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Fluoropolymer force fields derived from semiempirical molecular orbital calculations

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The van der Waals parameters for Lennard-Jones (6–12) and 6–9 potentials and equilibrium geometries for use in molecular mechanics and dynamics calculations on perfluoroalkanes and polytetrafluoroethylene (PTFE) have been derived from MOPAC AM1 (Austin model 1) semiempirical calculations on the model molecule perfluorohexadecane (PFHD). Parameters derived from MOPAC AM1 energies scaled to yield higher barriers to torsional motion, as suggested by *ab initio* results, provide a large *trans* barrier and stronger intermolecular attractions, which will probably be important for dynamics investigations into the nature of the solid-state phase transitions and helical defects. Reasonable intramolecular geometries and intermolecular packing arrangements are obtained with all parameter sets reported. Copyright © 1996 Published by Elsevier Science Ltd.

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INTRODUCTION

Polytetrafluoroethylene (PTFE) is a good model system with which to investigate structural transformations and their mechanisms in polymers. It is well characterized with respect to chemical and molecular structure. Its thermodynamic phase transitions are well documented[1]. The phase diagram contains the melt and four solid phases, which display a variety of structures, helical conformations and disorder types. However, the inter- and intramolecular contributions to disorder are not well understood, nor are the molecular mechanisms of the phase transformations. Investigations into the order–disorder and kinetic character of the phase transitions will provide knowledge that is useful for predicting and controlling the physical properties of PTFE and other polymers.

At 1 atm and below 292 K, PTFE is in phase II, characterized by a fairly well ordered triclinic unit cell containing two 13/6 (more precisely 54/25 or 473/219) helices of opposite hand[2,3]. Between 292 and 303 K, it is in phase IV, and above 303 K in phase I. X-ray data suggest that both of these phases are metrically hexagonal with one rotationally disordered stem per unit cell and that the helices are in the 15/7 conformation[4,5]. The rotational disorder in phase I is greater than in phase IV[2,5]. Modelling results on non-disordered 15/7 helices have found low-energy structures consisting of both left- and right-handed helices in the perfect unit cells. At higher temperatures, the time-average conformation in phase I becomes 2/1, but the rotational disorder and metrically hexagonal structure remain[5–7]. Axial disordering by small translations along the helical axes is also probable as temperature is increased[2,6]. Therefore, when PTFE melts at 600 K, it is highly disordered.

Previous modelling studies have successfully described the perfect solid phases of PTFE[2,6–8]. However, the intra- and intermolecular contributions to disorder and their role in the phase transitions are not well understood. Molecular mechanics and dynamics simulations are potential tools with which to investigate the phenomena involved in fluoropolymer phase transitions. However, before such calculations can be undertaken, reliable force-field parameters must be obtained. They must yield not only the proper helical conformation for a single chain, but also minimum-energy crystalline structures that are consistent with diffraction data. Previous studies of molecular packing using chains with a fixed helical conformation have given results in good agreement with available experimental data[2,6–8]. However, introducing conformational freedom while using available force fields resulted in reversion to a planar zig-zag conformation in the solid state. Recently, modifications to commercial force fields were successful in preserving the helical conformation in the solid state, but the predicted unit-cell dimensions were significantly smaller than the observed values[9]. Therefore, the force fields should be modified further if accurate modelling of

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PTFE and its phase transformations is to be achieved. Van der Waals parameters are of particular interest since they are most responsible for the intermolecular crystal packing interactions of most synthetic polymers.

METHODS

One approach to developing a reliable force field is to perform *ab initio* or semiempirical molecular orbital (MO) energy calculations and geometry optimizations on (small) model molecules for the polymer of interest. Molecular mechanics force fields can then be fitted to the quantum-mechanical data, while insisting that agreement with experimental cell dimensions, conformation and vibrational frequencies be maintained. Molecular mechanics force fields typically have a form such as that used in SYBYL[10] or Biosym Discover[11]. The total energy is given by the sum of several contributions:

$$E = E_s + E_b + E_t + E_{es} + E_{vdW} \qquad (1)$$

with the terms on the right-hand side given by:

$$E_s + \sum\left[\tfrac{1}{2}K_s(x_i - x_0)^2\right] = \text{bond stretching energy} \qquad (2)$$

where K_s = stretch constant and x_0 = equilibrium bond length;

$$E_b = \sum\left[\tfrac{1}{2}K_b(\theta_i - \theta_0)^2\right] = \text{angle bending energy} \qquad (3)$$

where K_b = bend constant and θ_0 = equilibrium bond angle;

$$E_t \sum\left\{\tfrac{1}{2}K_t[1 + \cos(3\tau)]\right\} = \text{torsional energy} \qquad (4)$$

where K_t = torsional barrier and τ = torsion angle (3 is a periodicity factor);

$$E_{es} = S_{es}q_1q_2/(\varepsilon_{es}r) = \text{electrostatic energy} \qquad (5)$$

where S_{es} = unit conversion constants, q_1, q_2 = fractional charges assigned to the atoms, ε_{es} = dielectric constant of the medium and r = distance between charges q_1 and q_2; and

$$E_{vdW} = \text{van der Waals energy}$$

There are three common equations for describing the van der Waals interactions. They are the Lennard-Jones (6–12) potential, the 6–9 potential and the Buckingham exponential–6 potential. The Tripos force field utilizes the first, which is given in SYBYL 6.01 as:

$$E_{vdW} = \sum\{\varepsilon_{vdW}[(r_{min}/r)^{12} - 2(r_{min}/r)^6]\} \qquad (6)$$

where ε_{vdW} is the depth of the potential well for a pair of atoms, r_{min} is the distance at which the interaction energy between the two atoms has a value of $-\varepsilon_{vdW}$, and r is the distance between the two atoms. The CFF91 force field[11] available through the Biosym *Discover* module utilizes the 6–9 non-bonded potential in the form:

$$E_{vdW} = \sum\{\varepsilon_{vdW}[2(r_{min}/r)^9 - 3(r_{min}/r)^6]\} \qquad (7)$$

