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Conformational Characteristics of Poly(tetrafluoroethylene) Chains Based upon ab Initio Electronic Structure Calculations on Model Molecules

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ABSTRACT: Conformational characteristics of poly(tetrafluoroethylene) (PTFE) chains have been studied in detail, based upon ab initio electronic structure calculations on perfluorobutane, perfluoropentane, and perfluorohexane. The conformational energy contours confirm the well-known minima of the trans states at ±17° but also show that the gauche states split as well, with minima at ±124° and ±84°, in order to relieve steric crowding. The directions of such split distortions from the perfectly staggered states are strongly coupled for adjacent pairs of bonds in a manner identical to the intradyad pair of poly(isobutylene) chains. These conformational characteristics are fully represented by a six-state rotational isomeric state (RIS) model comprised of t_+, t_-, g^+_+, g^+_-, g^-_+, and g^-_- states, located at the split energy minima. The resultant 6×6 statistical weight matrix is described by two first-order interaction parameters and two second-order interaction parameters; the ab initio estimated first-order interaction energies are ca. 0.6 kcal/mol for the g^+_+ states and ca. 2.0 kcal/mol for the g^+_- states, while the second-order interaction energies are ca. 0.6 kcal/mol for the $g^+_+g^+_+$ states and ca. 1.0 kcal/mol for the $g^+_+g^-_+$ states, according to MP2 level ab initio calculations using a D95+* basis set. This six-state RIS model, with no adjustment of the geometric or energy parameters as determined from the ab initio calculations, predicts the unperturbed chain dimensions, and the fraction of gauche bonds as a function of temperature, in good agreement with available experimental values. Compared with the previous four-state RIS model of Bates and Stockmayer, our six-state model differs significantly in that it fully takes into account the strong coupling of conformations for adjacent bond pairs, which leads to important differences in the nature and the magnitude of the interactions involving the gauche conformations between the two models.

Introduction

From crystallographic studies it has long been known that the backbone dihedral angles for the trans (t) conformation in perfluoroalkanes and poly(tetrafluoroethylene) (PTFE) are displaced by about 17° from a true trans ($t = 0°$).[1] This distorted t state ($t_\pm$), which is not observed in *n*-alkanes or poly(methylene), can be understood as a result of the greater van der Waals radius of the fluorine atoms relative to hydrogen atoms, the greater bond length for the C–F bond relative to the C–H bond, and the highly polar nature of the C–F bond, all of which lead to significant repulsive interactions in a trans conformation of PTFE that do not occur in the corresponding conformation of poly(methylene).

It has also been proposed that the types of strong steric interactions which lead to the distorted trans states in perfluoroalkanes will also lead to gauche (g) energies well above those found in *n*-alkanes.[2] However, the available experimental evidence for the value of gauche energy in perfluoroalkanes is inconclusive. For example, an analysis of the temperature dependence of specific IR bands in liquid perfluoropentane (PFP), perfluorohexane (PFH), and perfluoroheptane yielded values for the gauche energy ranging from 0.35 to 0.60 kcal/mol.[3] A more recent study of liquid perfluorobutane (PFB), PFH, and perfluorooctane yielded comparable gauche energies of 0.50–0.72 kcal/mol.[4] However, the latter study found gauche energies in the gas phase that ranged from 1.10 to 1.21 kcal/mol for the same molecules. This relative stability of the gauche state in the liquid phase relative to the gas phase was not seen in the first study.[3] Analysis of D-LAM Raman bands in liquid perfluoroalkanes ranging from C_9F_{20} to $C_{20}F_{42}$ in terms of a three-state rotational isomeric state (RIS) model yielded estimates of higher gauche energies than the above studies, with values ranging from 0.95 to 1.2 kcal/mol, depending upon the particular force constants used in the analysis.[5] A value of 1.1 ± 0.1 kcal/mol was estimated for the gauche energy in $C_{16}F_{34}$ and $C_{20}F_{42}$ as determined from infrared band intensities of vapor-deposited amorphous films analyzed using a four-state RIS model.[6] The gauche energies determined from the latter two studies are necessarily dependent upon the validity of the RIS models utilized in analysis of the experimental data.

The geometry and energy of the distorted t conformation and the g conformation in perfluoroalkanes have also been studied, to a limited extent, by ab initio electronic structure calculations.[7,8] Dixon[8] reported an energy of −0.38 kcal/mol for the distorted trans ($t_\pm = \pm 15.4°$) relative to the true trans ($t = 0°$) in PFB. He found that the energy of the g conformation in PFB lies 1.48 kcal/mol above that of the t_+ conformer at angle of ±116.7°. The energies were determined at the MP2 level using a double-ζ plus polarization basis set. The molecular geometries were optimized at the SCF level using a double-ζ basis set with polarization functions on the carbon atoms only.

The first rotational isomeric state (RIS) model for the conformational properties of perfluoroalkanes that in-

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Table 1. Conformational Energies and Geometries of Perfluorobutane

	ab initio energy[a] (kcal/mol)								ab initio geometry[b]		
	4-31G		D95+*		D95+(2*d*)		D95+(*df*)		torsion		valence
conformn	SCF	MP2	SCF	MP2	SCF	MP2	SCF	MP2	ϕ_{methyl}	ϕ_{cccc}	θ_{ccc}
t_+	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	8.8	13.5 (10.6)	114.6
t^c	0.15	0.27	0.11	0.23	0.14	0.19			0.0	0.0 (0.0)	115.2 (115.1)
$g^+{}_+$	1.73	1.15	1.02	0.47	1.03	0.49	0.98	0.38	9.0	124.4 (122.9)	118.1 (118.6)
$g^+{}_-$	2.06	1.70	1.94	1.71					−7.5	84.8 (81.5)	116.5 (116.0)

[a] Energies are relative to the t_+ conformer. D95+ was contracted as [4*s*3*p*] in all basis sets. Exponents for the diffuse functions were, for carbon, $\alpha_s = 0.0511$, $\alpha_p = 0.0382$, and for fluorine, $\alpha_s = 0.1211$, $\alpha_p = 0.0911$. Exponents for the polarization functions were, for carbon, $\alpha_d = 0.75$ for single d and $\alpha_d = 1.5, 0.375$ for 2d, $\alpha_f = 0.8$, and for fluorine, $\alpha_d = 0.9$ for single d and $\alpha_d = 1.8, 0.45$ for 2d, $\alpha_f = 1.85$. [b] Torsional angles and valence angles are from D95+* SCF-optimized geometries. Numbers in parentheses are from 4-31G-optimized geometries. ϕ_{methyl} refers to the twisting of the trifluoromethyl group. ϕ_{cccc} refers to the backbone torsion. [c] The *t* conformation is a saddle point.

