
G-T	0.5	0.9	1.8	0.92	1.74	1.38	0.27
TG†	0.3	1.1	2.2	1.49	2.67	1.93	3.65
GG†	3.1	14.6	18.3	3.96	13.40		3.95

[a] All energies in kcal/mol. [b] A, PRDDO optimization; B, rigid rotation of PRDDO optimized trans conformer; A′, STO-3G optimization; A″, MNDO optimization; B′, rigid rotation of PRDDO optimized trans conformer with $r(C_2C_3)$ = 1.54 Å.

Table V. Literature Values of Gauche-Trans Energy Differences

molecule	E(G-T), kcal/mol	method	ref
polytetrafluoroethylene	1.4-4.8	theory (empirical)	53
$H(CF_2)_nH$ (n = 4, 6, 8, 10)	0.7-1.4	dipole moments	39
$F(CF_2)_nF$ (n = 5, 6, 7)	0.2-0.7	IR	40
$CF_3CF_2CF_2CF_3$	1.1-2.3	theory (empirical)	54
$CH_3CCl_2CCl_2CH_3$	0.2-0.6	NMR	38
$CH_3CBr_2CBr_2CH_3$	0.7-1.8	NMR	38
CHF_2CHF_2	1.2	electron diffraction	41
	1.1-1.3	IR and Raman	47
	1.3	theory (empirical)	64
CH_2FCH_2F	−(0.6-1.4)	electron diffraction	43
	0 ± 0.2	IR and Raman	48
	+1.4	theory (empirical)	64
	1.0	theory (ab initio)	30

substituted *n*-butane in the previous section indicate that the theoretical methods being applied here deal adequately with the interactions involving the terminal methyl groups. It is therefore hoped that a comparison of calculated with experimental results for HCF_2CF_2H may be capable of extrapolation to $CH_3CF_2CF_2CH_3$ with minor differences.

Geometry optimizations of 1,1,2,2-tetrafluoroethane (TFE) by PRDDO and MNDO found the gauche-trans energy difference to be 0.0 and 0.1 kcal/mol, respectively. Application of STO-3G directly to the PRDDO-optimized rotamers (case A) yielded a gauche-trans energy difference of 0.50 kcal/mol. Optimization of the two structures by STO-3G (case A′) increased this energy difference only very slightly to 0.54 kcal/mol. When the extended 4-31G basis set[61] was applied to the STO-3G optimized conformers, an energy difference of 2.4 kcal/mol was calculated. Comparison of the above numbers to the experimental value of 1.2 ± 0.1 kcal/mol[41,47] indicates that STO-3G and 4-31G respectively underestimate and overestimate the true value.[65] On the above basis, then, one might expect the true gauche-trans energy difference in TFB to be somewhat higher than the 1.4 kcal/mol calculated by STO-3G optimization (A′).

The total SCF energies of *n*-butane, TFB, and TFE as calculated by the various procedures outlined above are presented in Table VI.

There is no available experimental estimate of the height of the trans → gauche barrier of TFB with which to compare the calculated value of 1.9 kcal/mol. A microwave study[50] of the two-carbon CH_2FCH_2F molecule found a barrier of 2 kcal/mol but with large uncertainty. A 4-31G calculation[30] of the same molecule yielded a somewhat higher barrier of 3.2 kcal/mol, whereas the molecular mechanics approach[66] recently found no indication of a barrier separating the two rotamers. As concerns the $(CF_2)_n$ polymer, an early empirical estimate[53] of the rotation barrier was extremely high (>50 kcal/mol). With regard to the geometry, electron-diffraction data[41] of TFE yield a value of ϕ in the gauche conformer of 78 ± 2°, which compares quite well with the STO-3G optimized values of 80° for the same molecule and 82° for TFB.

It has been noted from X-ray[45] and theoretical empirical data[54,55] that the perfluoro-substituted polymer of ethylene exists in a slightly twisted helical conformation as a result of a ϕ angle of ~165°. The calculations performed here give no evidence of a stable rotamer at ϕ = 165° for the four-carbon monomeric unit, indicating that the polymeric crystalline environment is perhaps responsible for this twist.