In this work, a general least-square method has been used to adjust force-field parameters (initially the K values and van der Waals terms, and eventually the equilibrium values as well) to values that yield both a suitable helical conformation and an adequate description of PTFE in the solid state. The parameters were adjusted against energy *versus* backbone torsion angle data from semiempirical MO calculations on perfluorohexadecane (PFHD), having 16 CF_2 units. The performance of the parameters was then tested with respect to intramolecular behaviour using SYBYL 6.01 and Biosym *Discover* 2.9.5/94.0, and with respect to intermolecular behaviour using CREAM, a program used previously for examining interactions between rigid helices[2,6]. Overall, the sequence by which the force-field parameters were derived was:

1. Least-squares fit of force constants for the molecular mechanics force field to conformational energy data from MO calculations. The functional form of the force field was that symbolized in equation (1), i.e. the sum of equations (2)–(5) and a van der Waals term, either equation (6) or (7).
2. Adjust equilibrium geometry parameters such that molecular mechanics calculations yield a minimum-energy structure consistent with that from the semiempirical MO calculations.
3. Check intermolecular interactions for agreement with crystallographic data.
4. Iterate as necessary.

Details are given below. This sequence resulted in force-field parameter sets designated set I (for 6–12 van der Waals term) and set II (for 6–9 van der Waals term). *Ab initio* data were then used to scale the semiempirical MO energies, after which the entire fitting sequence was repeated. The resulting parameter sets are designated set III and set IV.

Semiempirical MO calculations

Previous results (specifically, heats of formation, charges and geometries)[9] from semiempirical MO calculations on PFHD as a function of backbone torsion angle from MOPAC version 6.00 with the AM1 (Austin model 1) Hamiltonian were used to generate a conformational energy curve. The backbone torsion angles were fixed at specified values (all equal), while the energy was minimized with respect to the remaining geometrical parameters of the molecule. Symmetry constraints were imposed on C–C bond lengths and C–C–C bond angles in the semiempirical calculations.

Fitting of force field to AM1 MO data

The force-field was fit to the PFHD semiempirical MO conformational energy (heat of formation) data by least-squares adjustment of the force constants and van der Waals parameters. A generalized non-linear least-squares fitting algorithm[12] based on the Levenberg–Marquardt method was utilized. The initial equilibrium (x_0 and θ_0) values used in the force-field equations were taken to be those of the MOPAC AM1 minimum-energy geometry (see *Table 1* later). The initial force constants (K_s, K_b, K_t) were taken from spectroscopic results[13]. The force constants were constrained to stay within the experimental dispersion (uncertainty) range reported[13]. Limits were imposed on the van der Waals parameters such that interactions of reasonable magnitude were retained for C···C and F···C pairs.

For non-bonded (van der Waals and electrostatic) interactions, SYBYL 6.01 and Biosym *Discover* consider only 1,4 and higher pairs (i.e. atoms separated by three or more bonds). For unlike atoms (F···C in this case), the van der Waals well depth (ε) was taken as the geometric mean of the two like-atom depths[10].

Therefore for F···C:

$$\varepsilon_{FC} = (\varepsilon_{FF}\varepsilon_{CC})^{1/2} \qquad (8)$$

The $r_{\min}$ value for unlike-atom interactions was taken as the arithmetic average of the like-atom values. The energy calculations in the fitting routine conformed to these conventions. The CFF91 force field uses quartic, cubic and quadratic terms for bond stretching and angle bending interactions[11]. For this work, only the quadratic terms were used. Additionally, cross-terms (e.g. bond stretching–angle bending interactions) available in the CFF91 force field were not utilized.

The initial values for the fluorine van der Waals well depth and $r_{\min}$ were 0.082 kcal mol^{-1} and 3.45 Å, respectively[2]. For carbon, 0.097 kcal mol^{-1} and 3.85 Å were used[2]. For electrostatic interactions, the MOPAC AM1 charges were used with a fixed dielectric constant of 1.0. It should be pointed out that in non-linear and non-linearizable situations, initial trial parameters must be given, and the final result can be dependent on these initial values (i.e. local minima may be encountered). Various values of the initial parameters were used to try to avoid this problem.

The next step in the adjustment procedure was to use the least-squares determined values of the force constants and van der Waals parameters in the Tripos and CFF91 force fields in order to modify the equilibrium geometry values. These modifications were carried out until the minimum-energy helix produced by the force field in molecular mechanics calculations agreed reasonably with the minimum-energy geometry resulting from the MOPAC AM1 calculations. The Broyden–Fletcher–Goldfarb–Shanno (BFGS) minimization procedure was used with a gradient termination criterion of 0.01 kcal mol^{-1} Å^{-1} and a non-bonded interaction cut-off distance of 50 Å.

The adjusted parameters were next tested with respect to intermolecular interactions between two rigid, like-handed helices to ensure that crystallographically reasonable structures were generated. SYBYL and Biosym *Discover* were used to generate the minimum-energy helix structure using the optimized van der Waals and valence force-field parameters. These minimum-energy helices were then used for the rigid helix intermolecular interaction calculations. The criterion for acceptance of a set of parameters was that the minimum-energy distance between axes of like-handed molecules at an optimized setting angle be approximately 5.6 Å (i.e. near the distance observed experimentally for like-handed molecules). If this criterion was not met, constraints were placed on the van der Waals parameters and the entire adjustment process (steps 1–4 listed above) were repeated until crystallographic arrangements as well as intramolecular geometries were reproduced reasonably.