corporated the observed distorted $t_\pm$ conformations was presented over 20 years ago: the well-known four-state model of Bates and Stockmayer.[9,10] This model was parameterized so as to reproduce the dipole moments of a series of α,ω-dihydroperfluoroalkanes.[9] The four states, t_+, t_-, g^+, and g^-, explicitly account for the distortion of the trans state but do not allow for distorted gauche states. The model was found to reproduce the experimental data with a gauche energy of 1.4 ± 0.4 kcal/mol. This four-state RIS model predicts a value of approximately 30 for the characteristic ratio C_∞ ($C_\infty \equiv \langle R^2\rangle/nl^2$, where $\langle R^2\rangle$ is the mean-square end-to-end distance of the chains, n is the number of bonds, and l is the bond length, for large n) for PTFE at 600 K.[10] However, recent light scattering experiments have indicated that the characteristic ratio of PTFE is approximately 8 ± 2.5 at 600 K.[11]

The distorted trans state in PTFE is indicative of the existence of strong repulsive interactions in the staggered conformations due to steric crowding. In this regard, it should be noted that recent studies of chain conformations for some highly crowded polymers, such as poly(isobutylene)[12] and poly(methyl methacrylate),[13] indicate that all three staggered conformations (trans, gauche$^+$, and gauche$^-$ states) distort, resulting in a splitting of these conformations. In these polymers, adjacent pairs of conformations were found to split only in the same direction (both + or both −). Such coupled conformations are a natural consequence of attempts to minimize the strong steric overlap occurring in such sterically crowded molecules, as can be seen readily by examination of space-filling molecular models. No such detailed examination of conformational energies has been carried out for PTFE to investigate whether splitting of the gauche states occurs, in addition to the observed splitting of the trans state, in order to reduce steric repulsions in the gauche states.

We have performed a quantum chemistry study of the geometries and conformational energies of selected perfluoroalkanes as model molecules for PTFE, including extensive studies of the energies of PFB and PFP and complementary studies of selected conformations of PFH. The detailed results of these studies will be published separately. The results of these studies relevant to the parameterization of an RIS model for PTFE are summarized herein. In this paper, we present a six-state RIS model for PTFE based upon conformational geometries and energies of low molecular weight perfluoroalkanes as determined from the ab initio electronic structure calculations. The approach is similar to the one we used in successfully developing an RIS model for poly(oxyethylene) based upon ab initio electronic structure studies of model molecules.[14] As will be discussed in the next section, our model incorporates all of the important conformational characteristics of PTFE revealed by ab initio electronic structure studies, many of which are not accounted for in the original four-state model presented by Bates and Stockmayer.[9,10] Most importantly, our model predicts a characteristic ratio for PTFE consistent with recent experimental values using energy and geometric parameters determined from the ab initio conformational energies and geometries of perfluoroalkanes (PFB, PFP, and PFH).

Conformations of Model Molecules

We have investigated extensively, through ab initio electronic structure calculations, conformational energies and geometries of PFB and PFP as the primary model molecules for PTFE. PFB is the smallest perfluoroalkane containing a C–C–C–C torsion; study of this simple molecule reveals much about the shape of conformational space for perfluoroalkanes and PTFE. In order to examine interdependent conformational interactions present in perfluoroalkanes (and PTFE) longer than PFB, we have also investigated conformations of PFP. PFP is the smallest molecule which exhibits conformational interactions that depend not only on the state of the current torsion but also on the state of nearest-neighbor torsions (second-order interactions). Selected conformations of PFH were also investigated.

The geometries and energies of selected minimum energy and saddle point conformations of PFB, PFP, and PFH were determined from ab initio electronic structure calculations using both a 4-31G basis set and a D95+* basis set. The conformational energies and geometries for PFB, PFP, and PFH are presented in Tables 1, 2, and 3, respectively. The D95+* basis set is a Dunning[15] double-ζ basis set augmented with s and p diffuse and d polarization functions on all atoms. The diffuse and polarization function exponents are given in Table 1. Molecular geometries were optimized at the self-consistent-field (SCF) level for both basis sets. These geometries were subsequently used in MP2 level calculations of electron correlation effects. Both SCF and MP2 energies are given in the tables. Selected calculations for PFB using the larger D95+(2d) and D95+(df) basis sets were also performed. The representations (2d) and (df) indicate two sets of d polarization and a set of d and f polarization functions, respectively, on all atoms. The conformational energies determined using these basis sets, along with the exponents for the additional polarization functions, are given in Table 1. The energies and geometries of the model molecules are discussed below. More detailed results of the quantum chemistry calculations will be presented in a future paper.

Conformations of Perfluorobutane (PFB)

The geometries and energies of the low-energy conformers of PFB are summarized in Table 1. A complete

Table 2. Conformational Energies and Geometries of Perfluoropentane

		ab initio energy[a] (kcal/mol)				geometry[b]				
		4-31G		D95+*		torsion		valence		
conformn		SCF	MP2	SCF	MP2	ϕ_1	ϕ_2	θ_1	θ_2	θ_3
t_+t_+	minimum	0.00	0.00	0.00	0.00	17.0	17.0	114.3	113.5	114.3
tt	saddle point	0.92	1.19	0.75	0.89	0.0	0.0	114.9	114.6	114.9
t_+t_-	not stationary									
$t_+g^+_+$	minimum	1.47	0.94	1.16	0.56	14.3	124.2	114.6	117.3	118.2
$t_+g^+_-$	not stationary									
$t_+g^-_-$	not stationary									
$t_+g^-_+$	minimum	2.11	1.71	2.21	1.99	13.1	−83.9	114.4	114.9	115.9
$g^+_+g^+_+$	minimum	3.75	2.72	2.80	1.62	121.2	121.2	118.8	121.2	118.8
$g^+_-g^+_-$	minimum	4.25	3.52	4.36	3.92	88.8	88.8	115.6	117.0	115.6
$g^+_+g^+_-$	not stationary									
$g^+_+g^-_-$	saddle point	10.08	8.54	7.96	6.89	109.6	−109.6	120.3	122.9	120.3
$g^+_+g^-_+$	minimum	5.26	4.31	4.76	3.59	116.8	−77.3	119.5	118.8	115.3

[a] Energies are relative to the t_+t_+ conformer. A [5*s*3*p*1*d*] contraction of the D95+* basis set was used for the single point energy calculations. [b] Backbone torsional angles: $\phi_1 = C_1–C_2–C_3–C_4$, $\phi_2 = C_2–C_3–C_4–C_5$. Valence angles: $\theta_1 = C_1–C_2–C_3$, $\theta_2 = C_2–C_3–C_4$, $\theta_3 = C_3–C_4–C_5$, from D95+* [4*s*3*p*1*d*]SCF-optimized geometries.

