Molecular Mechanics (MM4) Study of Fluorinated Hydrocarbons

Kuo-Hsiang Chen, Jenn-Huei Lii, Gerald A. Walker, Yaoming Xie, Henry F. Schaefer, III, and Norman L. Allinger*

Center for Computational Chemistry, Chemistry Annex, University of Georgia, Athens, Georgia 30602-2526

Received: January 20, 2006; In Final Form: March 17, 2006

A molecular mechanics study of small saturated hydrocarbons (up to C-6) substituted by up to six fluorines has been carried out with the MM4 force field. A parameter set has been developed for use in the calculation of bond lengths, bond angles, torsion angles, conformational energies, barriers to rotation, dipole moments, moments of inertia, and vibrational frequencies for these compounds. The results are mostly in fair to good agreement with experiment and ab initio calculations. The high electronegativity of fluorine leads to serious geometric consequences in these compounds, but these consequences can be dealt with adequately by suitable cross-terms in the force constant matrix, and by recognizing that some of the reference bond lengths and angles (l_0, θ_0) and the corresponding stretching and bending constant parameters (k_s, k_θ) that are usually thought of as constants must in fact be treated as functions of the electronegativity of the substituents. Additionally, the heavy mass of the fluorine (relative to the mass of hydrogen in alkanes) leads to large values for other cross-terms that were found to be unimportant in hydrocarbons. Conformational equilibria for polyfluorinated compounds are affected by the *delta-two effect* well-known in carbohydrates. A few larger fluorinated and polyfluorinated alkanes, including perfluoropropane, perfluorobutane, and Teflon, have also been studied.

Introduction

The MM3 force field[1,2] has been the workhorse of small molecule calculations for quite some years. While it has given pretty good results for most molecules and molecular properties studied, it has some clear limitations. In an effort to overcome the major known limitations in MM3, the MM4[3−26] force field was developed, starting with hydrocarbons.[3−6] The structures and physical properties of hydrocarbons (alkanes) can be well described by molecular mechanics. That is, they behave in a very classical way. They form the backbone of organic molecules, and hence, it is important that they be well described by any force field that is to be generally used. Ab initio calculations at the triple-ζ level with some correlation (MP2 or DFT) give fairly good representations of structure that can be reasonably well corrected to equilibrium (r_e) geometries, that can in turn be converted into experimental structures (r_g, r_z, r_α) with the aid of vibrational corrections.[27,28] The experimental structures, plus these ab initio structures, have been used as the basis from which MM4 has been developed. The MM4 calculations were subsequently extended to the structures and properties of several classes of functionalized derivatives.[7−26] (See the Appendix for some definitions and an explanation of some abbreviations used throughout the paper.)

Fluorine compounds form a much more complicated set of substances to deal with in molecular mechanics than most compound classes, for several reasons. First, the fluorine is highly electronegative, so where in most other classes of compounds the substituents exert small electronegativity perturbations on the hydrocarbon skeleton, in fluorine compounds, these perturbations tend to be quite large. Second, there are many known compounds which contain not just one or two but many fluorines up to Teflon (perfluoropolyethylene) in the limit. Obviously, electronegativity effects from the fluorines become extremely strong in highly fluorinated compounds, and these effects were not dealt with very well by MM2[29] or MM3.[30] The fluorine[29] contains lone pairs of electrons, and thus can show negative hyperconjugative effects.[31] Additionally, the heavy mass of fluorine relative to hydrogen leads to changes in the vibrational spectra of these compounds, relative to hydrocarbons.

With most classes of compounds, heats of formation provide useful information for describing the location of structures on the energy axis of the energy surfaces. However, in the case of the fluoro compounds, adequate experimental information concerning heats of formation is not available. Attempts were made to utilize such information as it exists, but these compounds combust poorly, and the accuracy of the available information falls far short of that obtained for most other classes of compounds. Additionally, because of the strong electronegativity effect of fluorine, many terms describing the interactions between fluorines would be required to develop a bond-energy type of heat of formation calculation. Accordingly, we had to forego the use of this type of information for this class of compounds.

To extend the applicability of molecular mechanics treatments, we have in the present work developed an MM4 force field and parameter set for fluorinated hydrocarbons. The MM4 geometries, including moments of inertia, dipole moments, conformational energies, and vibrational frequencies, are reported here for a wide variety of fluorinated hydrocarbons and compared with extensive experimental and ab initio results. The ab initio calculations were carried out at the MP2/6311++G(2d,2p) level using the Gaussian 94 program.[32] This basis set is referred to locally as "big", and referred to in writing as "B", or MP2/B. Earlier studies have shown that this kind of calculation gives r_e single bond lengths between C, N, O, and F atoms with small systematic truncation errors (approximately 0.003−0.007 Å too long).[27] Hence, these big basis set calculations,

---

* To whom correspondence should be addressed.

10.1021/jp060430x CCC: $33.50

with the appropriate bond length corrections, are called “BC or MP2/BC calculations” and are so referred to throughout this paper.

In using experimental data to develop parameter sets for molecular mechanics methods, the accuracy and reliability of those data need to be known. For experimental measurements in general, this information is available because of extensive analogous independent studies. Unfortunately, the accuracy to be expected from BC calculations is generally less well-known. On the whole, we feel that in the present case the uncertainties in the structures and energies from BC calculations are generally similar to or somewhat greater than those from the best experimental values.

The Energy Surface and Force Field. The initial objectives of a molecular mechanics calculation are ordinarily to determine the spatial coordinates and energies of the stationary points of the system at hand. These are the points on the energy surface where the first derivatives of the energy with respect to the coordinates are all equal to zero. The remainder of the energy surface is of limited interest.

The second thing that we want to know is the value of the second derivative of the energy with respect to the coordinates at each stationary point, as these establish the vibrational properties, and hence much of the thermodynamics, of the system. The vibrational spectra required for most of the compounds discussed herein have been previously determined experimentally, and are recorded in the literature with full interpretations. There are occasional errors in this interpretations, which were uncovered and corrected by using ab initio calculations. This work will be described later, in the section labeled Vibrational Frequencies.

To define that portion of the energy surface which is normally of interest then, we have to determine the set of coordinates corresponding to the stable structures and transition states and the force constant matrix (**F** matrix) for each. The latter tell us about the variation of the energy around the stationary points. In developing a force field to describe a set of compounds, in this case fluorocarbons, we need to develop two groups of parameters, one of which involves coordinates and the second of which involves how the energy changes with the coordinates. And, of course, these are coupled.

We want to consider the MM3 treatment of fluorinated alkanes as a starting point.[30] There are several differences between the MM4 and MM3 force fields that are important for the present work, and these will be outlined here. Of course, it has been many years since MM3 was developed (1985−95), and more and better data and methods have become available since that time. It was desirable to try to fit with MM4 not only everything that was looked at with MM3 but also any available newer or significant previously unconsidered data as well. In particular, it has now become much easier to do higher level ab initio calculations than it was when MM3 was being developed. While we believe that at present molecular mechanics still needs to ultimately refer back to experimental data, we can use ab initio (BC) calculations to fill in many gaps in those data, and occasionally to correct inaccuracies in the experimental information.

When MM3[1,2] was originally being developed from MM2,[34] we spent some years gradually improving the MM2 results by adding to the force field various terms that had been omitted from MM2, and which were subsequently found to be important. When the results were deemed to be sufficiently improved over MM2, we stopped, defined that level as MM3, and used that standard subsequently. It was recognized later that there was something of a plateau in the development of molecular mechanics, and that MM3 had almost, but not quite, reached that plateau. After this became clear, it was decided to develop MM4 to fully reach that plateau. We define that plateau as what might be called *experimental accuracy* with respect to geometry and energy. Thus, we would like in general to calculate bond lengths with an accuracy of about 0.003 Å and bond angles to about 1°. Energies within the same molecule (conformational energies, rotational barriers) should be within a few tenths of a kilocalorie per mole for stationary points that are within a few kilocalories per mole of the global minimum. Additionally, to get good thermodynamics, we need to have the vibrational spectra calculated with an overall root mean square (rms) error of no more than about 25 cm^{-1}. To reach this level of accuracy, we had to add several previously unused cross-terms into the force constant matrix. Additionally, after some years of experience, certain features of the MM3 force field were found to be less accurate, or less complete than would be desired, so simultaneously, these small items were taken into account in the development of MM4. Major changes in MM4, relative to MM3, included the addition of bend−torsion−bend interactions to improve the spectroscopic frequency calculations and of torsion−bend interactions to improve the geometric calculations. The former have a pronounced effect on spectra, as they allow the coupling of bending motions (especially the 1,4 bending motions) to vary as a function of torsion angle. While this was an important thing to include in a force field in order to fit vibrational spectra, it had almost no effect on structure. On the other hand, the torsion−bend interaction (unimportant in hydrocarbons) is also important for bond angles where the atom at the end of an angle supports a lone pair of electrons. Such angles, of course, are ubiquitous in compounds of oxygen, nitrogen, and sulfur, each of which is commonly found in organic molecules, and especially in biologically interesting molecules. However, many other atoms contain lone pairs, and this particular type of interaction is important for those as well. The inclusion of this interaction permits one to account for angular differences by up to 5° or so in cases where such variation is observed upon torsion. Such large variations are routinely encountered, and this is part of what might be called a *negative hyperconjugative effect* (which includes the anomeric[21] and Bohlmann effects[24,31]). If it is not properly included, major geometric errors in the calculated structures result.

There are torsion−stretch interactions analogous to these torsion−bend interactions. Again, they occur when there is an atom that has a lone pair of electrons attached to a bond being stretched. This interaction can lead to bonds being appreciably stretched as a function of torsion angle, and this in turn can have a significant effect on the energy of the system. The anomeric effect is probably the best known example here, where bond length and energy changes of about 0.02 Å and 2 kcal/mol may occur. These changes are far beyond ordinary experimental errors and must be included in any force field that is to be of experimental accuracy.

There are some parts of the calculations that are carried out differently in MM4 from the way they were with MM3. If we take the Bohlmann effect as an example, this is an effect wherein the bond length of a C−H bond is more or less stretched as torsion occurs about the bond that attaches the carbon to an atom carrying a lone pair.[31] The Bohlmann effect was calculated with MM3 using the standard equations from the initial geometry and the torsion angle in question. However, as the geometry optimization proceeds, the torsion angle changes, and therefore, the effect has to be recalculated at every iteration.

Thus, when one optimizes the effects of the forces acting, one is also changing the values of the "constants" in the equations that define those forces. Hence, the optimization has to be iterative, and it tends to be rather slow. A more efficient method is to calculate the Bohlmann effect (and other similar things) with the aid of a matrix element that goes directly into the force constant matrix. The latter scheme was used in MM4.[24] However, the latter scheme, while mathematically more precise and efficient by virtue of its noniterative nature, also has a drawback. With the MM3 method, one actually obtains numerical values that can be specifically assigned to each of these different effects for each bond for the molecule at hand. Such numbers are not readily available from the MM4 calculation because of the way they are mixed together with other things such as van der Waals and electrostatic interactions in the matrix element.

With these new features in MM4, one would expect in general to be able to fit the geometric and spectroscopic data much better for molecules containing one or a small number of fluorines. Indeed, this was found to be the case. The vibrational spectra are better calculated with MM4, as are the structures, as is most clearly evidenced by the moments of inertia. On the other hand, with only these improvements, the MM4 calculations on fluorides were still not very good for highly fluorinated molecules. Obviously, there were things that were happening in these molecules that led to much larger distortions in the geometries, energies, and spectra than had previously been recognized. Another important item was the van der Waals interaction function between fluorine and hydrogen. The availability of better ab initio calculations (BC) made it possible to refine this function relative to that used in MM3. The H/H interaction was earlier found to be somewhat different from that used in MM3,[3] and important for the present purposes, the F/H interaction was also.[8]

Results and Discussion

Parameter Optimization. MM3 was parametrized to fit data from experiment, and ab initio data were used only to a quite small extent, as the accuracy of the available ab initio data at that time was quite limited. When we did the parametrization of hydrocarbons with MM4, we tried to fit the parameters mainly to experimental data but made use of such ab initio data as were available, which were mainly at the MP2/6-31G* level. We now routinely use the MP2/6-311++G(2d,2p) level.

The parameters required for the force field calculation can be divided into groups, depending on whether they directly effect the coordinates or the force constant matrix. Those that effect the coordinates include such things as l_0 and θ_0, the normal strainless values for bond lengths and angles, for example. These things can be approximately determined for different atom combinations from simple molecules. The changes of l_0 brought about with electronegativity changes are known to be important from previous work.[35] It is also known that the changes in θ_0 brought about by electronegativity can be important in some cases,[20] and the present work emphasizes that fluorine is one of those cases.

The **F** matrix can be thought of in terms of two components, the diagonal part (stretching, bending, and torsion) and the off-diagonal part (coupling). The diagonal elements are normally much larger than the off-diagonal elements, and they need to be assessed first. The off-diagonal elements, usually neglected for the most part in simple force fields (except for the van der Waals and electrostatic components), can have a strong influence on molecular geometries, especially so if the molecules contain atoms that have lone pairs of electrons. Fluorocarbons, of course, have numerous lone pairs of electrons, and hence, some of these off-diagonal terms become important.

There is something of a hierarchy in the parameter optimization routine, as we carry it out. The moments of inertia of the molecules are most important for determining the structures, from our point of view. The stationary point energies are the other equally important feature, and they determine the important part of the vertical dimension of the potential surface. The moments of inertia are not optimized directly. Rather, the bond lengths, angles, and torsion angles are varied as they and the stationary point energies are optimized, to indirectly optimize these moments. Since these things are weakly coupled with the vibrational spectra, the latter must also be included in the iterative sequence.

As is customary, a preliminary (trial) parameter set has to be obtained somehow. In the case of the present work, it was obtained from MM3.[30] The bending, stretching, and torsional parameters were subsequently modified somewhat in order to reproduce better the vibrational spectra of several molecules, and numerical values were chosen for the cross-terms. After the spectra were roughly correct (the average rms errors in the frequencies of about 14 compounds were approximately 80 cm^{-1}), the geometric parameters were adjusted so as to give more nearly correct values for structures, torsional barriers, dipole moments, and moments of inertia. Refinement then proceeded iteratively, until all of these things were optimized within the limitations imposed by the terms included in the force field. All of the available pertinent experimental data were considered, as were BC calculations for important stationary points on the potential surfaces of key molecules, especially when such points were not covered by experimental information. When we were satisfied that the optimization had been completed, we arrived at the parameter set given in Supporting Information Table S1.

Parameter Set. Supporting Information Table S1 contains the MM4 parameters for the fluoroalkanes, including torsional parameters for FCCH, FCCF, and FCCC torsion angles, C−F stretching parameters (k_s) and natural bond lengths (l_0), and the electronegativity correction factors for shrinkage of C−C and C−F bonds, for use when the hydrogens of a hydrocarbon are replaced by fluorines. (The original hydrocarbon force field itself was, of course, used here unchanged.[3]) Also included are the electropositive correction factors for lengthening C−F bonds as one goes from a primary carbon atom, to a secondary carbon atom, and to a tertiary carbon atom. Similarly, the natural bond angles (θ_0) and bending parameters (k_b) for HCF, CCF, and FCF bond angles were included. The rotational barriers for simple compounds were also fit using torsional parameters. Since fluorine contains lone pairs of electrons, the torsion−bend and bend−torsion−bend parameters involving fluorine are important[3−5] and are included.