Single-chain molecular mechanics

Once parameters were obtained that yielded reasonable intra- and intermolecular behaviour, conformational energy curves for PFHD were calculated using the force fields. Optimized geometries from both the semiempirical MO calculations and molecular mechanics calculations in SYBYL or Biosym *Discover* were used. The latter were determined by fixing the backbone torsion angles (all equal) at the desired series of values, parallelling the procedure used in the semiempirical MO calculations. Again, the BFGS minimization routine, a 0.01 kcal mol^{-1} Å^{-1} gradient termination criterion and a 50 Å non-bonded cut-off distance were used.

Crystal packing calculations with PFHD

Using PFHD molecules minimized in SYBYL or Biosym *Discover* with the modified force fields, phase II crystal packing of rigid helices was investigated with both 6–12 and 6–9 van der Waals parameters. The energy of a hexagonal array of seven conformationally rigid PFHD chains was minimized with respect to separation of helical axes using steps of 0.01 Å and setting angles at steps of 6.67° (the 54/25 helix crystallographically permissible setting angle increment or notch). Note, however, that the minimum-energy helices (which were used) were not necessarily in the 54/25 conformation. Constraining the helices to the 54/25 conformation was not deemed necessary at this stage, since previous results have shown that the helical conformation and chain packing are intimately interrelated[9]. Future investigations will examine further the influence of solid-state packing on the helical conformation of PTFE chains. Displacements of the helices along their axes were not considered. Fluorine atoms capped the ends of the chains. Though they will have some influence, the crystal packing calculations should not be dramatically affected by these. A 50 Å non-bonded cut-off radius was used.

Scaling of semiempirical MO energies

The methodology for scaling the semiempirical MO energies using *ab initio* data is discussed below.

RESULTS OF FITTING

The conformational energy curve (relative heat of formation as a function of backbone torsion angle) generated from the MOPAC AM1 semiempirical MO calculations is shown in *Figure 1* (full curve). *Table 1* summarizes the MOPAC AM1 minimum-energy geometry and the barrier heights relative to the minimum. These geometric parameters, though different from values for PTFE derived from X-ray data[1], do yield a reasonable (but longer) CF_2 repeat distance of 1.313 Å with a 1.61 Å C–C bond distance and a C–C–C angle close to tetrahedral. These results agree well with previous MOPAC calculations on PTFE (cluster method) using the PM3 Hamiltonian in which the predicted backbone bond lengths and angles were 1.60 Å and 110° respectively[14]. However, *ab initio* calculations[15] (D95+* basis set, without considering electron correlation) on perfluoro-n-butane (PFB), perfluoro-n-pentane (PFP) and perfluoro-n-hexane (PFH) yielded geometries that were consistent with values typically reported from X-ray analysis of PTFE[1], with a shorter C–C length (1.55 Å) and wider C–C–C angle (114–115°). These give a slightly shorter CF_2 repeat distance (1.288 Å) with a backbone torsion angle of 162° (ref. 15).

The *trans* barrier (at 180°) and *trans–gauche* (*tg*, at 120°) rotational energy barrier appear to be underestimated by the MOPAC AM1 calculations when

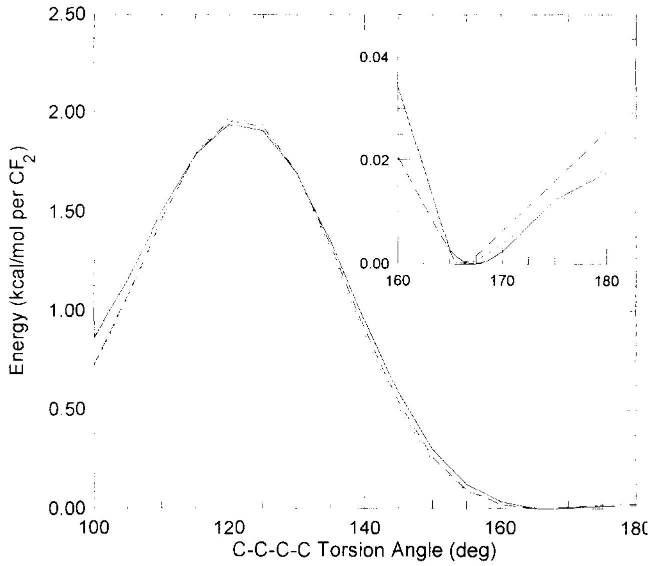

Figure 1 MOPAC AM1 conformational energy curve (—) for PFHD as a function of backbone torsion angle. Curve computed with parameter set I using the AM1 geometries (···). Curve computed with parameter set II using the AM1 geometries (- - -). The inset shows an expanded view of the minimum well and *trans* barrier

Table 1 MOPAC AM1 minimum-energy backbone geometry and rotational barriers for PFHD

C–C length	1.61 Å
F–C length	1.36 Å
C–C–C angle	109.6°
F–C–C angle	110.5°
F–C–F angle	104.4°
C–C–C–C torsion	167.4°
$-CF_2-$ repeat	1.313 Å
u/t (unit/turn)	70/33 (2.1212)
trans barrier	0.0175 kcal mol^{-1} per CF_2
tg barrier	1.939 kcal mol^{-1} per CF_2

compared to previously reported values[14,16–18]. Also, single-point energy calculations (using the D95+* basis set with electron correlation) on optimized PFB, PFP and PFH molecules give *trans* barriers that start at 0.0565 kcal mol^{-1} per CF_2 for PFB and increase to 0.223 kcal mol^{-1} per CF_2 for PFH[15]. Such behaviour indicates significant end effects and suggests that the *trans* barrier to rotation for PFHD would be higher than 0.223 kcal mol^{-1} per CF_2 if such calculations were extended to longer perfluoro-n-alkanes. This issue is addressed below.