Table 3. Conformational Energies and Geometries of Perfluorohexane

		ab initio energy[a] (kcal/mol)				geometry[b]		
		4-31G		D95+*		torsion		
conformn		SCF	MP2	SCF	MP2	ϕ_1	ϕ_2	ϕ_3
$t_+t_+t_+$	minimum	0.00	0.00	0.00	0.00	16.9	18.1	16.9
ttt	saddle point	1.73	2.09	1.34		0.0	0.0	0.0
$t_+g^+_+t_+$	minimum	1.34	0.79	1.27	0.77	13.7	124.0	13.7

[a] Energies are relative to the $t_+t_+t_+$ conformer. A [4*s*3*p*1*d*] contraction of the D95+* basis set was used for the single point energy calculations. [b] Backbone torsional angles: $\phi_1 = C_1–C_2–C_3–C_4$, $\phi_2 = C_2–C_3–C_4–C_5$, $\phi_3 = C_3–C_4–C_5–C_6$, from D95+* [4*s*3*p*1*d*]SCF-optimized geometries.

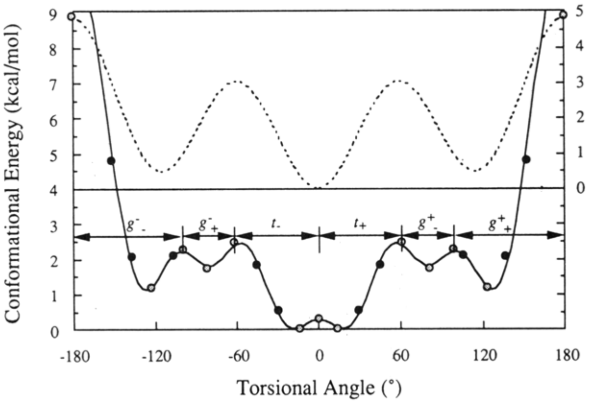


Figure 1. Conformational energy of PFB as a function of the C–C–C–C torsional angle. Circles are points from ab initio calculations (solid circles are with constrained torsion). The solid curve is a fit to the ab initio data. The dashed curve is the conformational energy of *n*-butane from the potential functions of ref 16. The latter curve has been displaced by 4 kcal/mol for clarity (reference to the right-hand ordinate). Conformational space associated with each state of PFB is indicated.

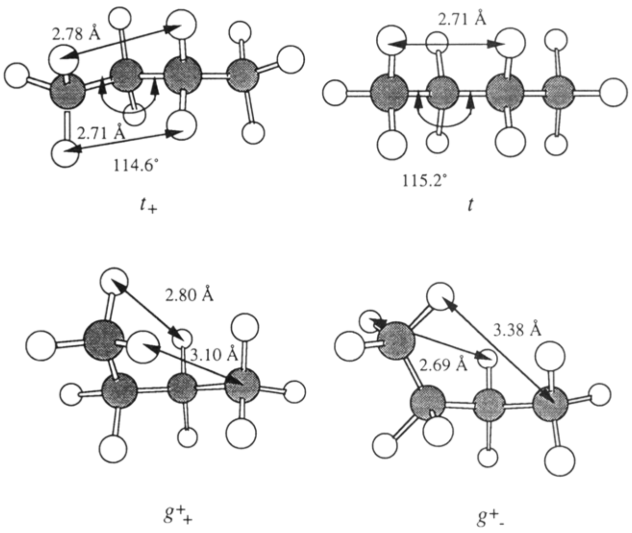


Figure 2. Schematic geometries of the low-energy conformations of PFB. The closest conformation-dependent fluorine–fluorine approaches are shown for the t, t_+, g^+_+, and g^+_- conformations. The C–C–C valence angles are indicated.

conformational energy map for PFB, showing the conformational energy of PFB as a function of the C–C–C–C torsional angle, is shown in Figure 1. The data for construction of Figure 1 consist of the energies and geometries of the low-energy conformers given in Table 1 plus energies and geometries of additional conformations determined by optimizing geometries at the SCF level using a 4-31G basis set, constraining the C–C–C–C torsional angle for the nonstationary points, and utilizing the resulting geometries for MP2 level calculations of the energy. The solid line is a fit of

$$E(\phi) = a_0 + \sum_{k=1}^{7} a_k \cos k\phi \qquad (1)$$

to the ab initio points indicated in Figure 1. Shown for comparison is the conformational energy of *n*-butane.[16] The splitting of the t, g^+, and g^- conformations into $t_\pm$, $g^+_\pm$, and $g^-_\pm$ conformations in PFB is clearly demonstrated.

Conformational Geometries. Examination of Table 1 indicates the C–C–C–C torsional angle and C–C–C valence angles for the low-energy conformers of PFB show only a weak dependence on the size of the basis set. The optimized geometries for the t, t_+, g^+_+, and g^+_- conformations of PFB, determined at the SCF level with a D95+* basis set, are illustrated in Figure 2. For the t_+ conformation, twisting of both the backbone and trifluoromethyl (TFM) torsions allows an interdigitation of relatively large fluorine atoms, thereby increasing the closest four-bond fluorine–fluorine distances, as indicated in Figure 2. This reduction in steric interactions, relative to the t conformation, relieves strain in the C–C–C valence angles. Similar four-bond interdigitation involving fluorine and carbon atoms results from the twisting of the backbone and trifluoromethyl groups in the g^+_+ and g^+_- conformations. In the g^+_+ conformation, the TFM groups twist in the same sense as for the t_+ conformation, as seen in Table