With hydrocarbons, a stretch−bend interaction where the bond being stretched was attached to the center atom, but outside of the angle being bent, was found to be unnecessary. However, with the molecules that contained three or four fluorines attached to a single carbon, that term becomes important,[36,37] and was included here. The comparison of the vibrations of tetrafluoromethane with those of methane itself is instructive. As the HCH angle in methane bends during a vibration, the carbon moves very little, and there is very little interaction between that bending and the stretching of the CH bonds that are not involved in the angle being bent. However, with tetrafluoromethane, the mass of fluorine and carbon are similar. Thus, when the FCF angle is being bent, the carbon moves quite a lot. Hence, the interaction between the FCF bending and the CF stretching (where the latter bond is not included in the angle being bent) becomes more important. Also, the spectrum of tetrafluoromethane cannot be fit even marginally well, unless that explicit interaction is included.

Having an initial parameter set, and a large trial set of compounds to be described with MM4, the structures and properties of the trial set were calculated in the usual way, and the parameters were adjusted in order to best fit those properties (structures, energies, vibrational spectra, etc.), as is ordinarily done. Additional compounds were then added to the trial set, to try to cover all eventualities. Various items came to our attention during this stage of the work, and particularly important is the following. Molecular mechanics normally makes the assumption that one can study small molecules, determine parameters, and use those parameters for the studies of large molecules. These parameters (those that go into the force constant matrix and those which determine the coordinates) are thought of as transferable constants. However, it became increasingly clear many years ago as we tried to improve our model that in some cases these items are not constants but functions of other variables. For example, l_0, the length of a bond of a given type, varies with the electronegativity of substituents that are attached to atoms forming that bond. Normally, the variation of most of these constants with their environment is relatively small, and in the past, it has typically been neglected by others. However, if we want a model that gives calculated results with an accuracy comparable with experiment, then in at least some cases we must take into account the variability of these constants with environment. An important quantity with fluorocarbons is the variation of the C−C stretching constant with the number of fluorines attached in the α and/or β positions of the bond (the total electronegativity effect). This item was noted and commented on earlier,[30] and will be discussed below under the C−C bond lengths.

When parameters are fit to a collection of experimental and ab initio data, there is always the problem of how to weight the various pieces of data. There is no really well-defined way for doing this, because the data are so diverse in nature, and the accuracy of a specific piece of data is often uncertain. Generally speaking, however, we feel that moments of inertia are the most important pieces of structural information. They are typically measured with high accuracy (five or six significant figures), and there is no uncertainty considering assignments (as there is with spectroscopic frequencies or radial distribution functions, for example). Thus, moments of inertia must be reproduced accurately if structures are to be reproduced accurately, and accordingly, they are heavily weighted. How much error one is going to accept in one piece of data relative to another is a judgment call. We have accordingly weighted the fits of the data, and the evaluation of the parameters, according to our best judgment. The results will be presented in the tables that follow and will be discussed.

TABLE 1: C−F and C−C Bond Lengths (Å) in Simple Fluoroalkanes

A. Methyl-, Ethyl-, Isopropyl-, and *tert*-Butyl- Compared to Experimental Data

compound	exptl	MM3/Δ	MM4/Δ
C−F Bond Lengths			
$CH_3F(r_g)$	1.391(1)[40]	1.389/−0.002	1.385/−0.006
$C_2H_5F(r_a)$	1.397(4)[41]	1.400/0.003	1.398/0.001
$(CH_3)_2CHF(r_g)$	1.405(2)[42]	1.408/0.003	1.408/0.003
$(CH_3)_3CF(r_a)$	1.425(24)[43] [a]	1.413/-	1.411/-
signed av		+0.001	−0.001
rms		0.003	0.004
C−C Bond Lengths			
$C_2H_5F(r_a)$	1.502(4)[41]	1.508/0.006	1.505/0.003
$(CH_3)_2CHF(r_g)$	1.514(2)[42]	1.512/−0.002	1.514/−0.000
$(CH_3)_3CF(r_a)$	1.520(24)[43] [a]	1.513/-	1.517/-
signed av		+0.001	+0.001
rms		0.004	0.002

B. Methyl-, Ethyl-, Isopropyl-, and *tert*-Butyl- Compared to MP2/BC Calculation

compound	MP2/BC	MM4/Δ
C−F Bond Lengths[b]		
CH_3F	1.387	1.380/−0.007
C_2H_5F	1.395	1.393/−0.002
$(CH_3)_2CHF$	1.404	1.402/−0.002
$(CH_3)_3CF$	1.413	1.407/−0.006
signed av		−0.004
rms		0.004
C−C Bond Lengths[b]		
C_2H_5F	1.507	1.501/−0.006
$(CH_3)_2CHF$	1.510	1.508/−0.002
$(CH_3)_3CF$	1.515	1.512/−0.003
signed av		−0.003
rms		0.003

[a] The experimental error in this value is quite large, and the MM4 value is in good agreement with that from BC calculation. Accordingly, this value is omitted in the calculation of the averages. [b] All values are r_e.

Molecular Geometries. While we were dissatisfied with the overall treatment of fluoroalkanes by MM3, there were parts of the treatment that were quite satisfactory, particularly those parts that involved rather simple compounds. When we redid the study of fluoro compounds with MM4, we wanted to fit the data that we had previously fit with MM3, that we regarded as satisfactory. There were two sets of compounds that we looked at first. One was the set of simple monofluorides where the alkyl group becomes increasingly complicated, namely, methyl-, ethyl-, isopropyl-, and *tert*-butyl fluorides. The second set consisted of the ethanes, where successive fluorines were substituted for the hydrogens in all possible ways, fluoroethane, 1,1-difluoroethane, 1,2-difluoroethane, etc., up to hexafluoroethane. At the time we developed MM3 (late 1980s), ab initio calculations (small basis Hartree−Fock) were of some use, but they were not of high accuracy. More recently, we have been using MP2/6-311++G(2d,2p) calculations (herein abbreviated as MP2/B or B) as our standard. With these calculations, we find that there are small systematic errors due to basis set and electron correlation truncation, of the order of a few thousandths of an angstrom in bond lengths for bonds between first row atoms and carbon. Since the errors appear to be systematic, they can be corrected (MP2/BC or BC). Our best value for the correction is −0.0063 Å for the C−F bond. No corrections are needed for bond angles. When we made our comparisons between experiment and MM4 calculations for the two series of small molecules mentioned above, we simultaneously made the corresponding comparisons between the MM4 and BC calculations. The resulting information is all summarized in Table 1.

C−C and C−F Bond Lengths. There are only three kinds of bond lengths in this series of molecules, C−C, C−F, and C−H. The C−H bond lengths are poorly determined by the ordinary experimental methods. They are best determined indirectly from the corresponding stretching frequencies. We have not explicitly studied C−H bond lengths in the present work, as they were studied in detail earlier.[31] Thus, we will begin by looking at C−C and C−F bond lengths in the two small sets of molecules.

In Table 1A are given the experimental data and MM4 results for the monofluoroalkanes with differing degrees of branching.

TABLE 2: Moments of Inertia of Fluoro Compounds (r_z)[a]

	ref 44		exptl	MM3/%	MM4/%
CH_3F	a	Ib,c	19.7908	19.879/0.45	19.801/−0.05
CH_2F_2	b	Ia	10.2838	10.356/0.70	10.257/−0.30
		Ib	47.6559	48.047/0.82	47.692/0.08
		Ic	54.6363	55.154/0.95	54.546/−0.17
CHF_3	c	Ia	48.8151	49.342/1.08	49.049/0.48
		Ib	48.8151	49.342/1.08	49.007/0.39
CF_4	d	Ia,b,c	88.1740	88.947/0.88	88.380/0.23
C_2H_5F	e	Ia	14.0108	14.403/2.80	14.046/0.25
		Ib	53.9665	53.655/−0.58	53.907/−0.11
		Ic	61.6328	61.621/−0.19	61.612/−0.03
CHF_2CH_3	f	Ia	8.8413	8.996/1.75	8.824/−0.19
		Ib	9.3634	9.284/0.85	9.354/−0.10
		Ic	16.2309	16.285/0.33	16.144/−0.54
CH_2FCH_2F (gauche)	g	Ia	4.8447	4.913/1.41	4.852/0.16
		Ib	16.7407	16.627/−0.68	16.777/0.22
		Ic	19.1513	18.865/−1.50	19.142/−0.08
CH_3CF_3	h	Ib,c	16.1812	16.090/−0.56	16.127/−0.34
CF_3CHF_2	i	Ia	136.921	134.348/−1.88	136.862/−0.04
		Ib	208.859	212.681/1.83	209.206/0.47
		Ic	251.934	254.502/1.02	250.938/−0.40
C_3H_7F (trans)	j	Ia	18.7269	18.903/0.94	18.636/−0.48
		Ib	134.6264	135.449/0.61	134.783/0.12
		Ic	143.9846	144.691/0.49	144.067/0.06
C_3H_7F (gauche)	k	Ia	34.8445	34.754/−0.26	34.842/−0.01
		Ib	99.3699	101.263/1.91	99.780/0.41
		Ic	117.5830	118.192/0.52	117.404/−0.15
2-fluoropropane	l	Ia	58.1303	59.518/2.39	58.325/0.33
		Ib	62.3722	61.710/−1.06	62.422/0.08
		Ic	105.1824	105.878/0.66	105.607/0.07
2,2-difluoropropane	m	Ia	98.1355	99.516/1.41	98.096/−0.04
		Ib	104.4144	102.910/−1.44	103.927/−0.47
		Ic	105.1637	104.114/−1.00	105.373/0.20
t-butylfluoride	n	Ia	107.250	108.201/0.89	107.208/−0.04
		Ib	107.250	108.201/0.89	107.224/−0.02
fluorocyclohexane (eq)	o	Ia	117.1650	117.216/0.04	117.519/0.30
		Ib	230.8944	233.052/0.93	230.983/0.04
		Ic	317.5257	319.400/0.59	318.217/0.22
fluorocyclohexane (ax)	p	Ia	141.8418	141.681/−0.11	142.573/0.52
		Ib	192.2603	195.193/1.53	192.453/0.10
		Ic	255.1289	257.836/1.06	255.083/−0.02
1,1-difluorocyclohexane	q	Ia	158.3370	158.287/−0.03	158.684/0.22
		Ib	287.1839	289.520/0.81	285.531/−0.58
		Ic	334.1793	334.659/0.14	332.915/−0.38
signed av				+0.52	+0.010
rms				1.108	0.266

[a] The moments are in atomic units except for 1,1-difluoroethane, 1,2-difluoroethane, and 1,1,1-trifluoroethane, which are in units of g × $cm^2 \times 10^{-39}$.

In Table 1B are given the corresponding BC data compared with the MM4 data for the same set of compounds. In Supporting Information Table S2A are given the MM4 data for the fluoroethanes compared with experiment, and in Supporting Information Table S2B are given the same data compared with MP2/BC calculations. The experimental data in Table 1 and Supporting Information Table S2 were all well fit with MM3, and as a starting point, we wanted to make sure that they were fit as well by MM4.

It should also be mentioned at this point that, in fitting the geometries of these small molecules, it is very important that the moments of inertia of the molecules also be fit at the same time. All of the experimental data available concerning moments of inertia of small fluoride molecules are assembled in Table 2. These data will be discussed later, but we call attention to the fact here that the data fit in Table 1 and Supporting Information Table S2 need also to produce structures that agree with the data in Table 2.

In Table 1A, which compares the MM4 calculations (and also MM3) with experimental bond lengths, for methyl-, ethyl-, isopropyl-, and *tert*-butyl fluoride, the MM3 numbers fit the experimental data quite well, both for the C−F and for the C−C bond lengths. The MM4 data are similarly good, with the exception of methyl fluoride, which will be discussed explicitly below.

When we turn to Table 1B, the results are very similar. The MM4 value for the C−F bond in fluoromethane is again too small, and the other C−F and C−C bonds scatter about somewhat but in general are in satisfactory agreement with the information in Table 1A.

It is, of course, necessary to fit the bond lengths not only at the energy minima but also across the remainder of the potential surface. This means that we must include torsion−stretch interactions if necessary, to account for bond length changes which occur as a function of torsion angle. The bond length changes for the C−C bond (0.016 Å), and for the C−F bond (0.0015 Å) in ethyl fluoride, are shown in Supporting Information Figures S1 and S2, respectively. There is a tendency of the bond lengths to stretch when the molecule is in an eclipsed form, relative to when it is in a staggered form, and part of this comes from van der Waals repulsion (or dipole−dipole repulsion in more complicated cases). The stretching from these sources is explicitly included in MM3 and MM4. The remainder is brought about with the torsion−stretch interaction. This latter stretching here comes partly from hyperconjugation and from the Bohlmann effect and was neglected in MM3.

Next, we examined the data involving the fluorinated ethanes (Supporting Information Table S2A) and noted that the agreement of MM4 with experiment is quite satisfactory, and slightly (insignificantly) better than it was with MM3. When the MM4 data are compared with the BC data (Supporting Information Table S2B), the results for the C−F bonds are satisfactory but the MM4 C−C bond lengths seem to be systematically too short by 0.007 Å. Overall, those C−C bond lengths agree adequately with experiment, with the signed average being −0.002 Å (Supporting Information Table S2A), and the moment of inertia data discussed later are well fit. Hence, it would seem that the systematic shortness of the MM4 calculated C−C bonds compared to those from the BC calculations (Supporting Information Table S2B) comes largely from a systematic error, with the BC values being too large. Some of this error may arise from the vibrational corrections required to get from the former set of numbers to the latter. If we examine the individual errors in the C−C bond lengths between MM4 and BC (Supporting Information Table S2B), the only MM4 number which is larger than the BC value is that from hexafluoroethane. This molecule is a special problem discussed later in this manuscript, for which the error is +0.004 Å.

We would like at this point to explicitly consider the structure of 1-fluoropropane. A number of important features are present in this particular small molecule, including a conformational equilibrium between anti and gauche forms. We wish to accurately fit the structure of these two conformations and especially their moments of inertia. The pertinent structural information is given in Table 11, and the moments of inertia are given in Table 2. First, we will simply note that the moments of inertia are adequately fit, with no moment for either conformation being in error by more than 0.5%. Besides the various effects which cause changes in bond lengths in ethyl fluoride, the addition of the C_2-C_3 bond leads to further kinds of torsion−stretch interactions and the β electronegativity effect. In Figures 1−3 are shown the bond length variations for the three skeletal bonds with respect to torsion angle. The bond length agreement between the MM4 results and the MP2/BC

TABLE 3: Molecular Structure of Fluoromethane

	exptl (r_0)[a]	MM3 (r_g)	MM4 (r_z)	exptl (r_g)[39]	MM4 (r_g)	exptl (r_e)[39]	MP2/BC (r_e)	MM4 (r_e)
C−F	1.3890(8)	1.389	1.385	1.391(1)	1.385	1.383(1)	1.387	1.380
C−H	1.0947(11)	1.108	1.099	1.108	1.108	1.086(2)	1.090	1.090
HCF		108.9	109.0	108.7(2)	109.0	108.8(3)	108.6	108.7
HCH	110.32(12)	110.0	110.0		109.9	110.2(3)	110.3	110.2

[a] Eggers, D. F. *J. Mol. Struct.* **1976**, *31*, 307.

TABLE 4: Molecular Structure of Difluoromethane

	exptl (r_z)[a]	MM3 (r_g)	MM4 (r_z)	MP2/BC (r_e)	MM4 (r_e)
C−F	1.360(1)	1.359	1.354	1.356	1.349
C−H	1.097(5)	1.108	1.094	1.089	1.087
HCF		109.9	109.1	108.6	109.1
FCF	108.11(16)	108.8	108.6	108.5	108.3
HCH	113.67	108.3	111.8	113.8	112.3

[a] Hirota, E. *J. Mol. Spectrosc.***1978**, *71*, 145.