Initial fits to the MOPAC AM1 data (using a force field in which the only non-bonded interactions considered were F···F) revealed that the periodic torsional terms in the functional form given in equation (4) increased the error between the original and fitted data and tended to force the minimum-energy backbone conformation to *trans*. Equation (4) implies a three-fold torsional potential with equilibrium torsion angles of 60° and 180°. This partially explains why the default Tripos force field predicts a planar zig-zag conformation for PTFE. Previous calculations on PTFE[16] also demonstrated that periodic torsional terms, whose functional forms are as in equation (4) above, made conformational predictions less satisfactory. The best agreement with X-ray data on PFHD and PTFE was obtained when the torsional barrier was set to zero[16]. While there is a certain elegance in having a force-field term to take into account every physically reasonable type of atomic interaction, the pragmatic approach of omitting the torsional terms from the force-field was taken in this work to achieve reasonable agreement with the semiempirical MO results. The force-field equation then becomes:

$$E = E_s + E_b + E_{es} + E_{vdW} \qquad (9)$$

The van der Waals parameters that result are expected to compensate for the effects of rotational barriers normally provided by the torsional energy term.

Reasonable agreement with the semiempirical MOPAC AM1 data could be attained only by a significant reduction of ε_{FF}, the F···F van der Waals well depth, by approximately an order of magnitude from typical initial values (0.08–0.10 kcal mol^{-1}). This is reflected in the final adjusted parameters reported in *Table 2a*. It may be argued that the shallow well depth might be a result of ignoring torsional energy terms and that their inclusion might give rise to deeper van der Waals well depths. This is true for C···C and C···F interactions, which are at attractive distances. However, it is not true for the repulsive, short-distance F···F interactions when reasonable r_{min} values are maintained. The initial fitting attempts (in which the torsional terms were included) resulted in unsatisfactory ε_{FF} values near 0.001 kcal mol^{-1} and ε_{CC} values near 1.0 kcal mol^{-1}. The F–F well depths listed in *Table 2a* are similar to the value (0.021 kcal mol^{-1}) used in modelling studies of poly(vinylidene fluoride)[19]. Thus there is evidence in the literature for ε_{FF} values of similar magnitude.

The adjusted valence force-field parameters are given in *Table 2b*. The resulting energies for PFHD, having AM1-optimized geometries and using the 6–12 (set I) and 6–9 (set II) potentials, are compared with the

Table 2 AM1-derived force-field parameters
(a) van der Waals parameters

	6–12[a]		6–9[b]	
Interaction	ε_{vdW} (kcal mol^{-1})	r_{min} (Å)	ε_{vdW} (kcal mol^{-1})	r_{min} (Å)
F···F	0.0115	3.207	0.0245	3.248
C···C	0.0050	3.400	0.0050	3.450
F···C[c]	0.0076	3.304	0.0111	3.349

[a] Set I
[b] Set II
[c] Calculated from equation (8)

(b) Valence force-field parameters. The equilibrium values below were used with both the 6–12 (set I) and 6–9 (set II) van der Waals potentials

		Force constant[d]	
Interaction	Equil. value	Set I	Set II
C–C stretch	1.61 Å	402.43	402.43
F–C stretch	1.36 Å	871.69	892.50
C–C–C bend	109.4°	0.0589	0.0532
F–C–C bend	110.0°	0.0486	0.0480
F–C–F bend	104.3°	0.0782	0.0782

[d] Stretch constants in kcal mol^{-1} Å^{-2}. Bend constants in kcal mol^{-1} deg^{-2}

original AM1 curve in *Figure 1*. Slightly better fits to the data were obtained when electrostatic interactions (using charges from the AM1-optimized geometry) were included. Accordingly, the parameters reported in *Table 2* are those obtained with consideration of electrostatic interactions. The statistical correlation coefficients for the fitted curves are both 0.997, indicating very good agreement.

The locations of the minima of the fitted curves along the backbone torsion angle coordinate are shifted to smaller values than that of the original AM1 curve (167.4°) as indicated in *Table 3*. Since the backbone torsion angle that generates a phase II helix is around 164.3° (ref. 6), these shifts are acceptable. *Table 3* also lists the fitted rotational barrier heights and their discrepancies with respect to the MOPAC AM1 barrier heights. Both the *trans* and *tg* barriers are adequately reproduced by the two parameter sets. While the *trans* barrier produced by parameter set II differs from the original AM1 *trans* barrier by +42.2%, this overestimation may be favourable since the AM1 barrier may in fact be too small (see below).

The conformational energy curves for PFHD resulting from molecular mechanics geometry optimizations with parameter set I and set II are shown in *Figure 2* (dotted and dashed curves). *Table 4* summarizes the minimum-energy geometry and rotational barrier heights. The helices resulting from set I and set II were close to the 54/25 (2.1600 units/turn) conformation having u/t ratios of 226/105 (2.1524 units/turn) and 491/228 (2.1535 units/turn), respectively. With set I, the *tg* barrier is underestimated by 9.2% (compared to AM1 results in *Table 1*), while the *trans* barrier is overestimated by 52.8%. With set II, both barriers are overestimated (*tg* 5.2%, *trans* 88.3%) compared to the results in *Table 1*. Again, overestimation of the *trans* barrier may not be detrimental. These differences in the rotational barrier heights indicate that the molecular mechanics calculations using the adjusted parameters result in slightly different minimum-energy geometries than do the MOPAC AM1 calculations. Relatively few, invariant force-field parameters cannot account for all of the interactions and changes in interactions implicit in molecular orbital calculations, especially when the conformation is far from the minimum to which the parameters were fitted.