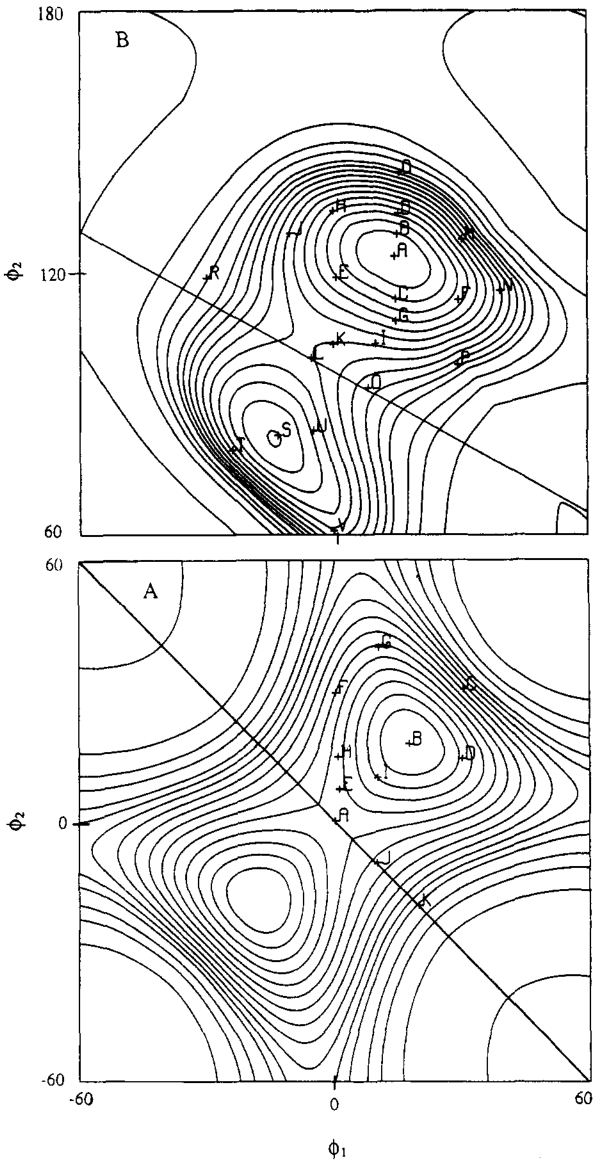


Figure 3. Conformational energy maps for the *tg* and *tt* regions of PFP. Points are from ab initio calculations. Contours were determined from a polynomial fit to the ab initio data (see text). (A) For *tt*: $A = 1.19$, $B = 0.00$, $C = 2.05$, $D = 0.49$, $E = 1.10$, $F = 1.56$, $G = 1.48$, $H = 1.07$, $I = 0.44$, $J = 1.59$, $K = 3.08$, all in kcal/mol. Contours are at 0.25–3.00 kcal/mol, spaced at 0.25 kcal/mol, 3.5 kcal/mol, 4.0 kcal/mol, 5.0 kcal/mol, and 10.0 kcal/mol. (B) For *tg*: $A = 0.94$, $B = 1.07$, $C = 1.54$, $D = 1.58$, $E = 1.80$, $F = 1.86$, $G = 2.11$, $H = 2.17$, $I = 2.71$, $J = 2.73$, $K = 2.80$, $L = 2.85$, $M = 2.94$, $N = 3.07$, $O = 3.27$, $P = 3.33$, $Q = 3.76$, $R = 6.18$, $S = 1.71$, $T = 2.88$, $U = 2.18$, $V = 2.77$, all in kcal/mol. Contours are at 1.20–3.95 kcal/mol, spaced at 0.25 kcal/mol, 4.45 kcal/mol, 4.95 kcal/mol, 5.95 kcal/mol, and 10.95 kcal/mol. The straight lines indicate the division of conformational space into t_+t_+ and t_-t_- states or $t_+g^+{}_+$ and $t_-g^+{}_-$ states.

1. For the $g^+{}_-$ conformations, the TFM groups twist in the opposite sense, maintaining the same sign of distortion as the neighboring $g^+{}_-$ state. Relative to the $g^+{}_+$ conformation, the geometry of the $g^+{}_-$ conformation results in a relief of steric interaction between a fluorine atom and a carbon atom at the expense of an increase of steric interaction between fluorine atoms, as can be seen in Figure 2. The distortion of the backbone torsion in the $g^+{}_-$ conformation is much greater than in the $g^+{}_+$ conformation when compared to the *g* conformation in *n*-butane, as shown in Figure 1. As a result, the $g^+{}_-$ conformation is higher in energy than the $g^+{}_+$ conformation. It is worth noting that the C–C–C valence angles in PFB are somewhat smaller than might be expected, given the presence of the relatively large fluorine atoms. The gain realized in increasing the C–C–C valence angle is tempered in the fully substituted perfluoroalkane molecules by a concomitant decrease in the F–C–F valence angle.

Conformational Energies. The energies of the low-energy conformers of PFB, relative to the t_+ conformer, are summarized in Table 1. While the energies (relative to t_+) of the *t* and $g^+{}_-$ conformations show only a weak dependence on the size of the basis sets used in the ab initio calculations, the energy of the $g^+{}_+$ conformer depends strongly on the basis set size, with a strong trend toward lower energies as the basis set is improved. The best representation of PFB considered, D95+(df), yields an energy for the $g^+{}_+$ conformer of 0.38 kcal/mol at the MP2 level, more than 0.75 kcal/mol lower than that yielded by the 4-31G basis set. Correlation effects were also found to be important. For example, with a D95+* basis set, the energy of the $g^+{}_+$ conformer of PFB relative to the t_+ conformer was 0.47 kcal/mol at the MP2 level and 1.02 kcal/mol at the SCF level. It should be noted that the geometry and relative energy for the $g^+{}_+$ conformer reported in Table 1 are significantly different from the values for the *g* conformer reported by Dixon.[8,17]

Conformations of Perfluoropentane (PFP)

Ab initio values for the energies of the important conformations of PFP and the corresponding backbone torsional angles are presented in Table 2. As in PFB, it is apparent that basis set size effects are important for the conformer energies but not the geometries; e.g., the 4-31G and D95+* MP2 energies of the $t_+g^+{}_+$ conformer differ by 0.4 kcal/mol but the backbone torsional angles were found to differ by less than 1°. When the D95+* SCF and MP2 energies for the $t_+g^+{}_+$ conformer are compared, it is apparent that electron correlation effects are also important in PFP.

Energy maps for the important low-energy *tt* and *tg* regions of the conformational space of PFP are shown in Figure 3. The *tt* region is split into t_+t_+ and t_-t_- minima while the *tg* region is split into a low-energy $t_+g^+{}_+$ minimum and a somewhat higher energy $t_-g^+{}_-$ minimum. The regions of conformational space associated with each conformation are shown in Figure 3. The conformational energies $E(\phi_1,\phi_2)$ for PFP were constructed as follows. For each map, polynomials of the form

$$E(r,\theta_{\text{fixed}}) = a_0(\theta_{\text{fixed}}) + a_1(\theta_{\text{fixed}})r^2 + a_2(\theta_{\text{fixed}})r^3 + a_3(\theta_{\text{fixed}})r^4 \quad (2)$$

were determined for eight values of θ_{fixed}, where

$$r = \sqrt{(\phi_1 - \phi_1^{\min})^2 + (\phi_2 - \phi_2^{\min})^2} \quad (3)$$

$$\theta = \arccos\left(\frac{\phi_1 - \phi_1^{\min}}{r}\right) \quad (4)$$

and $(\phi_1^{\min},\phi_2^{\min})$ corresponds to either the t_+t_+ or the $t_+g^+{}_+$ minimum. The polynomials were fit to ab initio energies determined with a 4-31G basis set at the MP2 level as described above. Selected ab initio points are shown on the conformational energy maps. The energy $E(\phi_1,\phi_2) = E(r,\theta)$ of a given conformation was then determined by fitting a cubic polynomial in θ to the $E(r,\theta_{\text{fixed}})$ values for the four θ_{fixed} values nearest θ.