TABLE 5: Molecular Structure of Trifluoromethane

	exptl (r_z)[44c]	MM3 (r_g)	MM4 (r_z)	exptl (r_e)	MP2/BC (r_e)	MM4 (r_e)
C−F	1.335(1)	1.340	1.333	1.3284(31)	1.329	1.329
C−H	1.097(7)	1.108	1.091	1.091(14)	1.088	1.084
HCF		110.3	110.0		110.5	110.2
FCF	108.49(15)	108.6	109.0	108.97(57)	108.5	108.8

TABLE 6: Molecular Structure of Tetrafluoromethane

	exptl (r_0)[44d]	MM3 (r_g)	MM4 (r_z)	MP2/BC (r_e)	MM4 (r_e)
C−F	1.319253(14)	1.325	1.320	1.317	1.316

TABLE 7: Molecular Structure of Fluoroethane

	ED (r_a)[40]	MM3 (r_g)	MM4 (r_a)	MW (r_s)	MM4 (r_s)	MP2/BC (r_e)	MM4 (r_e)
C−F	1.397(4)	1.401	1.398	1.398(5)	1.395	1.395	1.393
C−C	1.502(5)	1.510	1.505	1.504(4)	1.503	1.507	1.501
$C-H_{av}$	1.099(2)	1.110	1.104	1.095(2)	1.094	1.092	1.092
CCF	110.4(2)	108.6	109.4		109.2	109.4	109.1
CCH	113.6(4)	110.7	111.2(CH_2)		111.1	111.9	111.1
		111.5	111.8(CH_3)		111.5	110.3	111.5

TABLE 8: Molecular Structure of 1,1,2-Trifluoroethane

	ED (r_a)[71]	MM3 (r_g)	MM4 (r_a)	MP2/BC (r_e)	MM4 (r_e)
		Gauche			
C_1-F_{av}	1.353(4)	1.355	1.359	1.358	1.355
C_2-F	1.387(8)	1.383	1.385	1.380	1.381
C−C	1.500(5)	1.507	1.499	1.505	1.495
$C-H_{av}$	1.088(11)	1.105	1.099	1.091	1.087
CCF_{av}	109.0(5)	109.1	109.0	108.8	108.8
FCF	106.8(7)	108.0	107.2	108.0	106.9
CCH_{av}	108.9(14)	111.2	112.9	110.7	112.8
$\omega H-C_1-C_2-F$		42.8	50.8	53.8	50.7
		Anti			
C_1-F	1.353(4)	1.356	1.357	1.356	1.353
C_2-F	1.387(8)	1.384	1.383	1.375	1.379
C−C	1.500(5)	1.506	1.503	1.505	1.498
$C-H_{av}$	1.088(11)	1.105	1.100	1.087	1.088
CCF_{av}	109.0(5)	110.1	111.0	110.1	110.8
FCF	106.8(7)	108.7	107.6	107.8	107.4
CCH_{av}	108.9(14)	110.6	111.4	111.0	111.3
$\omega H-C_1-C_2-F$		180	180	180	180

TABLE 9: Molecular Structure of 1,1,2,2-Tetrafluoroethane

	ED (r_a)[73]	MM3 (r_g)	MM4 (r_a)	MP2/BC (r_e)	MM4 (r_e)
		Trans			
C−F	1.350(8)	1.349	1.353	1.351	1.349
C−C	1.518(5)	1.519	1.507	1.515	1.502
C−H	1.098(6)	1.104	1.096	1.085	1.084
CCF	108.2(3)	109.2	108.4	108.4	108.3
FCF	107.3(3)	107.5	107.4	108.4	107.2
CCH	110.3(10)	112.0	115.1	112.3	115.3
$\omega H-C-C-H$	180	180	180	180	180
		Gauche			
$C-F_{ave}$		1.354	1.354	1.350	1.348
C−C		1.510	1.510	1.518	1.506
C−H		1.103	1.098	1.086	1.805
CCF_{av}		110.5	110.5	109.0	110.3
FCF		107.7	107.7	108.8	107.5
CCH		112.2	112.2	111.8	112.3
$\omega H-C-C-H$	78(2)	69	69	65.6	69.2

TABLE 10: Molecular Structure of Perfluoroethane

	ED (r_g)[a]	MM3 (r_g)	MM4 (r_g)	MP2/BC (r_e)	MM4 (r_e)
C−C	1.545(6)	1.554	1.548	1.537	1.541
C−F	1.326(2)	1.321	1.328	1.325	1.322
FCF	109.1	107.5	109.3	109.3	109.3
CCF	109.8	111.4	109.6	109.6	109.7

[a] Gallacher, K. L.; Yokozeki, A.; Bauer, S. H. *J. Phys. Chem.* **1974**, *78*, 2389.

TABLE 11: Molecular Structure of 1-Fluoropropane

	MW (r_s)[44j]	MM4 (r_s)	MP2/BC (r_e)	MM4 (r_e)
		Trans		
C_2-C_3	1.534(1)	1.529	1.527	1.527
C_1-C_2	1.501(2)	1.505	1.509	1.503
C_1-F	1.401(3)	1.400	1.394	1.399
$C_3-H(a/g)$	1.084/1.093(2)	1.095/1.095	1.092/1.094	1.095/1.095
C_2-H	1.095(1)	1.097	1.094	1.094
C_1-H	1.094(1)	1.093	1.094	1.091
CCC	110.6(3)	110.3	110.8	110.1
CCF	110.0(4)	110.0	110.5	110.0
ωCCCF	180	180	180	180
		Gauche		
C_2-C_3	1.526(3)	1.529	1.525	1.527
C_1-C_2	1.506(2)	1.507	1.509	1.505
C_1-F	1.380(5)	1.400	1.397	1.399
$C_3-H(a/g)_{av}$	1.102_{av}	1.095/1.095	1.092/1.093	1.095/1.095
C_2-H_{av}	1.099_{av}	1.097	1.095	1.095
C_1-H_{av}	1.097	1.094	1.094	1.091
CCC	113.0(3)	111.6	112.5	111.4
CCF	110.1(6)	109.7	109.7	109.7
ωCCCF	62.6(5)	65.2	62.9	65.3

calculations, and experiment (microwave), as well as the moments of inertia, are all satisfactory.

Armed with the above information, we now wish to look at the bond lengths in the structures of all of the compounds examined in this work, apart from perfluoro compounds which will be discussed separately later. These structures are given individually in Tables 3−14 and Supporting Information Tables S3−S17. When we examine the C−C bonds and compare them with experiment, over the full set of compounds listed for which there are experimental data, there are 35 different C−C bonds, and the MM4 values, relative to experiment, show a signed average and rms values of +0.0004 and 0.0086 Å, respectively. The largest errors here come from the fluorocyclohexanes, where the experimentalists assumed that the C−C bond lengths in each molecule all had an identical value. (They could measure the average value but not the individual values, which are not resolved in the radial distribution function.) The MM4 calculations show this is not correct, of course, because the presence of the fluorine shortens nearby bonds. If those (experimental) errors are removed from the calculation, the rms value would become smaller, and the signed average error would still be negligible.

We can also make a comparison between the MM4 and BC values for the C−C bond lengths. Here, we find that over 63

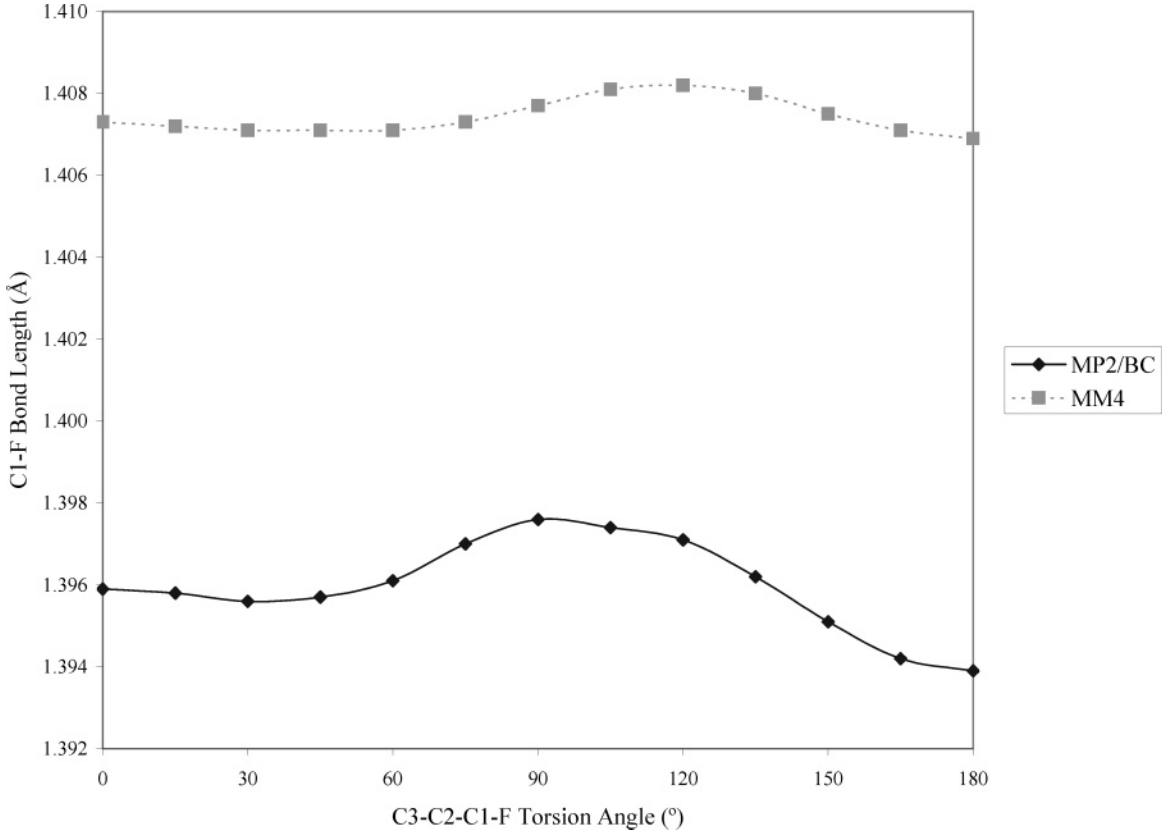


Figure 1. Propyl fluoride C1−F bond length variation with C3−C2−C1−F torsion angle.

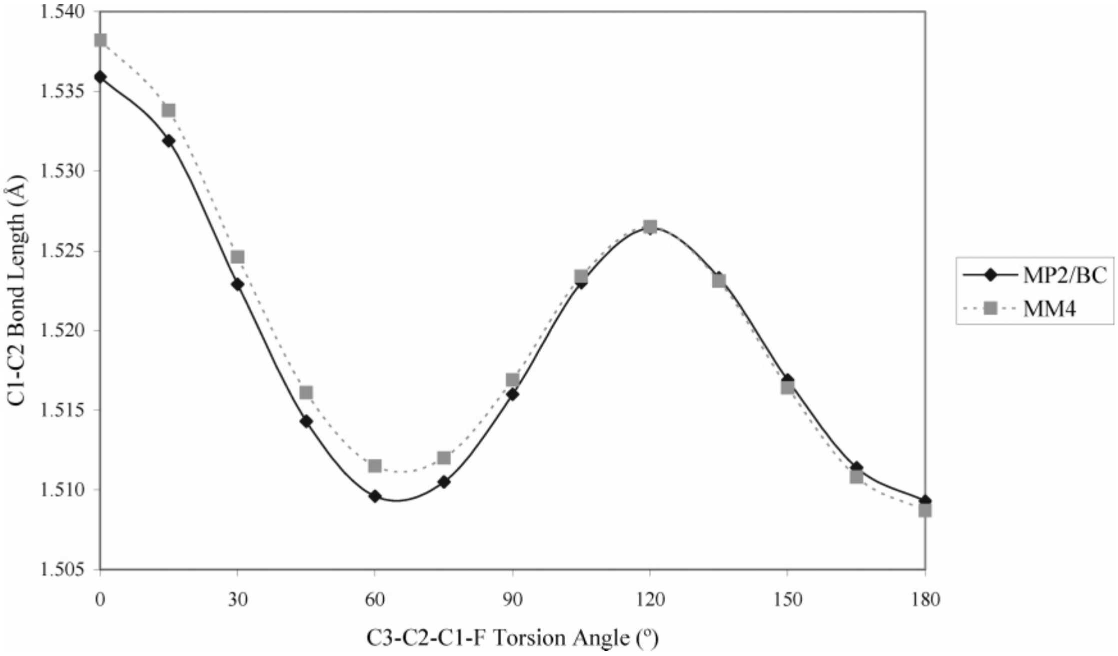


Figure 2. Propyl fluoride C1−C2 bond length variation with C3−C2−C1−F torsion angle.

bonds the signed average and rms errors are −0.0043 and 0.0065 Å, respectively. Thus, again, as in Table 1, the MM4 values for the C−C bond lengths are systematically smaller than the BC values by about 0.006 Å. However, since the MM4 values fit well to experiment, and especially to the moments of inertia, the errors appear to be primarily in the BC values, not in the MM4 values. The large fluorocyclohexane errors between MM4 and experiment mentioned above are not seen in the MM4 BC comparison, as expected. For the C−F bonds, if again we look first at the comparison of MM4 with experiment, the signed average over 43 bonds and rms values are +0.0027 and 0.0067 Å, respectively. If we look at a similar comparison of the MM4 values to the BC values, we find that the signed average and rms values are +0.0004 and 0.0045 Å, respectively. Thus, overall, the experimental (mostly electron diffraction) values are systematically a little smaller (0.0023 Å) than the ab initio values, and the latter have been fit more accurately, as required by the moment of inertia data. The rms value for the MM4 C−F bond lengths relative to the BC data is +0.0045 Å. The somewhat larger value when MM4 is compared with experiment

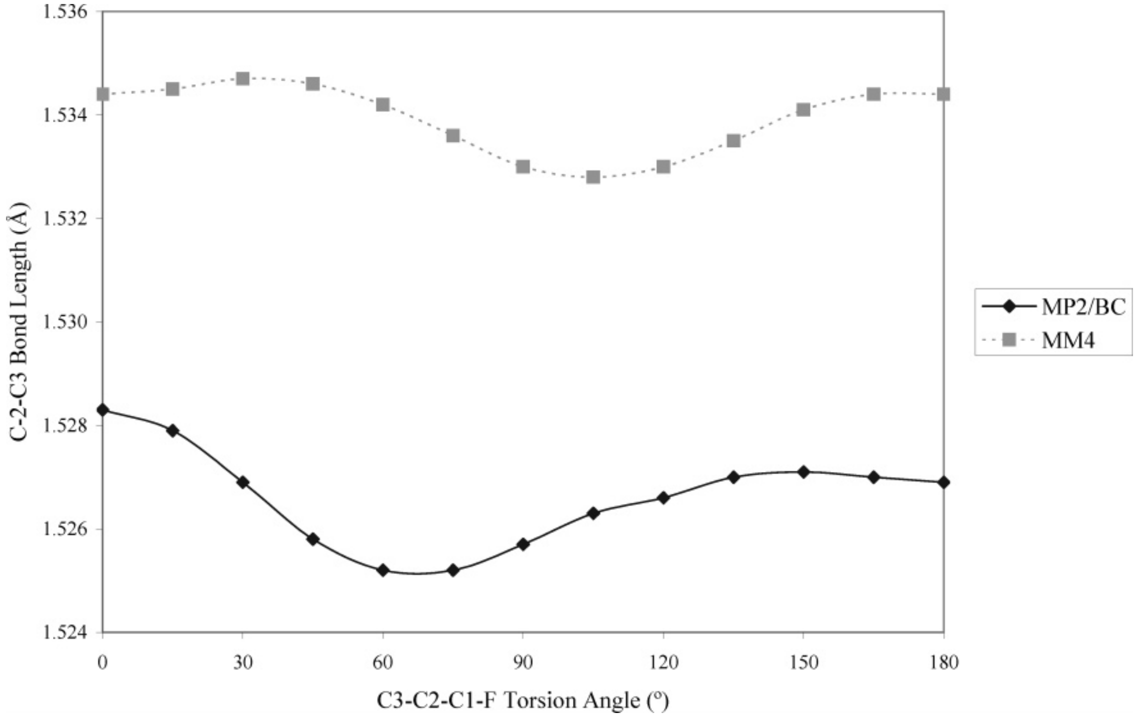


Figure 3. Propyl fluoride C2−C3 bond length variation with C3−C2−C1−F torsion angle.