Table 3 Fitted minimum-energy backbone torsion angles and rotational barrier heights

Parameter set	Torsion angle (deg)	Barrier^a *trans* (kcal mol^{-1} per CF_2)	*tg* (kcal mol^{-1} per CF_2)
I	166.0	0.0186 (+3.5%)	1.973 (+1.7%)
II	165.4	0.0256 (+42.2%)	1.957 (+0.9%)

^{a} Percentage error in parentheses

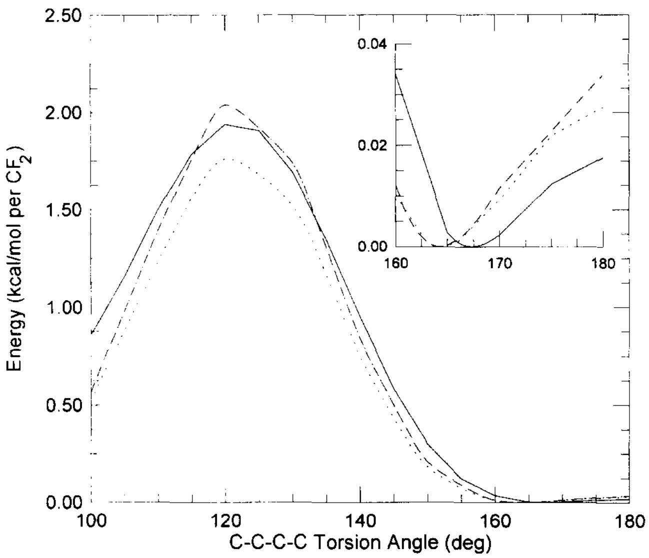

Figure 2 Conformational energy curves resulting from molecular mechanics calculations with paramer set I and set II compared to the MOPAC AM1 data: (—) MOPAC AM1; (···) set I; (- - -) set II. The inset shows an expanded view of the minimum well and *trans* barrier

Table 4 Minimum-energy geometry for PFHD using parameter set I in the Tripos force field and set II in the 6–9 force field

	Set I	Set II
C–C length	1.61 Å	1.61 Å
F–C length	1.36 Å	1.36 Å
C–C–C angle	109.7°	109.8°
F–C–C angle	110.6°	110.6°
F–C–F angle	104.5°	104.6°
C–C–C–C torsion	164.4°	164.3°
–CF_2– repeat	1.312 Å	1.313 Å
u/t (units/turn)	226/105 (2.1524)	491/228 (2.1535)
trans barrier^a	0.0275 (+52.8%)^b	0.0339 (+88.3%)
tg barrier^a	1.761 (−9.2%)	2.039 (+5.2%)

^{a} In kcal mol^{-1} per CF_2

^{b} Discrepancy between the barrier height listed and the corresponding MOPAC AM1 barrier in *Table 1* given in parentheses

Figure 3 shows the arrangement of right- and left-handed helices and the setting angles resulting from the crystal packing calculations. The setting angle relationships were the same for both set I and set II, as listed in *Table 5*, along with the projected unit-cell parameters predicted by the calculations. The projected cell dimensions are within 1.5% of experimental values obtained from X-ray diffraction analysis of phase II PTFE[3] and also agree well with previous calculations[2]. The relative setting angles along the a' direction ($\Delta\theta_a$) and b' direction ($\Delta\theta_b$) match previous modelling results[2]. This is not surprising since the minimum-energy helices from set I and set II were very close to the 54/25 conformation.

SCALED ENERGY BARRIERS

While the geometries predicted above are acceptable, the rotational barrier heights, especially the *trans* barrier, may require further scrutiny. With such a low *trans* barrier, an unrealistically large amount of conformational disorder might be observed in molecular dynamics simulations of PTFE. While a wide range of *trans* barrier heights for PTFE exists in the literature (0.265–1.888 kcal mol^{-1} per CF_2)[14,16–18], none are as low as the AM1 (or derived force field) values. *Ab initio* calculations on perfluorobutane (PFB) suggest that the *trans* and *tg* barriers for this small perfluoro-n-alkane are 0.0565 and 0.569 kcal mol^{-1} per CF_2 respectively[15]. This *tg*/*trans* barrier ratio of 10 (for PFB) compares to a ratio of 110 (for PFHD) from the AM1 calculations. For perfluoropentane (PFP) and perfluorohexane (PFH), *ab initio* calculations yield *trans* barriers of 0.178 and