Figure 1 reveals that in PFB the torsional states are split into $t_\pm$, $g^+{}_\pm$, and $g^-{}_\pm$ states, for a total of six states. Examination of Figure 3 and Table 2 reveals that the same torsional states are present in PFP. Due to second-order state of current torsional bond

state of previous torsional bond

	t_+	t_-	g^+_+	g^+_-	g^-_+	g^-_-
t_+	1	0	σ	0	σ'	0
t_-	0	1	0	σ'	0	σ
g^+_+	1	0	$\sigma\psi$	0	$\sigma'\omega$	0
g^+_-	0	1	0	σ'	0	$\sigma\omega$
g^-_+	1	0	$\sigma\omega$	0	σ'	0
g^-_-	0	1	0	$\sigma'\omega$	0	$\sigma\psi$

Figure 4. Six-state RIS statistical weight matrix for PTFE.

steric effects, however, certain torsional sequences are not allowed in PFP; i.e., certain conformations do not correspond to local minima on the conformational energy surface. For example, examination of Figure 3 demonstrates that no energy minimum corresponds to the t_+t_- conformer, consistent with our ab initio calculations. This result is at variance with the previous four-state RIS model,[9,10] where such sequences were allowed. The $t_+g^+_-$ and $t_-g^+_+$ conformations also do not correspond to stationary points on the conformational energy surface for PFP, as seen in Figure 3.

Conformational energy maps were not constructed for the relatively high-energy $g^\pm g^\pm$ and $g^\pm g^\mp$ regions of PFP conformational space. From Table 2, however, it can be seen that the $g^+_+g^+_+$, $g^+_-g^+_-$, and $g^+_+g^-_+$ conformations correspond to energy minima while the $g^+_+g^+_-$ and $g^+_+g^-_-$ conformations do not. Such couplings of conformational pairs are identical to those found for the intradyad conformations of poly(isobutylene),[12] as expected from the similar steric crowding for both polymers.

Six-State RIS Model

Below we develop a six-state RIS model for PTFE based upon analysis of the conformational energies and geometries of perfluoroalkanes as yielded by ab initio electronic structure calculation. In the appendix, a four-state RIS model deduced from the six-state RIS model developed here is presented and compared in detail with the six-state model and the previous four-state model.[9,10]

Statistical Weight Matrices. A six-state statistical weight matrix for PTFE is shown in Figure 4. Elements in the statistical weight matrix representing two bond sequences which do not correspond to minimum energy conformations in PFP were assigned a statistical weight of zero. The resulting statistical weight matix has only four parameters: two first-order statistical weights for the $g^\pm_\pm(\sigma)$ and $g^\pm_\mp(\sigma')$ states and two second-order statistical weights for the $g^\pm_\pm g^\pm_\pm(\psi)$ and $g^\pm_\pm g^\mp_\pm(\omega)$ states.

First-Order and Second-Order Parameters. The energies of g^+_+ and g^+_- conformers of PFB, the $t_+g^+_+$, $t_+g^-_+$, $g^+_+g^+_+$, $g^+_-g^+_-$, and $g^+_+g^-_+$ conformers of PFP, and the $t_+g^+_+t_+$ conformer of PFH are shown in Table 4, along with the representation of the conformational energies in terms of the energies of first-order and second-order conformation-dependent interactions. The ab initio energies are D95+* MP2 values taken from Tables 1–3. The first-order g^+_+ and g^+_- interactions are labeled σ and σ', respectively, with corresponding energies E_σ and $E_{\sigma'}$, while the second-order $g^+_+g^+_+$ and $g^+_+g^-_+$ interactions are labeled ψ and ω, respectively, with corresponding energies E_ψ and E_ω. The resulting RIS energy for each conformer, given as a sum of the energies for all of the conformation-dependent interactions present in the conformer, is also given in Table 4.

Table 4. RIS Representation of Model Molecule Conformers

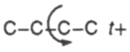
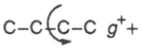
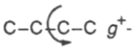
conformer	RIS representation	energies[a] ab initio	energies[a] RIS
PFB			
g^+_+	E_σ	0.47	0.5
g^+_-	E_{σ}'	1.71	1.7
PFP			
$t_+g^+_+$	E_σ	0.59 (0.56)	0.6
$t_+g^-_+$	E_{σ}'	(1.99)	2.0
$g^+_+g^+_+$	$2E_\sigma + E_\psi$	1.68 (1.62)	1.7
$g^+_-g^+_-$	$2E_{\sigma}'$	(3.92)	4.0
$g^+_+g^-_+$	$E_{\sigma}' + E_\sigma + E_\omega$	(3.59)	3.6
PFH			
$t_+g^+_+t_+$	E_σ	0.77	0.8

[a] Energies are relative to the t_+t_+ conformer for PFP, the t_+ conformer for PFB and the $t_+t_+t_+$ conformer for PFH, in kcal/mol. Ab initio energies are MP2 values using a D95+* basis set contracted to [4*s*3*p*1*d*]. Numbers in parentheses are for a [5*s*3*p*1*d*] contraction. E_σ = 0.5 kcal/mol (PFB), 0.6 kcal/mol (PFP), and 0.8 kcal/mol (PFH). $E_{\sigma'}$ = 1.7 kcal/mol (PFB) and 2.0 kcal/mol (PFP). E_ψ = 0.5 kcal/mol (PFP). E_ω = 1.0 kcal/mol (PFP).

As seen in Table 4, E_σ was found to increase somewhat in the order PFH > PFP > PFB. We believe this trend is due to end effects in the shorter PFB and PFP molecules. In PFB, the g^+_+ conformer involves interaction between the two TFM end groups, and in PFP, the $t_+g^+_+$ conformer involves interaction of one TFM end group with a difluoromethylene group. In the PFH $t_+g^+_+t_+$ conformer, the end groups do not interact with the central g^+_+ C–C–C–C bond. We believe the increased stability of the g^+_+ conformation when end groups are involved may arise from the much greater positive partial charge associated with a TFM carbon than an interior carbon, resulting in stronger carbon–fluorine electrostatic attractions. Also, the TFM torsions are less restricted than interior torsions. These effects will be discussed in greater detail in a future paper. Although we cannot perform MP2 calculations for PFH using a basis set larger than D95+* (due to the required computer resources), we can estimate that such calculations using a D95+(df) basis set would result in approximately the same ΔE_σ = (D95+(df) − D95+*) = −0.1 kcal/mol seen for PFB, from the energies in Table 1. We therefore estimate E_σ for PFH as 0.77 kcal/mol − 0.1 kcal/mol = 0.67 kcal/mol. This value is quite similar to the value of E_σ = 0.6 kcal/mol calculated for PFP with a D95+* basis set (see Table 4), indicating that in PFP for this basis set chain-end effects and basis set size effects approximately cancel. We therefore assign E_σ = 0.6 kcal/mol and $E_{\sigma'}$ = 2.0 kcal/mol, from the D95+*/MP2 conformer energies, as our best estimates for these energies. Although $E_{\sigma'}$ is considerably higher than E_σ, the difference is approximately kT at 600 K, and thus, we expect significant population of these states. The E_σ value is quite similar to the gauche energy determined from Raman spectroscopy studies on *n*-pentane.[18] This gauche energy is considerably lower than the values reported in earlier RIS and ab initio work on PTFE and perfluoroalkanes (1–2 kcal/mol).[2,8–10] (See below for a more detailed discussion of the gauche energy in perfluoroalkanes.)