TABLE 12: Molecular Structure of 2-Fluoropropane

	ED (r_g)[41]	MM3 (r_g)	MM4 (r_g)	MP2/BC (r_e)	MM4 (r_e)
C−F	1.405(6)	1.410	1.408	1.404	1.402
C−C	1.514(2)	1.512	1.514	1.510	1.508
CCC	114.6(15)	111.9	113.3	113.7	113.0
CCF	108.5(5)	108.7	108.0	107.8	107.9

TABLE 13: Molecular Structure of *tert*-Butyl Fluoride

	ED (r_a)[42]	MM3 (r_g)	MM4 (r_a)	MP2/BC (r_e)	MM4 (r_e)
C−F	1.425(24)	1.415	1.411	1.413	1.407
C−C	1.520(24)	1.514	1.517	1.515	1.512
C−H_{av}	1.09(2)	1.110	1.105	1.092	1.092
CCF	107.9(15)	107.8	106.7	106.5	106.8
CCC	110.0(15)	111.1	112.1	112.3	112.0
CCH_{av}	111.6(15)	111.7	111.9	110.2	111.5
HCH_{av}	107.2(15)	107.7	107.0	108.7	107.4

(0.0067 Å) is larger mainly because the signed average value is larger, so overall, the results are approximately equivalent.

Our conclusions are that the BC values for the C−F bond lengths are comparable in accuracy to those from experiment after the basis set/correlation error is taken into account and that MM4 reproduces both to approximately within the experimental error. The experimental work normally determines not only the structure but also some estimate of the error associated with that structure. The MM4 errors that we have here are reasonable in magnitude and similar to the errors quoted in the experimental papers. The ab initio accuracy is less certain, but with the stated corrections, it appears to be generally competitive with experiment. It is our view that overall the accuracy of the MM4 calculations is generally consistent with the error limits in the structural information available. Special cases will be discussed individually.

If we compare the data in Tables 1A and B and Supporting Information Tables S2A and B, we find that the C−F bond lengths given by experiment are close to those from the BC calculations. For the C−C bonds, the MP2/B calculations give bond lengths that are approximately 0.005 Å longer than those from experiment (Tables 1A and B and Supporting Information Tables S2A and B, where the comparisons are made via MM4). If we accept that the experimental values are the more accurate ones, it would appear that we need a correction factor of about −0.005 Å for C−C bonds to convert the MP2/B calculation to an MP2/BC calculation.

Let us now discuss explicitly the molecular structure of fluoromethane. The appropriate information is summarized in Table 3. There is considerable disagreement concerning the length of the C−F bond by various experiments and calculations. The experimental value for r_e is 1.383(1) Å, and we have no reason to question this value. However, the MP2/BC (r_e) value is 1.387 Å. (This includes a correction that has already been added to this latter value of −0.0063 Å.) Then, the MM4 value is 1.380 Å. One would conclude that the MM4 value is too short, by either 0.003 or 0.007 Å, depending on which of the previously cited values one prefers. Then, if we look at the experimental r_g value, we find 1.391(1) Å, while the r_g value from MM4 is 1.385 Å, a discrepancy of 0.006 Å. However, when we look at the moments of inertia determined experimentally, our r_z value (1.385 Å) gives I_b and I_c values that are too long by 0.05%, which corresponds to about 0.0004 Å. It is difficult to change the moments of inertia very much by repositioning the hydrogens, because of their small mass. The hydrogen positions for all of these calculations agree very well. The data with which we have to work clearly contain significant internal inconsistencies, and we cannot see how to fit this structure better with MM4. We were unable to improve the MM4 results by further parameter adjustment, because of the requirement of fitting the experimental moments of inertia.

Electronegativity Effect. Previous molecular mechanics programs (MM2[34] and MM3[1]) include corrections for the *primary electronegativity effect* on bond lengths.[35] This effect has been used to describe the shrinkage of C−C, C−H, and C−F bond lengths upon the substitution of hydrogen atoms by fluorines (or other electronegative substituents). An additional smaller shrinkage is observed in bond lengths when a fluorine (or other substituent) is substituted on a bond once removed, and this has been referred to as the β or *secondary electronegativity effect*.[31,37] This additional correction factor is also used in MM3 for substitutions of electronegative atoms, including for mutual

TABLE 14: Molecular Structure of Fluorocyclohexane

	Eq				Ax			
	MW (r_0)[44n]	MM4 (r_z)	MP2/BC (r_e)	MM4 (r_e)	MW (r_0)[44o]	MM4 (r_z)	MP2/BC (r_e)	MM4 (r_e)
C−F	1.404(20)	1.413	1.400	1.411	1.399(20)	1.414	1.406	1.411
$C-C_{av}$	1.526(fixed)	1.528	1.524	1.523	1.526(fixed)	1.528	1.524	1.524
$C-H_{av}$	1.096(fixed)	1.100	1.096	1.095	1.096(fixed)	1.100	1.095	1.095
CCC_{av}	111.4(15)	110.9	110.8	110.7	111.7(15)	111.5	111.3	111.4
CCF	108.7(20)	108.9	109.1	108.8	110.0(20)	108.8	108.1	108.7
HCF	109.2(20)	107.1	106.3	107.4	107.9(20)	106.8	106.0	107.0

bond length shrinkages that occur due to vicinal fluorine substituents. The equation used in both MM2 and MM3 for the primary electronegativity correction constant is

$$l_e = l_e(a) + 0.62 l_e(b) + (0.62)^2 l_e(c) + ...$$

where l_e is the primary electronegativity correction constant and *a*, *b*, *c*, ..., correspond to the first, second, third, ..., electronegative atoms attached to the bond under consideration.

The secondary electronegativity correction constant is generally given by

$$l_e' = 0.4 \Sigma l_e$$

where the summation is over all substitutions once removed from the bond in question.

The electronegativity corrected natural bond length (l_0') is then

$$l_0' = l_0 + l_e + l_{e'}$$

where l_0 is the ordinary natural bond length. The value of the constant 0.62 was originally chosen to fit MM2 structures to the data on the series of fluoroethanes,[35] and is in accord with the approximate values used by physical organic chemists long ago to represent the electronegativity effect in changing the acidities of halogenated acetic acids.[38] For the mutual interaction between vicinal fluorines with MM4, the best value for this constant is 0.67, and for the interaction of the fluorines with the C−C and C−H bonds, the values are 0.38 and 0.55, while the general value used elsewhere remains 0.62. The value of 0.4 was similarly chosen as a universal secondary constant to fit MM2 and MM3 data, and is in accord with data on β substituted acetic acid derivatives.[38] These values are reasonable measures of the "inductive effect" in organic molecules historically. However, the β substituent constant has been found (with the better MM4 force field) not to be really a constant either but to vary over the range 0.05−0.38, depending on the set of atoms involved (Supporting Information Table S1).

The electronegative shortening of the C−C bonds by the attachment of fluorine was earlier studied in detail with the fluoroethanes,[35] and these numbers were then applied to other cases. However, actually, we should have (but did not) also examined what happens when the fluorine is attached to a carbon that is involved with more than one C−C bond. Thus, isopropyl fluoride and *tert*-butyl fluoride would have their C−C bonds shortened by the electronegativity effect of the fluorine, but one would expect that this shortening should not be the same as it would be in fluoroethane. The reason is the same as the reason that the first fluorine added to an ethane molecule causes a large shortening but the second one causes a smaller shortening, etc. As electron density is withdrawn by the fluorines, and positive charge piles up on the carbon or carbons, the electronegativity effects become increasingly smaller with further substitution. A similar phenomenon is expected to occur when the number of carbon−carbon bonds involved at the center being substituted is increased. Thus, on the basis of the general applicability of numbers cited earlier, we might expect that whatever electronegative shortening results from attaching a fluorine to ethane, it would be only 0.38 times that much if a second C−C bond were involved, as in isopropyl fluoride. Of course, one bond would not shorten by 1.0 units, and the other by 0.38 units, but the effect would be averaged out, to 0.69 units. The fluorine added to isobutane to yield *tert*-butyl fluoride would similarly have a bond shortening effect of 1.0 + 0.38 + 0.144 = 1.524 units, and if additivity is assumed, and the three bond lengths shorten equally, each would be shortened by 0.508 units, not by the 1.0 units previously assumed. Taking these changes into account improves the MM4 bond lengths over those in MM3 for secondary and tertiary fluorides and for the corresponding geminal difluorides.

Electropositivity Effect. The general treatment of electronegativity effects on bond lengths was discussed earlier, and the general equation for multiple substitutions (with the same substituents) was described.[35] If the substituents were to differ in electronegativity, that with the largest effect is put first, and the others in order, according to diminishing electronegativity. Of course, it may be that there are electropositive atoms attached, in which case the effect is in the opposite direction, and causes the bond to lengthen. In MM2 and MM3, these electronegativity and electropositivity constants were simply put in decreasing order of their absolute values. Since we studied no cases with both electronegative and electropositive substituents on the same bond, no problem was observed using this scheme until recently. However, the physical cause for this effect is that the electronegative substituent pulls electrons away from the bond, and as one pulls more and more electrons from the bond, the process becomes increasingly difficult; hence, the effect diminishes with further substitution. However, if one then adds an electropositive atom into that group, it tends to donate electrons, so its effect is certainly not diminished, and rather has an increasing effect on the overall result. Accordingly, in MM4, if there are both electropositive and electronegative substituents on the same bond, they are treated separately by the method discussed above. A total effect is calculated for electronegativity and another total effect for electropositivity for each bond, and then these effects are summed to give l_e.

Bohlmann Effect. This effect (which is a hyperconjugative effect) was originally discovered by Bohlmann, and was useful in stereochemical assignments in alkaloids. As discovered, this effect produces changes in the stretching frequencies of C−H bonds, if they are properly oriented with respect to the lone pair on an amino nitrogen attached to the carbon.[31] Since a fluorine contains lone pairs of electrons, it will exert a hyperconjugative effect in the usual way. A difference between fluorine and nitrogen is that the lone pairs on fluorine point equally in all directions radially to the bond, and hence do not have the usual stereospecific result that is associated with the Bohlmann effect with nitrogen. However, they would be expected to lead to bond length and bond angle changes, as is normally found with the Bohlmann effect.

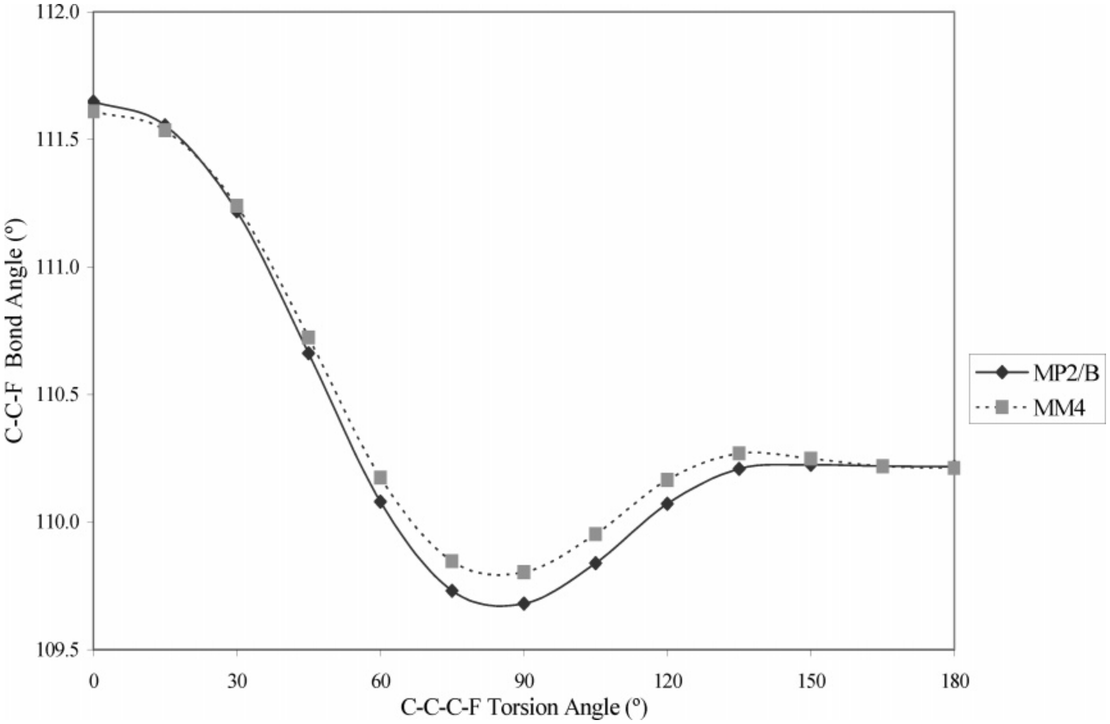


Figure 4. Propyl fluoride C−C−F angle variation with C−C−C−F torsion angle.

The Bohlmann effect by the fluorine on hydrogen is mixed in with the electronegativity effect, which it opposes. It cannot be separated from the latter in a unique way (see however ref 30), so it is simply given the value zero, and the observed effect is assigned totally as the electronegativity effect.

Bond Angles. The general theory of geometric changes with electronegativity holds that the replacement of a hydrogen by an electronegative substituent, for example of methane to give methyl fluoride, leads to bond length and angle changes in the following way.[43] The electronegative substituent pulls electrons toward it, and since p electrons are more polarizable than s electrons, the bond from carbon to the fluorine obtains higher p character, which leaves higher s character for the remaining (H−C) bonds. The increased s character leads to shorter C−H bonds. These bond length effects were well taken into account already with MM2 and MM3, and they are similarly taken into account here. However, note that according to theory, these changes affect not only bond lengths but also bond angles, and these expected angular changes were not explicitly examined with MM3 or other force fields. In the present case, the extra s character in the C−H bonds will cause the H−C−H angles to open up and the H−C−F angles to close down. If the angular change from this effect were to be small, since the H−C−F value for θ_0 is an adjustable parameter, its adjustment would be adequate to account for what is observed. Thus, in MM3, and in all other existing force fields known to the present authors, no account of this bond angle deformation was explicitly allowed for, as the parametrization of θ_0 appeared to adequately take care of the problem. However, if one considers this effect as it occurs in propyl fluoride, the geometry about the carbon to which the fluorine is attached can be dealt with as previously, but what about the C−C−C angle? Earlier work has shown that the β carbon is affected to about 0.4 the amount that the α carbon is affected by electronegative substituents with respect to bond length,[35] but the corresponding bond angle changes were previously ignored. These bond angle changes are pretty small, but when they involve heavy atoms and highly electronegative substituents, they may not be negligible. Thus, we found with propyl fluoride the C−C−C angle shrinks, as demanded by the theory of electronegativity, so that to represent it adequately requires reducing θ_0 for C−C−C by −2.45°. This is a sufficiently large number that, if it is not taken into account, one simply cannot fit the moments of inertia of propyl fluoride, or of other molecules that contain three carbons in a row with fluorine attached on the end (propyl fluoride derivatives). In our present set of compounds for which experimental moments of inertia are available, the only other compounds affected are the cyclohexyl fluorides. When the magnitude of the effect is adjusted so as to fit the propyl fluoride data, the cyclohexyl fluoride data are also fit. Since fluorine is the most electronegative element, the corresponding changes induced by oxygen and other less electronegative elements are expected to be smaller than this, but not necessarily negligible. Indeed, the corresponding number for oxygen is −1.80°.[20]

As bond lengths are affected by torsion angle, so are bond angles. In fact, the effect generally tends to be much more conspicuous with the bond angles than with the bond lengths. Thus, there are torsion−bend interactions which need to be taken into account. In Supporting Information Figure S3 is shown the variation of the C−C−F angle with torsion in ethyl fluoride. The total variation here is rather small, about 1°, and it is adequately taken into account as shown. The corresponding variation of the C−C−H bond angle with torsion is much larger, over 3°, and this is shown for ethyl fluoride in Supporting Information Figure S4. The V_2 shape[100] of the curve is characteristic of hyperconjugation ($H^+C{=}CF^-$).