Conclusions

As noted above, energy profiles obtained for *n*-butane using the rigid rotor approximation differ significantly from those calculated with extensive geometry optimization only in the gauche → gauche transition region. These deviations can be reduced drastically by CCC bond angle variations alone. However, comparisons of curves A and B in Figure 2 illustrate that the rigid rotor approximation is a poor one for TFB throughout the full range of ϕ. Although the gauche → gauche barrier (ϕ = 0°) is most dramatically affected, there are important differences in the trans-gauche transition region as well. The data in Table III indicate that a number of geometrical parameters require variation as their optimized values are quite different for several rotamers. The parameters showing the most variation are CC bond lengths and the CCC bond angles.

The rotational energy profiles calculated by PRDDO for *n*-butane agree well with ab initio results but the former method as well as MNDO provides poor relative energies in the trans → gauche regions for the fluoro-substituted TFB and TFE molecules. Both of these approximate procedures severely underestimate the gauche-trans energy difference. However, application of ab initio treatments to geometries optimized via PRDDO furnish results in reasonable agreement with those obtained by more costly ab initio optimization as well as available experimental data.

Table VI. Total Calculated Energies[a] of Trans Conformers

	n-Butane	
PRDDO	A	−157.0768
STO-3G	A	−155.4652
	2,2,3,3-Tetrafluorobutane (TFB)	
PRDDO	A,B	−550.6455
	B′	−550.6431
STO-3G	A,B	−545.2940
	A′	−545.2961
	1,1,2,2-Tetrafluoroethane (TFE)	
PRDDO	A	−472.6650
STO-3G	A	−468.1164
	A′	−468.1182
4-31G	A′	−474.0287

[a] All energies in atomic units.

Use of the extended 4-31G basis set provided no significant improvement of the minimal basis set results for *n*-butane. In addition, when applied to the fluoro-substituted TFE molecule, 4-31G yielded a substantially poorer estimate of the experimentally obtained gauche-trans energy difference than did the smaller STO-3G basis set, in accord with previous findings for 1,2-difluoroethane.[63]

The data provided in this paper for TFB await experimental verification but may serve to furnish a first approximation adequate for statistical treatments of relevant polymers.

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Diffusion in Rigid Bilayer Membranes. Use of Combined Multiple Pulse and Multiple Pulse Gradient Techniques in Nuclear Magnetic Resonance

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Abstract: Combined NMR multiple pulse homonuclear decoupling and multiple pulse gradient techniques have been used to determine the self-diffusion coefficients at 25 °C of the phospholipids in the $L_{\beta'}$(gel) phase of L-α-dipalmitoylphosphatidylcholine in a 15% (w/w) D_2O model membrane and of potassium oleate in a 30% (w/w) D_2O lamellar phase (above the phase transition). The values found, 1.6×10^{-10} and 1.3×10^{-8} cm^2 s^{-1}, respectively, are considered in reasonable agreement with values obtained by other investigators using fluorescence photobleaching recovery. The technique has the advantage that it monitors lipid protons and hence avoids possible complications of added probes. The use and limitations of the method are discussed, and the values found for diffusion are compared with those determined or estimated by other methods.

The importance of lateral diffusion of lipids, proteins, and other membrane components is well established.[2,3] Diffusion is a fundamental aspect of embryological development, cell fusion, membrane phase separations, membrane transport processes, and immunochemistry.[3] Lipid water multibilayer systems, such as L-α-dipalmitoylphosphatidylcholine (DPL)/H_2O system, have been extensively studied as models of cell membranes.[2c] Such systems, lyotropic liquid crystals, have the capability of maintaining orientational order while allowing for flow.[2c] One of the most useful parameters used in inferring microscopic details about the dynamics of flow in such systems is the self-diffusion coefficient. While pulsed NMR spin-echo methods have been a traditionally useful tool for determining self-diffusion in liquids,[4] relaxation due to dipolar interactions generally precludes their use in solids and in relatively rigid phases such as glasses and model membrane multibilayers. In order to apply this NMR technique in such systems, the dipolar broadening must be removed in some fashion. One method of achieving this, applicable to the special case of membranes where the lipids are above the chain melting phase transition (T_c), is to use oriented samples and the angular properties of the dipolar Hamiltonian.[5,6] Another, and much more general, approach is to utilize the multiple pulse techniques developed in the early 1970s to attenuate dipolar

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