The energy of the PFP $g^+_+g^+_+$ conformer (see Table 3) yields E_ψ = 0.5 kcal/mol when a value of E_σ = 0.6 kcal/mol, appropriate for PFP, is used. We therefore make the simplifying assumption that $E_\psi = E_\sigma$. This assumption is also consistent with the 4-31G PFP energies in Table 2. The second-order ψ interaction arises from the close

Table 5. RIS Energies and Geometric Parameters

parameter	value
E_σ	0.6 kcal/mol
$E_{\sigma'}$	2.0 kcal/mol
E_ψ	0.6 kcal/mol
E_ω	1.0 kcal/mol
C–C	1.53 Å
C–C–C	116°
	17°
	124°
	84°

approach of CF_2 groups separated by four skeletal bonds in the $g^+{}_+g^+{}_+$ conformation. The resulting increase in steric interaction is evident in the increased strain in the C–C–C backbone valence angles in the $g^+{}_+g^+{}_+$ conformation compared to the $t_+g^+{}_+$ conformation, as can be seen in Table 2. This type of interaction is not present in *n*-pentane due to the much smaller size of the hydrogen, the shorter C–H bond length, and the smaller torsional angles for the gauche state in alkanes compared to the $g^+{}_+$ state in perfluoroalkanes. This effect was not considered in the previous four-state RIS model.[9,10] This type of interaction does not occur in the highly distorted $g^+{}_-g^+{}_-$ conformation, where the CF_2 groups are not brought into close enough contact, resulting in correspondingly less strain in the C–C–C valence angles, as shown in Table 2. For this reason, no second-order ψ term is associated with the $g^+{}_-g^+{}_-$ conformational sequences.

Finally, the energy of the PFP $g^+{}_+g^-{}_+$ conformer is 3.59 kcal/mol, yielding $E_\omega = 1.0$ kcal/mol. At high temperatures this state can be expected to influence the conformational properties because of its highly compact nature (see discussion below). This state was also not allowed in the previous four-state RIS model.[9,10]

Statistical weights are associated with each of the first-order and second-order energy parameters as follows:

$$\sigma = \exp(-E_\sigma/kT) \tag{5}$$

$$\sigma' = \exp(-E_{\sigma'}/kT) \tag{6}$$

$$\psi = \exp(-E_\psi/kT) \tag{7}$$

$$\omega = \exp(-E_\omega kT) \tag{8}$$

Because of the differences in the shape and extent of conformational phase space for the t_+, $g^+{}_+$, and $g^+{}_-$ states (e.g., see Figure 1), it is possible that the statistical weights given in eqs 5–8 do not accurately represent the relative importance of the states, i.e., that preexponential factors significantly different from unity may be required to adequately describe the relative statistical weights of the states. The total integrated weights for the t_+, $g^+{}_+$, and $g^+{}_-$ conformations of PFB, determined from the conformational energy given by eq 1, and for the t_+t_+, $t_+g^+{}_+$, and $t_+g^-{}_+$ conformations of PFP, determined from the conformational energies given by eqs 2–4, were therefore determined. Comparison of the relative integrated weights with the Boltzmann weights (eqs 5–8) at 600 K using energies from the small basis set conformational yields preexponential factors for the σ and σ' interactions of about 0.9. As discussed above, the calculations employing the 4-31G basis set give conformational geometries which agree well with those found using the larger D95+* basis set. However, the conformational energies were found to depend on the size of the basis set. Considering the relatively large uncertainties in the conformational energies resulting from the use of the 4-31G MP2 conformational energies in constructing the PFB and PFP conformational energy surfaces, we feel these results are accurate only to the point that they indicate there is no large variance from unity for the preexponential factors; i.e., the relative weights of the states are reasonably well represented by Boltzmann factors. For the purposes of RIS calculations we therefore assume preexponential factors of unity for all interactions including the second order ψ and ω interactions. The final first- and second-order interaction energies for our six-state RIS model are summarized in Table 5. In the appendix a four-state RIS model, deduced from our six-state RIS model, is presented and compared in detail with the six-state model and the previous four-state model.[9,10]

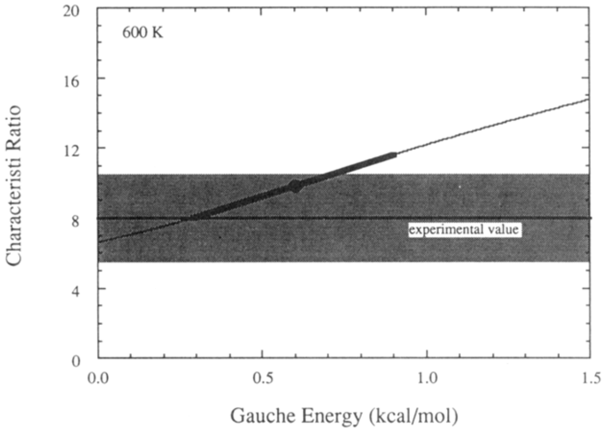


Figure 5. Characteristic ratio of PTFE as a function of E_σ at 600 K. The solid circle corresponds to our best estimate of E_σ = 0.6 kcal/mol. The heavy solid curve indicates the range of characteristic ratio values corresponding to an uncertainty in E_σ of ±0.3 kcal/mol. The horizontal line is the experimental value of ~8, with the shaded region indicating an uncertainty of ±2.5.