The C−C−F angle in propyl fluoride varies with the torsion angle over about 2°, and this is shown in Figure 4. There is some steric repulsion at 0°, leading to the angle opening maximum. However, there also is a V_2 component to this change, which is clearly a result of a resonance effect. The C−C−C bond angle also varies considerably with torsion angle, over a range of about 3° (Figure 5). In this case, the curve is somewhat more complicated, with significant V_1, V_2, and V_3 components. There is an apparent discrepancy in the 0−60° torsion range between the MM4 and BC calculations, but this

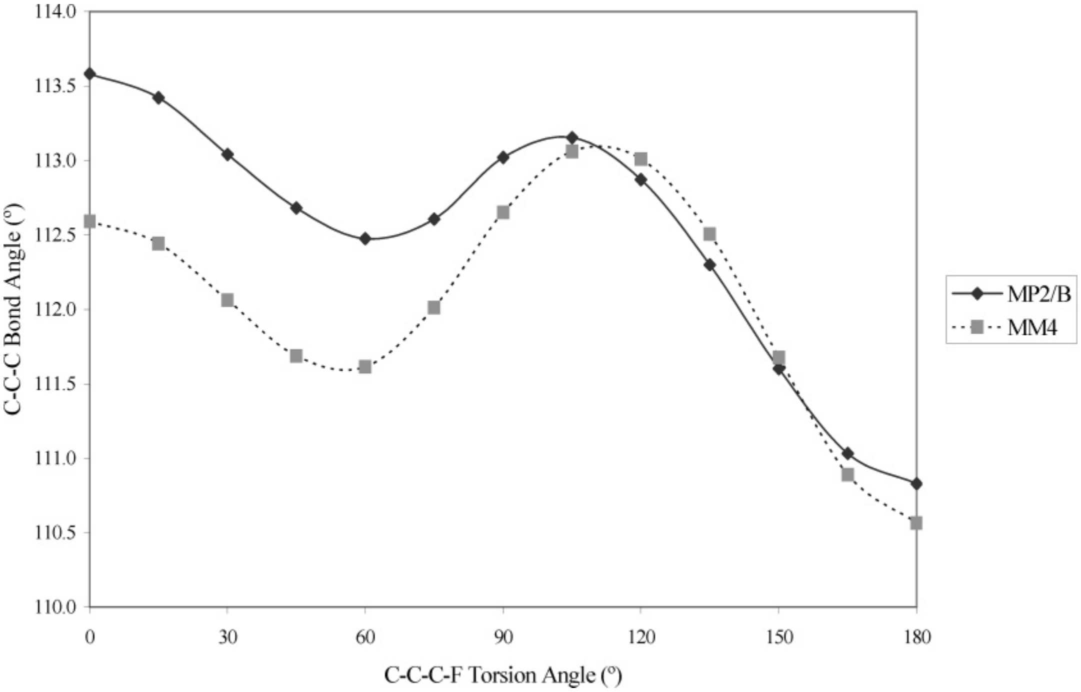


Figure 5. Propyl fluoride C−C−C bond angle variation with C−C−C−F torsion angle.

is required to fit the moments of inertia of propyl fluoride derivatives, specifically the fluorocyclohexanes. Thus, it is believed that the error here is more from the BC calculations than from the MM4 calculations.

Next, we may examine the bond angles that MM4 calculates for the alkyl fluorides overall, compared to the experimental values (Tables 3−14 and Supporting Information Tables S3−S17). The situation can be summarized rather easily. The accuracy is similar for the C−C−C, C−C−F, or F−C−F angles. In each case, the MM4 values differ from the experimental values with a rms value of about 1°. They similarly differ from the BC values by about 1°. When all of the bond angles between heavy atoms are compared, the MM4 values show discrepancies from experiment of greater than 3° in only 4 cases (out of 105). There are discrepancies of 2−3° for an additional 5 cases. However, all of these cases involve molecules for which it would be difficult to accurately determine the bond angles by the methods used. Hence, we turned to the BC calculations for these angles. It was found that MM4 showed differences for all of those angles from the BC values of less than 1.6°. Thus, it would seem that the largest discrepancies in bond angles in these molecules between MM4 and BC/experiment are less than 2°, and mostly less than 1°. The still larger discrepancies between MM4 and experiment are due to experimental error. However, we also know that changing bond angles between heavy atoms by 1° can lead to rather large changes in moments of inertia. Thus, it in fact seems unlikely that there are many errors even as large as 1°.

An item that limits the accuracy to which MM4 can calculate bond angles in the present case stems from the way the different types of angles were specified in MM4 (as inherited from MM3 and MM2). We consider a bond angle of the type C−C−X and assign it an angle type, depending on the other two atoms attached to the central carbon. Types 1, 2, and 3 respectively are defined as having zero, one, or two hydrogens in those two positions. In the case of fluorocarbons, if one has no hydrogen attached at that central position, one is dealing with an angle of type 1. Thus, the structure in question could be *tert*-butyl fluoride, where the two attached atoms are carbon, 1,1,1-trifluoroethane, where the two attached atoms are fluorine, 2,2-difluoropropane, where one attached atom is fluorine and one is carbon, or isopropyl fluoride, with one fluorine and two carbons. These are all considered the same angle type by the program, and hence, a single bending parameter (θ_0) value has to be used for the F−C−F angle of each type and for the C−C−F angle of each type. We know now that when electronegative substituents are attached, they change the values for θ_0, and as shown later in this paper, to some extent they are also expected to change the value for the bending constant. Thus, we are trying to represent four different kinds of structures with a single set of parameters. As it turns out, this works pretty well, although it introduces a little error into the force field that cannot be removed, as long as one retains these present angle type constraints. In practice then, we average out the parameters as best we can to accommodate everything at the same time.

Moments of Inertia. If the necessary experimental data are available, as they are in the case of fluoroalkanes, then the most important thing to fit in determining the structural parameters for the force field is the set of moments of inertia data. Various experiments that determine geometries are subject to a wide variety of problems and resulting errors. The ab initio calculations, although in principle accurate, with real current-day basis sets and electron correlation treatments are not usually as good as the best experiments, although they are often better than many experiments. Certainly, they augment the experiments. However, the moments of inertia of molecules are typically measured to five or six significant figures. They are clear, unambiguous, very accurate, and thus need primary consideration. The comment is often made that a molecule has only three moments of inertia, so that a wide variety of structures can fit those moments of inertia. Hence, one cannot tell if the structure is correct, even if the moments of inertia are well fit. That is certainly true. However, if one does not fit the moments of inertia, then for sure the structure is wrong. Thus, the moments of inertia are a necessary, but not sufficient, condition for establishing the structure. When one has as much data as we have in the case of the fluoroalkanes, to fit *all* of the moments of inertia with a transferable force field does not leave much room for error in the structures. Accordingly, we feel that fitting these data is of primary importance. While the word "geometry" is usually thought of as being indicative of bond lengths, angles, and torsion angles, the moments of inertia limit in a demanding way the amount of parameter adjustment that is possible.

We made use of moment of inertia data for 15 molecules and 17 total conformations (Table 2). In some cases, one or more of the moments of inertia cannot be measured by the usual method using microwave rotational frequencies because the molecule lacks a dipole moment, or because of the orientation of the dipole moment with respect to the principal axes. While such moments have sometimes been determined in various ways, we have not ordinarily used such numbers, because they may not be comparable in accuracy with the rest of the moment of inertia data. (Ab initio moments of inertia as normally reported also lack the required accuracy. Such accuracy can be obtained if one uses an infinite basis set and complete correlation.[45] However, few such numbers are presently available.) Thus, the total number of independent experimental moments of inertia is less than 3×17 and is in fact 47 in the present work. These 47 moments of inertia were calculated with MM4, and the values were compared to those determined by microwave spectroscopy. These are normally r_z quantities. Even if the structure determined is r_s, the moments themselves are r_z. Our molecular mechanics programs all use r_g as the standard, since at the time the decision was made as to what kind of units to use for bond lengths (about 1970), the most data, and the most accurate usable data, that were available were in r_g units from electron diffraction. We continue to use this as the standard. Hence, we have to interconvert r_g and r_z here. Additionally, we make use of other kinds of microwave data (r_s), older electron diffraction data (r_a), X-ray data (r_α), and ab initio data (r_e). To utilize all of these data, since there may be differences of up to 0.005 Å or so in going from one to the other for most bonds measured (and differences sometimes of as much as 0.030 Å), one must have a fairly accurate interconversion scheme in order to obtain meaningful numbers. Most of these interconversions were worked out by Kuchitzu, and they are published in various places, most conveniently in the book by Cyvin.[46] A computer program for carrying out these interconversions was written by Hedberg and Mills.[47] These interconversions were formulated in the days of hand calculation, and some of them contain assumptions and approximations that proved not to be the best after computer calculations became available. We have gone through this work again, and in some cases were able to obtain somewhat better formulas for carrying out the interconversions. These are all included in the MM4 program, so that the interconversions are made automatically.

Ab initio calculations with currently used basis sets and electron correlation treatments normally do not give very accurate values for r_e bond lengths. (An excellent example of how accurate r_e bond lengths can be calculated has been published by Stanton et al.[45a] However, such calculations are very computationally intensive, and have so far been applied to only small molecules containing no more than three first row atoms.) Thus, correlation and basis set truncation errors need to be corrected for, before making comparisons of the ab initio values with the MM4 r_e values. In the present work, we have made all of these corrections to the best of our current knowledge. It is impossible to accurately know just what all of these errors amount to. In a way, the MM4 force field is a test of how well all of these corrections can be made, because the numbers all have to be converted to a common basis before comparisons can be made. The accuracy of MM4 is then limited, not only by the inherent accuracy of the molecular mechanics approximations but also by the accuracy of the experimental and ab initio data, and the accuracy of the vibrational corrections that are required to convert those data to common units. We have done about as well as we can do with all of these problems. It has often been remarked that one should simply optimize everything simultaneously by least-squares methods, but that can be done adequately only when the errors in the various quantities are known. In the case of MM4, the accuracy of the molecular mechanics is approximately down to the accuracy to which these errors are known, and hence, it does not seem possible at present to determine the MM4 force field and the results calculated from it, much more accurately than we have done up to this point, with the exception of vibrational frequencies (and a few special cases to be discussed later). With additional small transferable cross-terms, too small to affect structures, it would presumably be possible to improve the frequency calculations with negligible effects on everything else. However, this improvement would be labor intensive, and of limited use, so we have not pursued it.

For the fluoride moments of inertia overall, the MM4 signed average error was +0.00%, and the rms error was 0.27%. The largest absolute error was 0.58%. Thus, the MM4 moments of inertia over this set of compounds are similar in accuracy to those determined by MM4 for other classes of compounds. By way of reference, over the same set of compounds, MM3 gave individual signed errors that ranged from −1.88 to +2.80%. The signed average and rms errors were +0.52 and 1.11%, respectively. Most of the large errors in the MM3 moments of inertia resulted from the lack of torsion−bend (Bohlmann) interactions in MM3 that made it impossible to fit simultaneously the moments of inertia of different conformations for a molecule even as simple as fluoropropane.

Conformational Energies. *Torsional Angles.* The V_1, V_2, and V_3 torsional parameters were optimized for MM4 to give the best fit to experimental and BC values of the conformational energies and rotational barriers for the fluoroethane series, following the same scheme that was previously used for MM3. With MM3, the torsional barriers were generally calculated to be somewhat lower than the experimental values in order to get better vibrational frequencies. In MM4, a V_6 term has been added to change the shape of the potential well slightly, so one can now calculate both better rotational barriers and torsional frequencies simultaneously (see later). (These torsional frequencies are important because they are very low, and hence affect the entropies and the thermodynamics of the molecules.)

Rotational Barriers and Conformational Energies (Monofluorides). The torsional energies are most important in determining the relative energies of the stationary points, that is, the conformational energies. (We loosely use the term "energy", but MM4 calculates the energy, enthalpy, and free energy of molecules routinely, and the comparisons that need to be made between MM4 and experiment are sometimes one or the other of these, depending on the experiment. (When no comment is made, the appropriate quantity was always fit to the experimental value.) The details of these calculations are outlined in earlier papers.[3−6] It is indicated in Table 15 just exactly what it is that is being compared in each case. Unfortunately, the word "energy" is sometimes used in the literature to represent any one of the three options mentioned, and it is not always clearly indicated which usage is meant, but this can usually be determined from the experimental details. The energy results obtained in the previously described geometric optimizations will be summarized here (Table 15).

TABLE 15: Rotational Barriers and Conformational Energies of Fluoro Compounds[a]

		exptl	MP2/B	MM3	MM4
C_2H_5F		2.30−4.26	3.42	2.87	3.07
CHF_2CH_3		3.21	3.35	3.28	3.89
CH_2FCH_2F	ΔH_{t-g}	0.80(9)[77]		0.18	0.76
	ΔE_{t-g}		0.70	0.19	0.66
	$\Delta E_{g\rightarrow t}$	2.36	3.19	2.12	2.67
	$\Delta E_{g\rightarrow g}$	5.72	8.12	6.62	5.91
CF_3CH_3		3.45−4.06	3.33	3.62	4.13
CHF_2CH_2F	ΔE_{t-g}		1.45	0.95	0.82
	ΔH^{b}_{t-g}	0.90(30)[71]		1.02	0.89
	$\Delta E_{g\rightarrow t}$		2.60	1.04	2.52
	$\Delta E_{g\rightarrow g}$		5.60	5.95	4.96
CHF_2CHF_2	ΔE_{g-t}		1.54	0.06	1.50
	ΔH^{c}_{g-t}	1.17(20)[73]		0.16	1.56
	ΔE_{c-t}		7.31	7.30	6.37
	$\Delta E_{t\rightarrow g}$		3.93	2.43	4.51
CF_3CH_2F		4.2	4.15	3.65	4.20
C_2F_5H		3.5−4.4	4.02	3.48	4.28
C_2F_6		3.91	4.33	3.02	4.45
C_3H_7F	ΔH_{t-g}	0.47(31)		0.16	0.27
	ΔE_{t-g}		0.26	0.18	0.22
	$\Delta E_{g\rightarrow g}$		4.93	4.74	4.51
	$\Delta E_{g\rightarrow t}$		3.86	2.70	3.64
2-fluoropropane		3.65(30)	3.34	3.15	3.34
2,2-difluoropropane		3.45	3.31	3.61	3.68
fluorocyclohexane	ΔG_{a-e}	0.4(3)[d]		−0.35	0.03
	ΔE_{a-e}		0.04	−0.49	0.11

[a] Energy (or enthalpy or free energy) differences between conformations are subscripted with a minus sign (t−g), whereas energy barriers between two conformations are subscripted with an arrow (e→g). [b] At 265 K. [c] At 253 K. [d] Wiberg's best value from QM calculation is 0.15 kcal/mol and exptl number is 0.26(2) without reference.