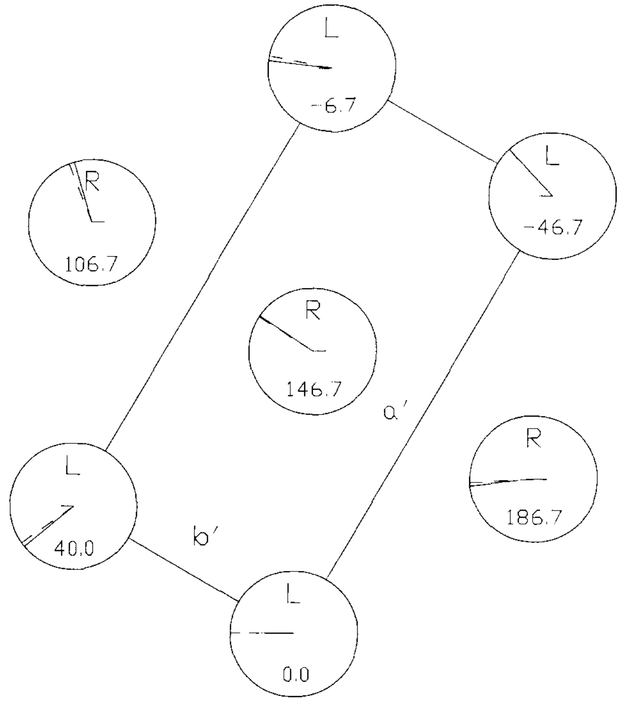

Figure 3 Minimum-energy phase II unit cell predicted with the adjusted van der Waals parameter sets I and II (both sets produced the same setting angles). The orientation of the projected unit cell is shown with the long axis being a' and the short b'. R and L designate right- and left-handed helices respectively. The shorter radial lines represent the 0.0° setting angle reference, while the longer radial lines and numbers give the setting angle obtained with the packing calculations. The broken lines indicate experimental results[13]

Table 5 Projected phase II unit-cell parameters predicted with van der Waals parameter sets I and II

Set	a' (Å)	b' (Å)	γ' (deg)	$\Delta\theta_a$ (deg)	$\Delta\theta_b$ (deg)
I	9.54	5.72	91.2	−46.7	40.0
II	9.47	5.65	91.0	−46.7	40.0
Experimental[a]	9.649	5.648	90.0	−46.4	35.8
Prev. calc.[b]	9.60	5.62	91.4	−46.7	40.0

[a] From ref. 3
[b] From ref. 2

0.223 kcal mol^{-1} per CF_2 (ref. 15). The *tg* values are not available. It seems prudent to use these *ab initio* results to correct for some of the apparent deficiencies in the AM1 data. This was accomplished by using the *ab initio* values to scale the AM1 data.

Scaling procedure

It was first necessary to estimate how the *ab initio* generated barriers for PFB, PFP and PFH would extrapolate to PFHD. Semiempirical MO calculations were used for this purpose under the assumption that *ab initio* calculations would follow a similar trend. Using MOPAC version 5.01 with the AM1 Hamiltonian, *trans* and *tg* barriers for a series of perfluoro-n-alkanes from PFB to perfluoroeicosane (PFE) were determined. The results of these calculations are shown in *Figures 4a* and *4b*. As the number of carbon atoms in the backbone increases, the rotational barrier heights (per CF_2) increase and then begin to level off when PFE is reached. The very limited *trans* barrier data available from *ab initio* calculations[15] suggest a similar trend as shown in *Figure 4a*, albeit with a much larger increment per backbone atom.

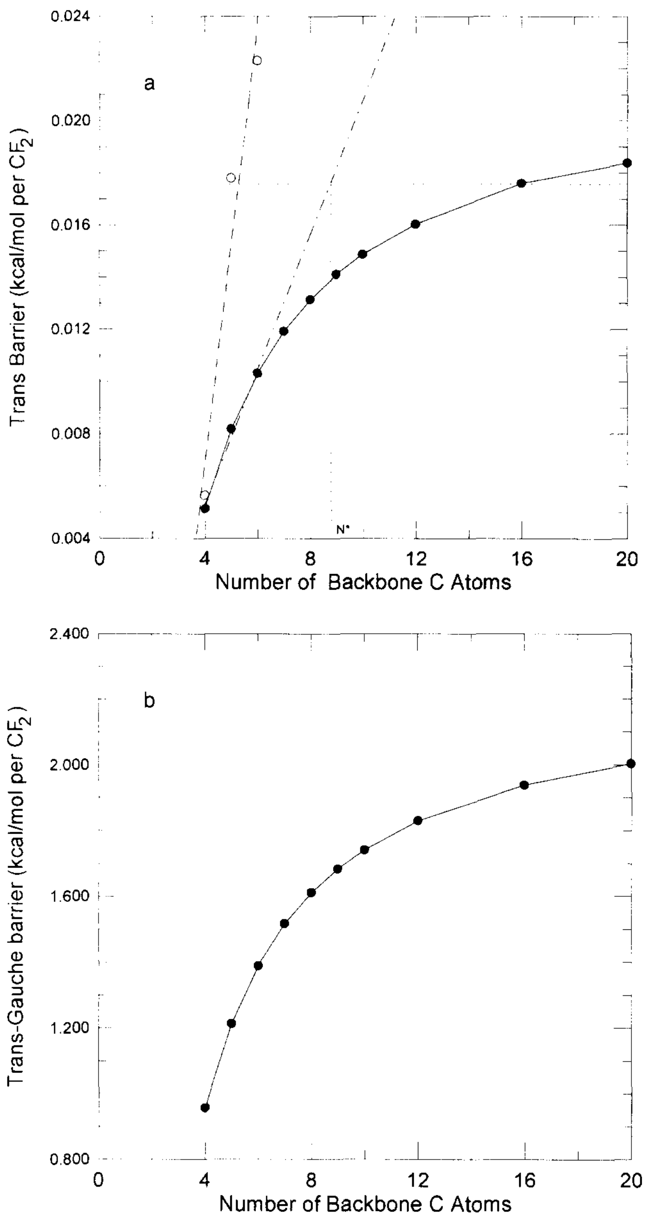

Figure 4 MOPAC AM1 calculations depicting the variation of rotational barriers for a series of perfluoro-n-alkanes from perfluorobutane to perfluoroeicosane. (a) The *trans* barrier. The open circles are *ab initio* data[15] for PFB, PFP and PFH, scaled down by a factor of 10. Also shown are the linear fits and intersections described in the scaling procedure applied to the AM1 data. (b) The *trans–gauche* barrier

To scale the AM1 *trans* barrier, the following procedure was used. A least-squares straight line was fitted through the three *ab initio* data points. The same was done with the PFB, PFP and PFH AM1 data points (see *Figure 4a*). Though a logarithmic function would most likely provide a good fit through the AM1 data points, the lack of *ab initio* data points makes this linear estimation a better choice. The backbone length at which the line through the AM1 points intersected the PFHD *trans* barrier height was determined. This value ($N^* = 8.76$) was then used in the equation of the straight line fitted to the *ab initio* points to estimate the *ab initio trans* barrier for PFHD. This estimated *trans* barrier was 0.465 kcal mol^{-1} per CF_2. The AM1 data on the *trans* side of the minimum-energy conformation were scaled (by a factor of 25.83) to yield a *trans* barrier of 0.465 kcal mol^{-1} per CF_2.