Characteristic Ratio of PTFE

For PTFE, the principal measured property that can be calculated with our six-state RIS model is the characteristic ratio. The energy parameters (determined as discussed above) and geometric parameters (average ab initio values weighted over the conformations of PFP) are given in Table 5. Standard methods were used in the RIS calculations.[2] Our model yields a characteristic ratio of 9.8 at 600 K, as compared with 8 ± 2.5 from recent light-scattering experiments.[11] The sensitivity of the predicted characteristic ratio to the gauche energy E_σ at 600 K is shown in Figure 5. Here it was assumed that $E_\psi = E_\sigma$ while $E_{\sigma'}$ and E_ω were fixed at the values given in Table 5. The range of the characteristic ratio for an estimated uncertainty of ±0.3 kcal/mol in E_σ, due to basis set size, electron correlation, and basis set superposition effects,[19] is indicated. The prediction of our model using the parameter values listed in Table 5 falls within the range of experimental uncertainty. Using a E_σ value of 0.3 kcal/mol, the lower end of the estimated uncertainty range, yields a computed characteristic ratio near 8. We expect that E_σ is likely to be somewhat less than our predicted values of 0.6 kcal/mol due to finite basis set effects. In contrast, using the value of E_σ = 1.4 kcal/mol, typical of previous estimates for the gauche energy,[9,10] which lies well outside of the estimated range of uncertainty in the ab initio conformer energies, yields a characteristic ratio near 15.

The predicted temperature dependence of the characteristic ratio of PTFE using the parameters given in Table 5 is shown in Figure 6. For comparison, the characteristic ratio of poly(methylene) as predicted by a three-state RIS

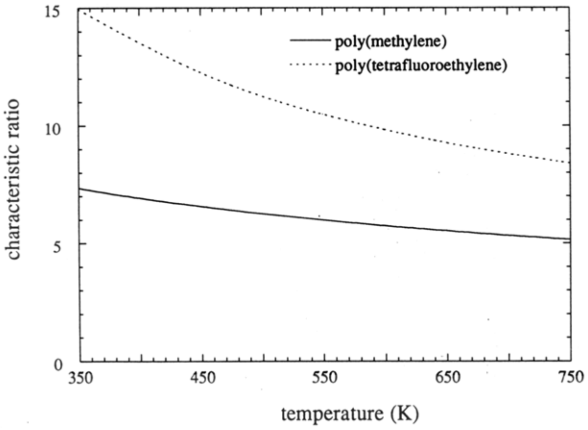


Figure 6. Predicted temperature dependence of the characteristic ratio of PTFE from the six-state RIS model. Shown for comparison is the predicted characteristic ratio of poly(methylene).

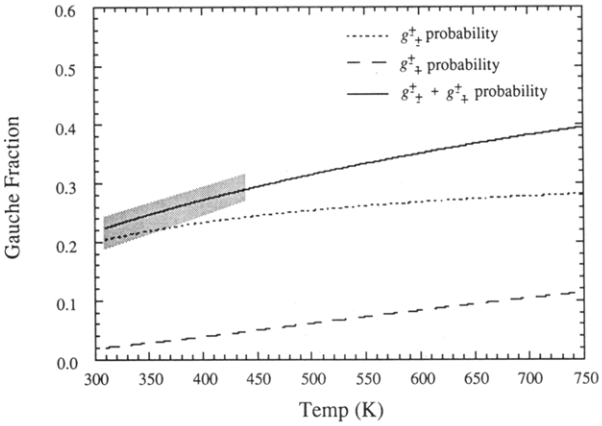


Figure 7. Gauche probability for PTFE as a function of temperature. The shaded region corresponds to predictions based upon analysis of D-LAM frequencies for a series of perfluoroalkanes (ref 5).

model[2,20] is also shown. It can be seen that the characteristic ratio of PTFE is approximately twice that of poly(methylene) at the lower temperatures and exceeds that of poly(methylene) by about 50% at higher temperatures. The predicted temperature coefficient for the mean square end-to-end distance of PTFE, $(d \ln \langle R^2 \rangle / dT)1000$, is -1.2 at 600 K.

For $E_\sigma = 0.6$ kcal/mol, the characteristic ratio is fairly insensitive to $E_{\sigma'}$, with a variance of around ±3% at 600 K for values in the range of $E_{\sigma'} = 2.0 \pm 0.3$ kcal/mol. The increase in the population of $g^+{}_-$ conformations which results from a decrease in $E_{\sigma'}$ comes partly at the expense of the $g^+{}_+$ conformations. Because of their smaller torsional angle, $g^+{}_-$ conformations are relatively inefficient in reducing the characteristic ratio as compared to $g^+{}_+$ conformations. The net result is a slight decrease in the characteristic ratio with decreasing $E_{\sigma'}$, due mainly to an increased population of the compact $g^+{}_+g^-{}_+$ conformations. The characteristic ratio is somewhat more sensitive to E_ω. Because of the low E_ω energy (1.0 kcal/mol), the $g^+{}_+g^-{}_+$ conformations in PTFE are only 3.6 kcal/mol higher in energy than the t_+t_+ conformations, comparable to the 3.0 kcal/mol energy difference between the g^+g^- and tt conformations in poly(methylene).[2,20] At 600 K, $g^+{}_+g^-{}_+$ conformations account for about 3% of the conformational pairs. A decrease in E_ω leads to an increase in the population of $g^+{}_+g^-{}_+$ conformations without decreasing the population of $g^+{}_+$ states. In the range of $E_\omega = 1.0 \pm 0.3$ kcal/mol, the variance in the characteristic ratio is around ±6%. If $g^+{}_+g^-{}_+$ conformations are disallowed ($\omega = 0$), the predicted characteristic ratio increases by about 25%.

Gauche Energy and Gauche Probability

In comparison to experimental values, our value for the gauche energy of $E_\sigma = 0.6$ kcal/mol is consistent with estimated values for the gauche energy in liquid PFP, PFH, perfluoroheptane, and perfluorooctane based upon the temperature dependence of selected IR and Raman bands, where values ranging from 0.35 to 0.72 kcal/mole are reported.[3,4] One of these studies found[4] a significantly higher gauche energy in the gas phase, with an average stabilization of the gauche conformation of almost 0.6 kcal/mol in the liquid as compared to the gas phase. The other study indicates that no significant differences between gas- and liquid-phase spectra are apparent.[3] Although a gauche bond does result in a net dipole moment in perfluoroalkanes, our electronic structure calculations indicate that the magnitude of the dipole moment is quite small, around 0.2 D for the $t^+{}_+g^+{}_+$ conformation of PFP. As dipole–dipole interactions will depend upon the product of the dipole moments, a stabilization of the gauche state in liquid perfluoroalkanes on the order of 0.6 kcal/mol appears highly unlikely.

The gauche energy has also been estimated from an analysis of D-LAM Raman bands in liquid perfluoroalkanes ranging from C_9F_{20} to $C_{20}F_{42}$.[5] In terms of a three-state RIS model the analysis yielded gauche energies of 0.95 and 1.2 kcal/mol, depending upon the force constants employed. For example, at 440 K, the melting point of $C_{20}F_{42}$, these energies yield a gauche probability $p_{g^\pm}$ (probability of $g^\pm$) from the three-state RIS model of $p_{g^\pm} = 0.27$ and 0.32, respectively. At this temperature, the predicted gauche probability from our six-state model, using the energies given in Table 5, is $p_{g^\pm} = 0.29$. The gauche probability from our six-state model as a function of temperature is shown in Figure 7. Also shown is the range of gauche probabilities as determined from the analysis of the D-LAM frequencies. Our lower gauche energy, in conjunction with a six-state RIS model, yields gauche probabilities consistent with the analysis of the D-LAM Raman bands. Figure 7 also reveals that at lower temperatures the high energy $g^+{}_-$ and $g^-{}_+$ states account for only a small fraction of total gauche population. The importance of the high energy gauche states increases with increasing temperature.