MM4 gave a barrier of 3.07 kcal/mol for fluoroethane, which is within the range of values found experimentally (2.30−4.26 kcal/mol[40,52−63]) and slightly lower than the MP2/B value (3.42 kcal/mol). The barrier calculated by MM3 was still smaller, 2.87 kcal/mol.

The next higher homolog, fluoropropane, has a C−C−C−F torsion profile which is qualitatively well-known, having stable anti and gauche conformations, separated by syn and skew barriers, of which the former is somewhat higher (Figure 6). While one might have anticipated that the anti form would be more stable than the gauche form, it is actually the other way around, although the energy differences are small. The numbers are given in Table 15.

The 1-Fluoropropane−Cyclohexyl Fluoride Problem. There has been a long recognized problem concerning 1-fluoropropane and cyclohexyl fluoride. (A similar problem also exists for the corresponding compounds of the other halogens, and some other substituents (including hydroxyl) as well, and what follows is probably very general.) It is quite certain from experiment (gas phase) that 1-fluoropropane has a lower enthalpy in the gauche conformation than in the trans conformation,[48] and ab initio calculations agree. Since the gauche conformation is a *dl* pair of molecules, while the trans is a single molecule, the free energy difference favors the gauche conformation by even more. On the other hand, cyclohexyl fluoride has been found to be somewhat more stable (lower enthalpy) in the equatorial (trans) conformation by low temperature NMR studies, both in solution and in the gas phase.[49] The principles of conformational analysis suggest that this really should not be. If the gauche fluoropropane is more stable, then the corresponding conformation (axial) of the cyclohexyl fluoride should also be more stable. Thus, there has simply been a disagreement here for a long time, between the conformational analysis calculation and experiment. The values for the enthalpies in question are of modest size, with the gauche 1-fluoropropane being lower in enthalpy by 0.47 (31) kcal/mol, and the equatorial cyclohexyl fluoride more stable by 0.4 (3) (ΔG) kcal/mol.[50] Since there are two gauche interactions in the latter, from conformational analysis, they would lead to a calculated expected enthalpy difference of 0.94 kcal/mol, while the observed value is 0.4 kcal/mol with an opposite sign, leading to a discrepancy of 1.34 kcal/mol between what would be expected and what is found. The simple conformational analysis calculation thus appears to be wrong by about this amount. The experiments have been carried out many times and by using different techniques, in different solvents, different temperatures, etc., with similar results. Overall, the average experimental errors here are expected to

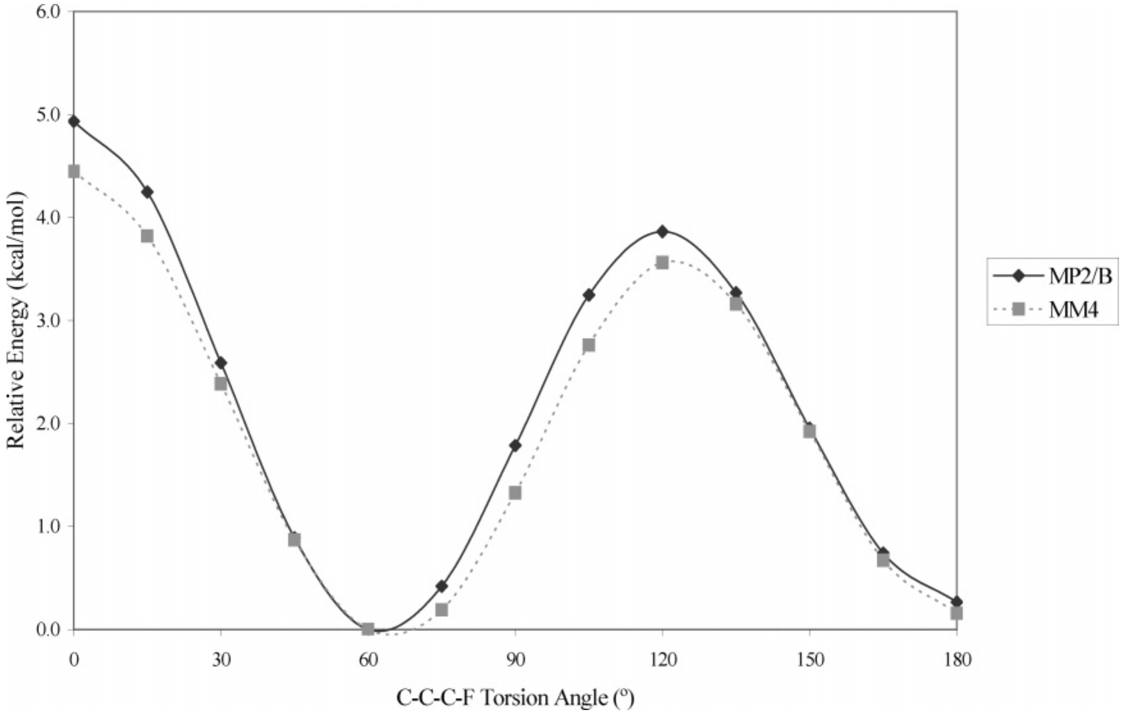


Figure 6. Propyl fluoride C−C−C−F torsion potential.

total not more than about 0.3 kcal/mol, so there has clearly been a problem here for a long time.

When we did the MM3 work on alkyl fluorides, our best estimation of the situation was that the problem here was probably due largely to solvation. Subsequently, however, high level ab initio calculations by Wiberg[51] have convinced us that the equatorial cyclohexyl fluoride is indeed the stable conformation in the gas phase, as well as in solution, and that the solvation energy is not really significant in shifting the conformational equilibrium with these compounds. Despite a lot of tinkering with parameters in MM2 and MM3, we were never able to reproduce the experimental results, i.e., propyl fluoride stable gauche and cyclohexyl fluoride stable equatorial. The same qualitative situation was also observed experimentally and by ab initio calculations for the corresponding systems where F was replaced by Cl, or by OH or OCH_3. Additionally, the N−H of piperidine has the H preferentially equatorial (and the lone pair axial) while the predominant conformation of ethylamine has the lone pair in the anti position. Thus, there are numerous examples where the stable cyclohexyl conformation is found to be opposite that predicted by conformational analysis based on small molecule analogues.

Our inability to fit the propyl fluoride/cyclohexyl fluoride conformational data with MM2 and MM3 was been a long-standing puzzle. However, in 1993, Houk suggested[52] with reference to the propyl alcohol/cyclohexanol case that the problem might be due to induced charges and that it might be solved by allowing for the effects of these charges in an explicit way. MM4 does include effects of induced dipoles that were not included in earlier force fields, and indeed, recent MM4 studies on propanol/cyclohexanol showed[15] that the induced dipoles caused the problem for the hydroxyl case to disappear with this force field. The experimental data were fit without any special effort. A detailed examination of the MM4 calculations showed why. The induced dipoles included in MM4 (but not in earlier force fields) stabilized the equatorial cyclohexanol conformation by about 1 kcal/mol relative to the axial conformation, without a corresponding change in propyl alcohol, which caused the problem to disappear.[20] What about the present case (propyl fluoride/cyclohexyl fluoride)? We were surprised to note that here the induced dipoles, while large, have a negligible effect on the equilibrium. The propyl fluoride/cyclohexyl fluoride problem remained.

If we accept the above as correct, then the only way that we have been able to devise that will enable us to fit simultaneously both the propyl fluoride data and the cyclohexyl fluoride data is with the aid of a torsion−torsion interaction. There is a $C_3-C_2-C_1-F/C_5-C_6-C_1-F$ interaction with the fluorine in cyclohexyl fluoride, but not in fluoropropane. Accordingly, we chose a value for that interaction (Supporting Information Table S1) so that after we first fit the propyl fluoride data by adjusting the torsion potential the results of the cyclohexyl fluoride calculation could be made to match the observed energy difference. We expect that the value of this interaction constant will be torsion angle dependent. Since we have only two points on the curve (anti and gauche), it could be fit with either a V_1 or a V_2 term. We arbitrarily chose a V_1 term, as it seems physically more reasonable. (We can similarly fit the other C−C−C−X data for the other cases previously mentioned with appropriate torsion−torsion terms.) In principle, these terms also affect the vibrational spectra, but such effects appear to be negligible.

Thus, we can say that we have a general solution for the propylX/cyclohexylX problem that has plagued molecular mechanics for many years. One obtains a certain result with the propylX unit. However, when two of these are placed together in such a way as to generate $C_a-C_b-C_cX-C_d-C_e$, those two units ($C_a-C_b-C_c-X$ and $X-C_c-C_d-C_e$) interact in a way that we can represent with a torsion−torsion interaction element in the force constant matrix. Thus, in a sense, this solves the problem. However, this example illustrates both a strength and a weakness of molecular mechanics. We solve the problem, and we can apply this information to other related cases, as is usual with molecular mechanics. However, we do not from this information alone gain any understanding of just why it is that these two torsion units interact as they do. Thus, there still remains a gap between what we know and what we would like to know.

Rotational Barriers and Conformational Energies (Polyfluorides). The barriers in 1,1-difluoroethane and 1,1,1-trifluoroethane are somewhat larger than that in fluoroethane, and unexceptional. A similar situation exists with 2-fluoropropane and 2,2-difluoropropane (see Table 15).

The barrier in 1,1,1,2-tetrafluoroethane calculated by MM4 (4.20 kcal/mol; Table 15) agrees with experiment. The MM4 result for the pentafluoroethane barrier (4.28 kcal/mol; Table 15) is in good agreement with experiment (3.5−4.4 kcal/mol[40]), as is the perfluoroethane barrier (4.45 kcal/mol; Table 15) compared to the experimental result (3.91 kcal/mol[64]). It is noteworthy that this barrier (and the barriers of the fluoroalkanes in general, with the conspicuous exception of 1,2-difluoroethane) is not much larger than that for ethane itself. Additional data on rotational barriers are given in Table 15.

Gauche Effect. It has been known experimentally for a long time that 1,2-difluoroethane is more stable in the gauche conformation than in the trans conformation. A similar effect, or at least the tendency, is observed for some other 1,2-dihaloethane derivatives, and for other compounds where the halogens are replaced by other electronegative atoms. The relatively uncommon situation of having a gauche conformation more stable than a trans conformation has been referred to as “the gauche effect”.[65] Early ab initio calculations were unable to reproduce this result at the Hartree−Fock level and consistently calculated (with small up to modest (double-ζ) basis sets) that the anti conformation was more stable.[8]

1,2-Difluoroethane was used to examine the FCCF torsional parameters, and the results[66] are listed in Table 15 and shown in Figure 7. In 1,2-difluoroethane, the gauche effect[29] stabilizes the gauche conformer relative to the trans one (vide infra). To reproduce this effect, a large positive V_2 term was used for the FCCH torsional parameter. The $V_1/V_2/V_3$ FCCH parameters were chosen so as to give a trans − gauche enthalpy difference of 0.76 kcal/mol for the difluoride, which is close to the results from both experiment (0.80(9))[67] and large ab initio calculations.[68] The MM3 result was clearly too low (0.18) but was a compromise required to fit other results. These other results were substantially affected by the delta-two effect (later), which had not been recognized as being important at the time. That effect was properly included in MM4, and hence, a better fit was possible here.

The gauche-to-trans barrier in 1,2-difluoroethane calculated by MM4 (2.67 kcal/mol; Table 15) was in fair agreement with the microwave (2.00 kcal/mol[69]) and ED (2.36 kcal/mol[70]) results and a little too low when compared with the MP2/B result (3.19 kcal/mol[32]). MM4 calculates the cis barrier height to be 5.91 kcal/mol, while MP2/B gives 8.12 kcal/mol. We noted this discrepancy but were unable to improve it without other undesirable consequences. The MM4 values are mostly close to the experimental values and differ more from the ab initio

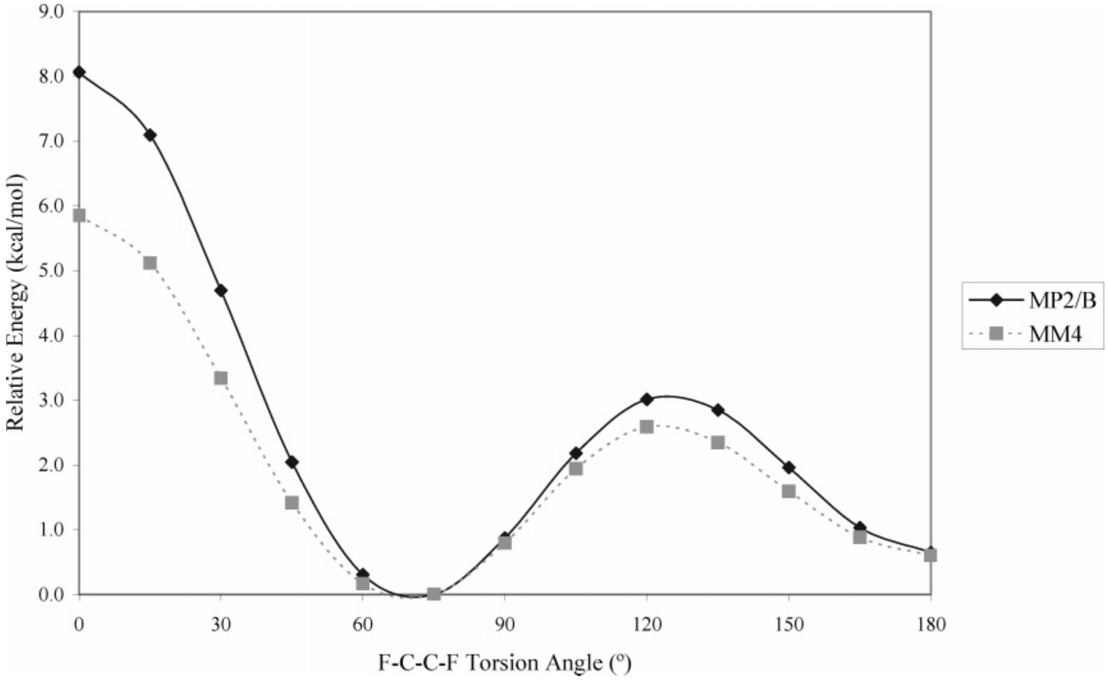


Figure 7. 1,2-Difluoroethane F−C−C−F torsion potential.

values. Other consequences stemming from the gauche effect will be discussed below.

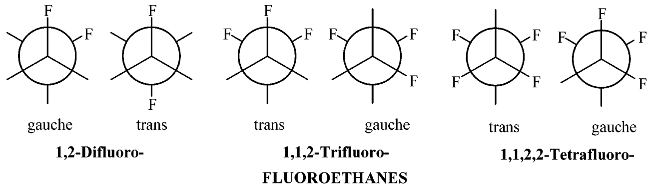
To reproduce the gauche effect in molecular mechanics, one can adjust the torsional energy profile for a linkage such as F−C−C−F so as to fit experiment. Negative V_1 and/or V_2 terms can yield this result. However, since there is clearly a strong hyperconjugative effect which tends to make hydrogen more stable in a position either cis or trans to fluorine, one can alternatively express the effect in terms of the H−C−C−F torsion. We have chosen to have a large component of the latter, for reasons of having a more physically understandable model.[29,30]

In a recent study, Wiberg et al. examined the gauche effect using very large basis sets and correlated levels up to MP4.[68] They concluded that the gauche effect is not due to any type of stabilization in the gauche conformation but is due to a destabilization of the trans conformation by highly electronegative substituents. In the trans conformation, the electronegative substituents tend to bend the central C−C bond in opposite directions, so that the bonding orbitals from the carbons do not point along a common line and the bond is bent. In the gauche conformation, they are bent in a similar direction, remain more nearly collinear, and overlap better than in the trans conformation, where they are bent in opposite directions. Thus, there is a destabilization of the trans conformation relative to the cis conformation.