The AM1 data in *Figures 4a* and *4b* suggest that the *tg*/*trans* ratio decreases as the chain length increases. However, the absence of *ab initio* data with which to draw comparisons, and the fact that calculations utilizing the AM1 Hamiltonian may be suspect with respect to the predicted rotational barriers obtained, make it difficult to determine the behaviour of the *tg*/*trans* barrier ratio as a function of chain length. Therefore, using the value from *ab initio* calculations on PFB, the *tg* barrier was assumed to be 10 times the *trans* barrier, giving a value of 4.65 kcal mol^{-1} per CF_2. Accordingly, on the *tg* side of the minimum-energy conformation, the AM1 data were scaled (by a factor of 2.40) to yield a *tg* barrier of 4.65 kcal mol^{-1} per CF_2. *Figure 5* (full curve) shows the result of this scaling procedure.

Fitting of force field to scaled AM1 data

The force field (using the 6–12 or 6–9 non-bonded potentials) was fitted to the scaled AM1 data using the same procedure as above. The same molecular mechanics and crystal packing calculations as above were also performed with the parameter sets derived from the scaled AM1 data. Initial attempts at fitting this scaled curve resulted in good agreement with the *tg* barrier, but a poor *trans* barrier. Since its value is probably more important for future work, the *trans* barrier height was given a heavier weighting relative to the other data points so that it could be reproduced as accurately as possible while keeping the *tg* barrier within 150% (arbitrarily chosen).

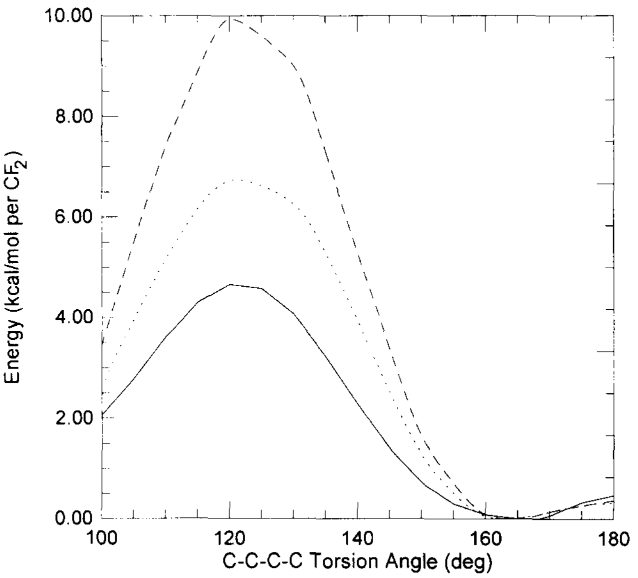

Figure 5 Scaled MOPAC AM1 conformational energy curve (—) for PFHD as a function of backbone torsion angle. Conformational energy curve (spline-smoothed) for PFHD as a function of backbone torsion angle generated by molecular mechanics calculations with parameter set III in SYBYL (···). Conformational energy curve generated with set IV in Biosym *Discover* (- - -)

Table 6 Force-field parameters derived from scaled AM1 data
(a) Van der Waals parameters

	6–12[a]		6–9[b]	
Interaction	ε_{vdW} (kcal mol^{-1})	r_{min} (Å)	ε_{vdW} (kcal mol^{-1})	r_{min} (Å)
F···F	0.2500	3.074	0.3328	3.200
C···C	0.0500	2.805	0.0500	3.000
F···C[c]	0.1118	2.940	0.1290	3.100

[a] Set III
[b] Set IV
[c] Calculated from equation (8)

(b) Equilibrium bond lengths and angles. The values below were used with both the 6–12 (set III) and 6–9 (set IV) van der Waals potentials

		Force constant[d]	
Interaction	Equil. value	Set III	Set IV
C–C stretch	1.595 Å	402.43	402.43
F–C stretch	1.36 Å	861.85	892.65
C–C–C bend	107.5°	0.0366	0.0336
F–C–C bend	110.0°	0.0466	0.0466
F–C–F bend	104.4°	0.0646	0.0782

[d] Stretch constants in kcal mol^{-1} Å^{-2}. Bend constants in kcal mol^{-1} deg^{-2}

Fitting the scaled AM1 data resulted in the parameter sets (III and IV) given in *Table 6*. Electrostatic interactions (AM1 charges) were included. Overall, the agreement was less satisfactory than that obtained with the original AM1 data. Much higher *tg* barriers (11.3 and 11.0 kcal mol^{-1} per CF_2 respectively) were generated by parameter set III and set IV when used with AM1-optimized geometries. The *tg* barrier is inextricably linked to the magnitude of the *trans* barrier when a force field with invariant force constants and non-bonded parameters is used. If intramolecular energy contributions dictate the number of defects in the solid state, the higher *trans* barrier height (compared to sets I and II) should give more meaningful results in molecular dynamics simulations, at the price of being less accurate in describing transitions that might occur in the melt.