Finally, the gauche energy has been estimated from the fraction of fully extended chains (chains containing no gauche bonds) of $C_{14}F_{30}$ and $C_{16}F_{34}$.[6] The analysis is based upon the intensities of infrared bands of amorphous films formed by vapor deposition under vacuum onto the surface of a CsI crystal at 8 K. It was determined that approximately $7.0 \pm 2.1\%$ of the $C_{14}F_{30}$ chains were fully extended, while only $4.5 \pm 1.4\%$ of the $C_{16}F_{34}$ chains were fully extended. In terms of the four-state RIS model of Bates and Stockmayer,[9,10] these fractions yield a gauche energy of 1.1 ± 0.1 kcal/mol. Assuming the temperature of the vapors correspond to the respective melting points of the perfluoroalkanes, our six-state model, using energies given in Table 5, yields an extended fraction of 1.9% in $C_{14}F_{30}$ and 0.7% in $C_{16}F_{34}$, much lower than the experimental values. The key assumption in this analysis is that the conformers in the amorphous film are the same as in the vapor before deposition. This was seen to be the case for alkanes longer than $C_{10}H_{22}$.[6] However, rotational energy barriers in perfluoroalkanes are lower than in the corresponding alkanes (see Figure 1), and the deposition temperatures were significantly higher in the perfluoroalkanes. It therefore appears quite possible that some state of current torsional bond

state of previous torsional bond

	t_+	t_-	g^+	g^-
t_+	1	0	σ	0
t_-	0	1	0	σ
g^+	1	0	$\sigma\psi$	$\sigma\omega'$
g^-	0	1	$\sigma\omega'$	$\sigma\psi$

Figure 8. Four-state RIS model for PTFE.

annealing could occur in the amorphous perfluoroalkane glasses before the temperature drops sufficiently to freeze out conformational transitions. Such an effect would account for the higher fraction of extended conformations seen experimentally than predicted by our model.

Conclusions

We have presented a six-state RIS model for PTFE based upon ab initio electronic structure calculations on model molecules. Our analysis of ab initio values for the conformational energies of PFH, PFP, and PFB yields a gauche energy of $E_\sigma = 0.6$ kcal/mol. This value is consistent with estimates based upon IR and Raman spectroscopy studies of liquid perfluoroalkanes. Our six-state RIS model includes the splitting of the g^+ and g^- states, seen in both PFB and PFP, in addition to the splitting of the t states. The occurrence or nonoccurrence of a minimum energy conformation for each two-bond rotational isomeric state in PFP was determined through ab initio electronic structure calculations. As a result of these studies, several states and second-order interactions were included in the model which were not considered in the previous four-state RIS model,[9,10] and conversely it was determined that t_+t_- conformations, which were included in the previous four-state model, should be excluded. Most importantly, our model, without adjustment of geometric or energy parameters estimated from ab initio electronic structure calculations on small molecules, predicts the characteristic ratio of PTFE at 600 K consistent with recent experiments.

Appendix

It is of interest to attempt to reduce the six-state model presented above to a four-state model where the $g^+{}_-$ and $g^-{}_+$ states combine with the $g^+{}_+$ and $g^-{}_-$ states, respectively. Such a model is illustrated in Figure 8. Here, the g^+ and g^- states are assumed to have the geometry of the $g^+{}_+$ and $g^-{}_-$ conformations, respectively, and the E_σ and E_ψ values are same as in Table 5. Conformations of the type $g^+{}_+g^-{}_+$ are represented as g^+g^-, requiring a new second-order parameter ω' with energy $E_{\omega'} = 2.4$ kcal/mol. The resulting four-state model yields a characteristic ratio of 9.4 at 600 K, with $(\mathrm{d}\ln\langle R^2\rangle/\mathrm{d}T)1000 = -1.5$, in reasonable agreement with the predictions of the six-state model (9.8 and -1.2, respectively). At 440 K, the four-state model predicts a gauche probability $P_{g^\pm} = 0.28$, with $(\mathrm{d}\ln p_{g^\pm}/\mathrm{d}T)1000 = 1.5$, in good agreement with the six-state predictions of 0.29 and 1.5, respectively. The gauche probability $p_{g^\pm}$ from the six-state model is the sum of the probability of $g^\pm{}_\pm$ and $g^\pm{}_\mp$ states (see Figure 7). As the latter states have been shown to be relatively inefficient in reducing the characteristic ratio, a larger characteristic ratio would be expected from the six-state model for the same gauche fraction, as is seen. This effect is augmented to some degree by the more extended nature of the $g^+{}_+g^-{}_+$ conformations in the six-state model compared to the g^+g^- conformations in the four-state model.

The above four-state model differs significantly from the earlier four-state model of Bates and Stockmayer.[9,10] The latter model, with the reported value of $E_\sigma = 1.4$ kcal/mol and a t_+t_- energy of 1.2 kcal/mol,[9,10] using our geometric parameters, predicts a characteristic ratio of 22.6 for PTFE at 600 K. Using our gauche energy of $E_\sigma = 0.6$ kcal/mol and disallowing t_+t_- conformations, as indicated by our ab initio calculations, the Bates and Stockmayer model yields a characteritic ratio of 9.1 and $(\mathrm{d}\ln\langle R^2\rangle/\mathrm{d}T)1000 = -0.5$. The predicted characteristic ratio is in reasonable agreement with the predictions of our four-state model due to the offsetting effects of disregarding the second-order ψ interaction, with the effect of decreasing the characteristic ratio by increasing the gauche probability, and of disallowing g^+g^- conformations, with the effect of increasing the characteristic ratio by removing these compact conformations. The discrepancy in the temperature dependence of the characteristic ratio indicates the importance of including g^+g^- conformations: the increasing population of these relatively high energy conformations with increasing temperature yields a strong negative temperature dependence of the characteristic ratio.

The good agreement for the conformational properties of PTFE studied here as predicted by the six-state RIS model and the four-state RIS model implies that the detailed characteristics of the split gauche conformations are not important for these properties. However, many other properties, such as local chain dynamics, require an accurate description of the local conformational energetics and geometries. It is important, therefore, that the local conformational properties of the molecules be well understood, even if simplified models are sufficient for predicting some properties.

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