The MM4 calculated torsional potential for 1,2-difluoroethane is generally satisfactory and shows the gauche effect correctly, but there is a rather large and unexplained discrepancy in the energy at the cis conformation. The MM4 calculation gives a barrier height of only about 6 kcal/mol here, somewhat higher than butane (about 5.2 kcal/mol). However, the MP2/B value is much higher, 8 kcal/mol. While this could be fit better by MM4, such a large energy cis relative to gauche (or trans) would carry over to compounds such as hexafluoroethane, predicting enormous rotational barriers, which are not observed. Thus, the discrepancy here is unexplained.

There are torsion−stretch and torsion−bend effects here, which carry over from those described under fluoroethane, and there is an extra torsion−bend effect involving both fluorines simultaneously. These lead to torsion−stretch and torsion−bend results, as shown in Supporting Information Figures S5−S7. The MM4 data do not fit the ab initio data as well as one would like, which suggests that more may be going on here than meets the eye.

While our interpretation of the nature of the gauche effect is still incomplete, its energetic results can easily enough be reproduced in molecular mechanics by adjusting the torsional potential. We did this earlier with MM3. However, it has turned out that that was not the whole story. There were a few more highly fluorinated compounds that remained distinct problems after this treatment. Two such compounds that we have studied here are 1,1,2-trifluoroethane and 1,1,2,2-tetrafluoroethane.



Consider the energy difference between the C_s (trans) and C_1 (gauche) conformations in 1,1,2-trifluoroethane (Table 15). If the gauche arrangement leads to stability, we would expect the conformation called trans would be more stable than the one called gauche (see the Newman projections). The conformational energy difference is (0.9−1.5 kcal/mol by experiment[71] and 1.45 by ab initio calculations), favoring the gauche (C_1) form. This is contrary to what is suggested by conformational analysis and the MM3 results with 1,2-difluoroethane. With the latter, the conformation with the fluorines gauche is more stable, but in the present case, the conformation with the more fluorines gauche is the less stable (Table 15).

A similar problem also exists in the MM3 results for 1,1,2,2-tetrafluoroethane (Table 15). Experimentally, the trans conformer (i.e., hydrogens are trans) was found to be more stable (ΔH) by 1.16[72] and 1.17[73] kcal/mol. The BC calculations agree fairly well with the experiments and give the gauche−trans energy difference as 1.54 kcal/mol. However, as in the 1,1,2-

trifluoro example above, the gauche conformation has more gauche interactions, and a negative energy is expected here. The problem for molecular mechanics was to fit 1,2-difluoroethane in such a way that 1,1,2-trifluoroethane and 1,1,2,2-tetrafluoroethane could be well fit simultaneously. We were not able to adjust the torsional parameters for MM3 so as to get more than a qualitative agreement with the experimental results. If the "experimental" values for ΔH between the two conformations in the above tri- and tetrafluoroethanes were taken as 0.90 and 1.17 kcal/mol, and the gauche difluoroethane is -0.80 kcal/mol, the overall best MM3 values were 1.02 and 0.16 and -0.18 kcal/mol, respectively. These gave errors of 0.12, -1.01, and 0.62 kcal/mol for the three compounds, which in turn gave a distressingly large rms error of 0.69 kcal/mol. What is the problem?

Delta-Two Effect. The 1,1,2,2-tetrafluoroethane shows an unexpected stability of conformations that at first sight is reminiscent of 1,1,2,2-tetramethylethane. In the case of the fluoro compound, the trans conformation (C_s) is unusually stable. The C_2 conformation has one additional gauche interaction between fluorines, and since gauche interactions are stabilizing here, it might be supposed that the C_s conformation would be unstable by 0.5 kcal/mol or so, whereas in fact it is more stable by 1.0 kcal/mol. In the corresponding tetramethylethanes, the gauche conformation between methyls is typically unstable by 0.8 kcal/mol. One might therefore suppose from conformational analysis that the C_s conformation, which has one less gauche conformation, would be more stable by 0.8 kcal/mol. Actually, the stabilities (enthalpies) are equal.

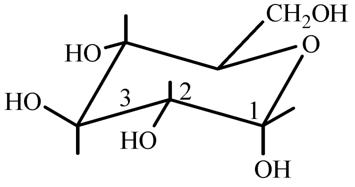
Although there is a superficial resemblance between the tetrafluoro- and tetramethyl ethanes, the underlying reasons for the above two conformational situations must be quite different. The alkane case is easily understood. The bulk of the instability in the gauche conformation comes from van der Waals repulsion between gauche methyl groups. The isobutane structural units are not exactly tetrahedral, and the tertiary centers are flattened somewhat (the C$-$C$-$C bond angles are about 111°). In the C_s conformation, this flattening brings the gauche methyls a good deal closer to one another, and they cannot get away from one another by twisting. Any twisting to relieve the strain on one side increases the strain on the other side. Thus, the symmetrical conformation has its enthalpy raised by this extra repulsion. The unsymmetrical conformation can twist the methyls apart to some extent and reduce this repulsion. Thus, the stabilities of the two conformations are found to be quite similar, as the two (more severe) gauche repulsions in the anti form just balance the three (more modest) repulsions in the C_2 form. This case is well understood, and the correct result was given automatically by MM3.

With the tetrafluoro compound, first, the fluorine atom has a much smaller van der Waals volume than does the methyl group, so that any steric effects would be expected to be relatively small. Second, the bond angles are close to tetrahedral, so that any steric effects do in fact appear to be small. The results in the alkane case are completely determined by steric effects, but that cannot be the case with the fluorides. The C_s conformation is not destabilized in 1,1,2,2-tetrafluoroethane, as in the alkane, but is stabilized, by about 2 kcal/mol. (Instead of being 1 kcal/mol less stable than the gauche conformation from the gauche effect, it is 1 kcal/mol more stable.) Thus, the question is where does this extra stability come from? Conformational analysis offers us no clue. Conformational additivities suggest that the C_s conformation will be less stable, and detailed MM4 calculations bear out this conclusion, unless something additional is added to the force field. If this extra stability is not from a steric effect, it would seem to be from a stereoelectronic or electrostatic effect. However, electrostatics has already been included in MM4, including induced dipoles. Thus, it would appear that these results stem from still another stereoelectronic effect.

The physical situation which underlies the conformational behavior of 1,2-difluoroethane and the related tri- and tetrafluoro compounds described in the preceding paragraphs can be summarized as follows. If there are just two fluorines in a gauche conformation, as in the case of 1,2-difluoroethane, the *gauche effect* stabilizes the gauche conformation (or alternatively destabilizes the anti conformation). With the other two more highly fluorinated derivatives discussed above, from this information and by the usual rules of conformational analysis, the conformation with the larger number of gauche effects should be the more stable one. However, this is not the case. Thus, with those two compounds, something else occurs, the result of which wipes out the stabilizing influence of the gauche effect, and in fact introduces a corresponding destabilizing effect.

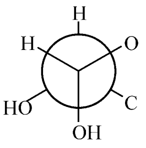
As it turns out, there is a long known and well established analogy in the carbohydrate field where a similar stereoelectronic effect is called the *delta-two effect*. The latter specifically involves conformations with three interacting oxygen atoms, instead of fluorines as in the present case. However, one would certainly expect similarities between oxygen and fluorine in any stereoelectronic effect.

Let us first review this delta-two effect. In the hexapyranose structures of carbohydrates, the anomeric hydroxyl group (for example, the one at C-1 in the glucose structure shown) is normally somewhat more stable in the alpha position (axial), as shown. This tends to be true in general, no matter what stereochemistry the rest of the molecule has.

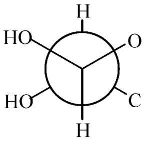


α-D-Glucose

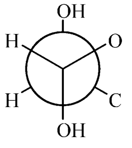
This stability is due mainly to the *anomeric effect*, which involves an energy of about 1$-$2 kcal/mol in the gas phase. The C-1 axial hydroxyl is usually more stable, but the β (equatorial) isomer is also usually found in equilibrium with it. However, there was long ago found one partial exception to the above, in that if there were a β hydroxyl at C-2 (axial), then little or none of the β C-1 isomer would be found. The conclusion drawn by Reeves[74] as early as 1956 was that there was some kind of a destabilizing effect if there were β-hydroxyls at C-1 and C-2 at the same time. He referred to this as the *delta-two effect*. This can be most easily understood with the aid ofNewman projections. Looking down the C-1$-$C-2 bond of α-D-glucose and α-D-mannose, we see the following:



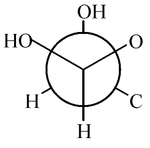
α-D-Glucose



β-D-Glucose



α-D-Mannose



β-D-Mannose

The β-D-mannose alone shows the delta-two effect (the vicinal oxygen between the geminal oxygens). It is destabilized by 0.8

kcal/mol, relative to the glucose case.[75] No physical interpretation of this effect appears to have been given previously in the literature. However, whatever the cause, the nature of the effect can be calculated in molecular mechanics as being due to a torsion−torsion interaction, involving three electronegative atoms (where two are geminal and the third is vicinal to the geminal pair). This effect appears to be related to the gauche effect and is of opposite sign with respect to the energy.

We were able to show with model studies[20,23] that this effect can be represented by a torsion−torsion interaction between the two O−C−C−O groupings, and it has a (gas phase) value of about 2 kcal/mol, which adds into the other energy terms present in the calculation in MM4. The delta-two effect is an apparent consequence of the electronegativity of the atoms involved, as it also occurs here with the analogous fluorine compounds. What is needed here to make the MM4 calculations agree with experiment is a similar effect, a torsion−torsion interaction between two FCCF groupings, where the two groupings differ only by the position one atom, which is a fluorine of the geminal difluoro grouping. Thus, the interaction here involves fluorines instead of oxygens but is otherwise the same as in the mannose case discussed above. The numerical values used for the fluoride (11 1 11 1 11 in Supporting Information Table S1) have the values 0.319 and 0.205 for V_1 and V_2 for the fluorine case. In the oxygen case, only the gauche conformation was fit, not the whole torsion potential, and only a V_2 term was used, with a value of 0.570. Thus, the sign of this term is the same for fluorine and oxygen, and the magnitude of the effect is quite similar at the gauche conformation. Thus, the delta-two effect in carbohydrates is also found here with fluorines. In each case, the effect destabilizes the delta-two conformation by about 2 kcal/mol.

Consequently, we added this delta-two torsion−torsion interaction term into the MM4 calculations for fluorides. As shown in Table 15, with this term included, the conformational results for 1,1,2-trifluoroethane and 1,1,2,2-tetrafluoroethane are much improved from the MM3 values. For MM4, the best values for the conformational energies of the tri- and tetrafluorides and for the 1,2-difluoride were 0.89, 1.56, and 0.76 kcal/mol, respectively. The errors were then −0.01, +0.39, and −0.04, rms 0.19 kcal/mol, so the fit is now satisfactory. (The MM3 errors were +0.12, −1.01, and +0.62, rms 0.69 kcal/mol, without the delta-two effect term.)

Dipole Moments. The dipole moments of 14 fluorinated hydrocarbons were calculated by MM4 and compared with the available experimental data[76] and ab initio calculated values at the MP2/B level,[32] and the results are summarized in Table 16. The experimental measurements utilized here for comparison were determined from the Stark Effect by microwave spectroscopy. (The measurement of dipole moments by polarization methods is complex and subject to considerable error, so we have not used such data here.) The fit of MM4 to experimental data was improved by including induced dipoles (polarization) in MM4. The MP2/B calculated dipole moments are also listed. Note that they are quite poor, being some 10−15% too large. This is largely a basis set/correlation truncation problem, and these values can be empirically corrected, since the bulk of the error is systematic. In Table 16 are given the corrected MP2/B moments, where the factor 0.87 is used. Note that these corrected MP2/B values have a rms deviation from experiment of only 0.07 D, which is approximately the experimental error. The rms deviation of MM4 from experiment is a reasonable 0.15 D.

TABLE 16: Dipole Moments of Fluoro Compounds

	exptl[a]	MP2/B	0.87 MP2/B	MM3	MM4
CH_3F	1.79(10)	2.177	1.894	1.82	1.614
CH_2F_2	1.96(2)	2.299	2.000	2.13	1.773
CHF_3	1.645(9)	1.912	1.556	1.93	1.469
C_2H_5F	1.96(1)	2.253	1.947	1.82	1.773
CF_2HCH_3	2.30	2.610	2.271	2.15	2.300
CF_3CH_3	2.35(2)	2.653	2.308	2.05	2.571
C_2HF_5	1.54	1.836	1.597	1.85	1.557
C_3H_7F(t)	1.85(2)	2.309	2.007	1.82	1.847
i-propylfluoride	1.96(3)	2.264	1.861	1.82	1.866
2,2-difluoropropane	2.40(2)	2.735	2.331	2.19	2.545
t-butylfluoride	1.959(5)	2.249	1.954	1.82	1.926
fluorocyclohexane (eq)	2.11(3)	2.492	2.168	1.82	2.067
(ax)	1.81(3)	2.085	1.813	1.82	1.815
1,1-difluorocyclohexane	2.556(10)	2.961	2.577	2.20	2.858
signed av			+0.006	−0.068	−0.015
rms			0.070	0.213	0.148

[a] Microwave values only.

TABLE 17: Vibrational Spectrum of Fluoromethane

IR(g)[74]	B. P.[33]	MM3/Δ	MM4/Δ	sym	assignment
3006	2984	3017/11	3016/10	*E*	C−H str.
2964.5	2912	2913/−52	2954/−11	*A*1	C−H str.
1466.5	1447	1421/−46	1448/−19	*E*	CH_3 def.
1464	1467	1437/−27	1552/88	*A*1	CH_3 def.
1182.3	1169	1043/−139	1172/−10	*E*	HCF bending
1048.6	1045	1035/−14	1072/23	*A*1	C−F str., HCH bending
rms		72	32		
signed av		−48	+7		

TABLE 18: Vibrational Spectrum of Difluoromethane

IR(g)[74]	B. P.[33]	MM3/Δ	MM4/Δ	sym	assignment
3015	2986	2992/−23	3015/0	*B*1	C−H str.
2949	2926	2939/−10	3001/52	*A*1	C−H str.
1508[a]	1495	1428/−80	1430/−78	*A*1	HCH bending
1430	1458	1530/105	1502/72	*B*2	HCF bending
1262[a]	1240	1256/−6	1324/62	*A*2	HCF bending
1165	1162	934/−231	986/−179	*B*1	HCF bending
1090	1091	1071/−19	1060/−30	*B*2	C−F str.
1070	1084	1097/27	1150/80	*A*1	C−F str.
529	517	570/41	533/4	*A*1	F−C−F bending
rms		91	80		
signed av		−22	−2		

[a] Liquid Raman spectrum.