Molecular mechanics

Set III (in SYBYL) and set IV (in Biosym *Discover*) were used to generate conformational energy curves (optimizing all geometric variables except the specified backbone torsion angle) as a function of backbone torsion angle for PFHD. These curves are shown in *Figure 5* (dotted and dashed curves) and the minimum-energy geometry is reported in *Table 7*. The helical conformations are 210/97 (2.1650 units/turn) and 460/213 (2.1596 units/turn) for set III and set IV respectively. The set III minimum-energy helix is close to the 13/6 (2.1667 units/turn) conformation, while the u/t ratio of the set IV minimum-energy helix is closer to that of the 54/25 conformation. The barriers to rotation are lower than the barriers obtained when the force-field parameters are used with fixed AM1 geometries. The molecular mechanics calculations allow optimized geometries that are more strained than the AM1 geometries (which relieves non-bonded repulsions). Again, a relatively simplistic force field with fixed parameters cannot reproduce all the details of molecular orbital calculations.

The *tg* barrier of 6.725 kcal mol^{-1} per CF_2 from set III is in fair agreement with the scaled AM1 *tg* barrier. Though the minimum-energy geometries obtained from molecular mechanics and semiempirical MO calculations differ greatly at the *tg* barrier (e.g. C–C length of 1.68 Å from set III *versus* 1.625 Å from AM1), dynamics simulations utilizing the adjusted parameters should not be adversely affected as molecules only rarely visit the peaks of energy barriers. The *trans* barrier of 0.313 kcal mol^{-1} per CF_2 (underestimated by 32.5% compared to the scaled AM1 *trans* barrier) seems more realistic than that previously obtained from the unscaled AM1 data.

The *trans* barrier obtained with set IV (0.358 kcal mol^{-1} per CF_2) agrees well with that from set III and the scaled AM1 *trans* barrier. However, the *tg* barrier (9.93 kcal mol^{-1} per CF_2) is significantly higher than the scaled AM1 barrier and that from set III. Part of the reason lies in the van der Waals parameters. The non-bonded parameters in set IV yield higher repulsive energies than those of set III in the range of approximately 2.25–3.0 Å. The shortest F–F distances generated by set III and set IV at the *tg* barrier were 2.41 and 2.31 Å respectively.

The crystal packing arrangements obtained with parameter sets III and IV are given in *Table 8*. The input molecules had the geometries listed in *Table 7* (obtained by molecular mechanics optimizations with set III and set IV). The projected unit-cell parameters obtained are within 1% of experimental values listed in *Table 5*. The relative setting angles along the a' (long) cell axis (eight 54/25 notches compared to seven) differ more from experimental[3] and previous modelling results[2] than the other unit-cell parameters. The setting angle along the b' axis predicted by set IV is also off by one notch. The results obtained with parameter set I and set II agree more closely with experiment and earlier modelling studies in that the setting angles along the a' axis maintain a seven notch (54/25) relationship, and those along the b' axis maintain a six notch relation. Taken together, the results show that the specific nature of the chain packing in the solid state is very sensitive to the nature of the helix. (The converse is also true!)

Whether the force field embodied in sets I and II or that described by sets III and IV will prove more accurate for molecular dynamics simulations in the solid state remains to be determined. While the larger *trans* barrier given by sets III and IV seems more reasonable based on single-chain properties, it is also quite possible that, in reality, chain packing effects play a strong (or stronger) role in resisting the formation of defects in the crystal. That is, PTFE maintains its phase II structure until near 19°C because (1) defects have relatively high *intra*molecular energies, (2) defects have relatively high *inter*molecular energies, or (3) both intra- and intermolecular effects are important. Only comparisons of experimental data with the results of MD simulations of the solid state using these force fields will be able to suggest which set is most appropriate.

Table 7 Minimum-energy geometry for PFHD using parameter set III in the Tripos and set IV in the Biosym Discover force fields

	Set III	Set IV
C–C length	1.61 Å	1.61 Å
F–C length	1.36 Å	1.36 Å
C–C–C angle	109.6°	109.6°
F–C–C angle	110.6°	110.6°
F–C–F angle	104.4°	104.5°
C–C–C–C torsion	163.2°	163.7°
$-CF_2-$ repeat	1.311 Å	1.311 Å
u/t (units/turn)	210/97 (2.1650)	460/213 (2.1596)
trans barrier[a]	0.313 (−32.5%)[b]	0.358 (−23.0%)
tg barrier[a]	6.725 (+44.6%)	9.932 (+113.6%)

[a] In kcal mol^{-1} per CF_2

[b] Discrepancy between the barrier height listed and the corresponding scaled MOPAC AM1 barrier given in parentheses

Table 8 Projected phase II unit-cell parameters predicted with van der Waals parameter sets III and IV

	Set III	Set IV
a' (Å)	9.59	9.53
b' (Å)	5.64	5.66
γ' (deg)	90.6	90.9
$\Delta\theta_a$ (deg)	−53.3	−53.3
$\Delta\theta_b$ (deg)	+40.0	+46.67

CONCLUSIONS

Van der Waals parameters for Lennard-Jones (6–12) and 6–9 potentials and equilibrium geometries for use in molecular mechanics and dynamics calculations on perfluoroalkanes and PTFE have been derived from semiempirical calculations on the model molecule perfluorohexadecane. The approach used is best described as a pragmatic one utilizing a combination of least-squares refinement and manual adjustment of force-field parameters. Reasonable intramolecular geometry and intermolecular packing arrangements are obtained with all parameter sets reported. Parameters derived from MOPAC AM1 energies scaled to *ab initio* results provide a higher *trans* barrier and stronger intermolecular attractions, which will probably be important for dynamics investigations into the nature of the solid-state phase transitions and helical defects.

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