Vibrational Frequencies. Force parameters derived for MM4 were adjusted in order to get the best fit to the associated vibrational frequencies. With the earlier MM3 work, there were occasional discrepancies with the experimental frequency assignments. Recently, Baker and Pulay published a study of the vibrational spectra of some simple alkyl fluorides determined by DFT(B3PW91/6-31G*) methods, applying a direct scaling of force constants technique.[33] We will refer to this as the B. P. method throughout this manuscript. Their results agreed well with experiment over a range of compounds, with an rms error in the calculated spectra of about 9 cm^{-1}. The present work suggests that, with a larger and more diverse set of fluoro compounds, the rms error is somewhat larger, in the range 20−30 cm^{-1}, but the results are good enough to be very useful. Accordingly, we carried out B. P. vibrational calculations for the substituted methanes and ethanes studied herein. The calculations lead to the conclusion that a few of the experimental frequencies were misassigned. The MM4 comparisons with experiment were changed accordingly. The MM4 spectra of 14 alkyl fluorides are listed in Tables 17−22 and Supporting Information Tables S18−S25, compared with the observed data[77−90] and the calculated B. P. results.[33] The earlier MM3 results are also given.[30]

TABLE 19: Vibrational Spectrum of Trifluoromethane

IR(g)[74]	B. P.[33]	MM3/Δ	MM4/Δ	sym	assignment
3035	3009	3006/−29	3058/33	$A1$	C−H str.
1375	1392	1487/112	1407/32	E	HCF bending
∼1152	1138	1136/−16	1126/−26	E	C−F str.
∼1152	1114	1040/−112	1172/20	$A1$	C−F str.
699.2	679	599/−100	609/−90	$A1$	FCF bending
507.6	498	554/46	577/70	E	FCF bending
rms		77	50		
signed av		+5	+13		

TABLE 20: Vibrational Spectrum of Tetrafluoromethane

IR(g)[74]	B. P.[33]	MM3/Δ	MM4/Δ	sym	assignment
1283	1267	1468/187	1294/11	$T2$	C−F str.
908.5[a]	869	734/−175	899/−10	$A1$	C−F str.
637.1	614	560/−77	589/−48	$T2$	FCF bending
435[a]	427	523/88	532/97	E	FCF bending
rms		136	54		
signed av		+36	+8		

[a] Gas Raman spectrum.

TABLE 21: Vibrational Spectrum of Fluoroethane

IR (g)[75]	B. P.[33]	MM3/Δ	MM4/Δ	sym	assignment
3012	3002	2996/−16	2990/−22	A''	CH$_3$ and CH$_2$ str.
3003	2992	3000/−3	2986/−17	A'	CH$_3$ and CH$_2$ str.
3003	2947	2973/−30	2977/−26	A''	CH$_3$ str.
2941	2925	2923/−8	2948/7	A'	CH$_2$ and CH$_3$ str.
2915	2910	2902/−13	2899/−16	A'	CH$_3$ str.
1479	1501	1512/33	1538/59	A'	CH$_3$ and CH$_2$ def.; C−F, C−C str.
1449	1470	1463/14	1494/45	A'	CH$_3$ def. and CH$_2$ Sci. C−F str.
1449	1454	1453/4	1451/2	A''	CH$_3$ def.
1395	1409	1434/39	1453/58	A'	CH$_2$ and CH$_3$ def.; C−C str.
1365[a]	1374	1373/8	1360/−5	A'	CH$_3$ and CH$_2$ def.; C−F str.
1277	1273	1242/−35	1300/23	A''	CH$_2$ twist
1171	1173	1100/−71	1098/−73	A'	C−F str.
1108	1037[b]	1032/−76	1068/31	A'	C−C str., CH$_3$ wag
1048	1115	1003/−45	1126/78	A''	CH$_3$ rock
880	872	909/29	921/41	A'	CH$_3$ wag, C−C str.
810	798	842/32	768/−42	A''	CH$_3$ wag
415	404	423/8	410/−5	A'	CCF skeletal bending
278[a]	261	240/−38	240/−38	A''	CH$_3$ torsion
rms		35	40		
signed av		−9	5		

[a] Liquid Raman spectrum. [b] Pulay's value was used because of the experimental ambiguity.

TABLE 22: Vibrational Spectrum of Perfluoroethane[a]

IR(g)[74]	B. P.[33]	MM3/Δ	MM4/Δ	MM4/ Δ[c]	sym	assignment
1417[b]	1387/−30	1281/−136	1318/−99	/−69	A_{1g}	C−F str.
1250	1221/−29	1350/100	1271/21	/50	Eu	C−F str.
1250[b]	1221/−29	1454/204	1331/81	/110	Eg	C−F str.
1116	1102/−14	1115/−1	1188/72	/86	A_{2u}	C−F str.
807[b]	777/−30	647/−52	733/−74	/−44	A_{1g}	C−C, C−F str.
714	693/−21	620/−94	609/−105	/−84	A_{2u}	CF$_3$ def.
619[b]	597/−22	565/−54	580/−39	/−17	Eg	CF$_3$ def.
522	503/−19	562/40	575/53	/72	Eu	CF$_3$ def.
372[b]	373/2	378/6	343/−29	/−30	Eg	CF$_3$ rock
348[b]	339/−9	312/−36	350/2	/11	A_{1g}	FCF bending
219	209/−10	247/28	202/−17	/−7	Eu	CF$_3$ wag
68	51/−17	63/−5	64/−4	/12	A_{1u}	C−C torsion
rms	21	90	56	59		
signed av	−19	18	−4	+15		

[a] Also called hexafluoroethane and ethforane. [b] Raman gas spectrum. [c] MM4 fit to B. P. values instead of the experiment.

In hydrocarbons, some of the ordinary C−H bending frequencies are similar in magnitude to some of the usual C−C stretching frequencies, and there is much coupling between the two sets of vibrations. To obtain good predictions of the vibrational spectra, these couplings are explicitly taken into account with cross-terms in the force constant matrix. With fluorocarbons, since the mass of fluorine is similar to that of carbon, and quite different from that of hydrogen, the C−F bending frequencies in general are much lower than those for C−H, and do not couple in a major way with the C−C stretching frequencies. On the other hand, the C−F stretching frequencies do tend to couple with each other, and with the C−C stretching frequencies. There is also a particular type of C−F stretching frequency that couples rather strongly with a F−C−F bending frequency (discussed later). Thus, the frequency coupling problem with fluorocarbons is similar in severity to what is observed with hydrocarbons, but there are different sets of frequencies involved in the two cases. This necessitates the use of different kinds of explicit cross-terms in the force constant matrix for polyfluorinated hydrocarbons, other than those that are needed for the hydrocarbons themselves. Such terms were not included in the MM3 force field.

The result of all of this is that if a hydrocarbon is lightly fluorinated, it may be treated as a perturbed hydrocarbon as has been customary in the past, and the accuracy of the vibrational calculations is usually similar to what has been previously found for other classes of compounds with MM4, and somewhat better than that from MM3. However, when one considers heavily fluorinated hydrocarbon structures, rather different terms and treatments of the interactions are required, in addition to those used in hydrocarbons, if one is to obtain reasonable accuracy. The MM4 force field has been developed in such a way as to improve the spectroscopic results of the fluorocarbons relative to those from MM3.

Stretching Frequencies and Force Parameters. Earlier MM3 work on the C−H stretching frequencies in substituted molecules showed that the electronegativity of substituents affected not only the bond lengths but also the stretching force constants for these bonds as well.[31] The C−H frequencies were restudied with MM4. As shown in Table 23, over the group of compounds studied, there are 41 CH frequencies, and these are calculated with a signed average error of -3 cm^{-1} from MM4. We have not carefully studied the couplings of these vibrations with each other and other vibrations, so the overall rms error is 27 cm^{-1}. This probably could be improved but is adequate for our purposes and similar to what was obtained with MM3.[31]

We earlier presumed that the variation of the stretching parameter with electronegativity is general and that it applies to C−C bonds as well as to C−H bonds, although the latter were the only kinds of bonds previously studied. Our MM3 work on fluorocarbons[30] showed the desirability of extending the variation of stretching constant with bond length to C−C bonds in fluoroalkanes, but this effect was not taken into account in the original MM3 work. Without taking this effect into account, the C−C stretching frequencies are calculated with reasonable accuracy for molecules containing up to about three fluorines. However, as the number of fluorines increases further, the calculated frequencies become much too low (by over 100 wavenumbers in several cases). Calculated over the set of fluoro compounds shown in Table 24 in the ordinary way with MM4, the rms error for the C−C stretching frequency would be 63 cm^{-1}, and importantly, the signed average error would be -33 cm^{-1}. This means that, overall, these frequencies would be calculated too low, and in a rough way, the errors are larger when the number of fluorines is larger.

As the earlier work with the C−H bond showed, we expect that we can represent the electronegativity effect of the fluorine

TABLE 23: C−H Stretching Frequencies of Fluoroalkanes

compound	sym	exptl	MM4/Δ
fluoromethane	E	3006	3016/10
	A_1	2965	2954/−11
difluoromethane	B_1	3015	3015/0
	A_1	2949	3001/52
trifluromethane	A'	3035	3058/23
fluoroethane	A''	3012	2990/−22
	A'	3003	2986/−17
	A''	3003	2977/−26
	A'	2941	2948/7
	A'	2915	2899/−16
1,1-difluoroethane	A'	3018	3026/18
	A''	3001	3000/−1
	A'	2979	3002/23
	A'	2963	2919/−44
1,2-difluoroethane(g)	B	3001	2993/−8
	A	2995	2992/−3
	B	2995	2952/−43
	A	2958	2965/7
1,2-difluoroethane(t)	A_g	2974	2979/5
1,1,1-trifluoroethane	E	3042	3010/−32
	A_1	2974	2934/−40
1,1,1,2-tetrafluoroethane	A'	3015	3009/−6
	A''	2981	2985/4
1,1,2,2-tetrafluoroethane(t)	B_u	3001	3057/56
	A_g	2995	3059/64
1,1,2,2-tetrafluoroethane(g)	A	3003	3041/38
	B	2995	3035/40
pentafluoroethane	A'	3008	3047/39
2-fluoropropane	A'	2996	2992/−4
	A''	2996	2990/−6
	A'	2989	2988/−1
	A''	2989	2987/−2
	A'	2960	2965/5
	A''	2931	2901/−30
	A''	2931	2900/−31
2,2-fluoropropane	A_1	3018	3004/−14
	B_2	3018	3002/−16
	A_2	3018	3002/−16
	B_1	3018	3002/−16
	B_1	2959	2920/−39
	A_1	2959	2919/−40
rms			27
signed av			−3

TABLE 24: C−C Stretching Frequencies of Fluoroalkanes

compound	sym	exptl	B. P.[a]	MM3/Δ	MM4[a]/Δ	k_s
ethane	A_{1g}	995	968	960/−35	967/−28	4.550
fluoroethane	A'	1108	1037	1000/−108	1068/−40	5.710
1,1-difluoroethane	A'	1129	1107	1028/−89	1115/−14	6.265
1,2-difluoroethane(g)	A	1079[b]	1080	986/−94	1101/22	6.265
1,2-difluoroethane(t)	A_g	1052	1120	979/−152	1067/15	6.265
1,1,1-trifluoroethane	A_1	828	801	727/−101	884/56	6.476
1,1,1,2-tetrafluoroethane	A'	843	816	720/−123	863/20	6.556
1,1,2,2-tetrafluoro-ethane(t)	A_g	1106	1120	929/−177	1072/−34	6.556
1,1,2,2-tetrafluoro-ethane(g)	A	906	888	815/−91	930/24	6.556
pentafluoroethane	A'	867	847	716/−151	830/−37	6.587
perfluoroethane	A_{1g}	807	777	647/−160	733/−74	6.598
2-fluoropropane	A''	1144	1133	1086/−58	1135/−9	5.258
	A'	819	799	812/−7	862/43	5.258
2,2-fluoropropane	B_1	1269	1253	1202/−67	1284/15	5.641
	A_1	780	752	718/−62	837/57	5.641
rms			28	112	38	
signed av			−22	−103	+3	

[a] MM4 and B. P. assignments are based on the potential energy distribution contributions. [b] The original assignment was 865 cm^{-1}. In fact, these two motions are strongly coupled together and could be assigned either way. We prefer this assignment.

on the stretching constant as a linear relationship, as shown in eq 1.

$$k_{s(C-C)} = k_0 + \frac{8\pi c^2}{(-0.000\,102\,3)^2} \times 6.0 \times (l_0 - 1.639) \times \Delta l_{0C-C} + k_{C-C} \quad (1)$$

where $k_{s(C-C)}$ is the stretching parameter, k_0 is the standard C−C stretching parameter (4.550 dyn/cm), c is the velocity of light, 6.0 is the reduced mass of the C−C bond, −0.000 102 3 is a parameter that correlates bond length and frequency for C−H bonds,[31] which we have used unchanged here, l_0 has the value 1.5270 Å for the C−C bond, 1.639 is a parameter, Δl_{0C-C} is the change in bond length from l_0, and k_{C-C} is a stretching parameter with the value −0.30. In Table 24 are given the calculated C−C stretching frequencies for a set of fluoroalkanes, following the value for the reference compound ethane. Addition of fluorines causes $k_{s(C-C)}$ to initially increase, as we go down the table, from the bond length shrinkage due to the attached fluorines. However, after we reach the tetrafluoroethanes, adding still further fluorines causes the C−C bond to stretch slightly, because of the combined van der Waals and dipole/dipole repulsions between the fluorines. This causes the value of the parameter to decrease somewhat in the penta- and hexafluoro compounds, even though the additional fluorines are causing still further electronegativity increases. In the final column of Table 24, the value for the stretching force constant of the C−C bond is given for each molecule. Note that these vary substantially in fluoroethanes, from a minimum value of 5.710 in fluoroethane (compared to 4.550 in ethane itself) up to a maximum value of 6.598 in the perfluoroethanes. However, these stretching frequencies are now calculated with an accuracy comparable with that obtained for the other frequencies, with signed average rms and errors of +3 and 38 cm^{-1}, respectively, over the whole series of fluoro compounds listed in Table 24.

Since the increase in the stretching constant of the C−C bond with increasing fluorine substitution was not accounted for in MM3, we should expect that the C−C stretching frequencies calculated by MM3 will become increasingly too small relative to experiment as the degree of fluorination increases. This is what is found. If we look at the errors in the calculated MM3 C−C stretching frequencies (for compounds having only one conformation and an unambiguous structure), we find for the following compounds the respective errors as given. For fluoroethane, 1,1-difluoroethane, 1,1,1-trifluoroethane, 1,1,1,2-tetrafluoroethane, pentafluoroethane, and perfluoroethane (Table 24), the corresponding errors are −108, −89, −101, −123, −151, and −160 cm^{-1}. Some of this error is due to the lack of sretch−stretch interaction cross-terms between the C−C and C−F bonds and other problems, but the calculated frequencies are systematically too small, and the major trend is clearly an increase in frequency as one goes along the series. The corresponding MM4 errors are −40, −14, +56, +20, −37, and −74 cm^{-1}.

We also studied the spectra of the four fluorine substituted methanes (Tables 17−20) with MM4. The substituted methanes are special cases, and they were not studied earlier with MM3. In MM4, relative to MM3, we have added stretch−stretch and bend−bend interactions, both of which are important for these compounds. Additionally, stretch−bend interactions have been specifically parametrized in MM4, whereas just some general atom-independent parameters were used in MM3. As would be expected, these coupling vibrations between the fluorines and carbon have a substantial effect on the calculated vibrational spectrum. The rms errors for these four compounds with MM3 were 72, 91, 77, and 136 cm^{-1}, for an average rms error of 94 cm^{-1}. The corresponding MM4 errors were 32, 80, 50, and 54 cm^{-1}, for an average rms error of 54 cm^{-1}.

Overall, MM4 does not calculate the vibrational frequencies for fluorocarbons very well, but it does better than MM3 did. In lightly fluorinated compounds, the accuracy of the MM4 results is similar to that obtained for hydrocarbons, but for more highly substituted fluorocarbons, the MM4 results are less good. The rms errors for 14 structures obtained over 250 vibrations are 53 cm^{-1}, compared to 65 cm^{-1} with MM3. These numbers show that the spectra of this group are in poorer agreement with experiment than were the alkanes (35 and 25 cm^{-1}, respectively, for large sets of molecules with MM3 and MM4). Many reasons for this poor agreement are evident, as discussed earlier, and they could presumably be at least partly overcome with the aid of a more complicated force field than MM3. Clearly, more and/or stronger significant sretch−stretch interactions are needed, perhaps including vicinal in addition to geminal. Also, the variation of the force constants with the changing electronegativity of the total substitution appears to be important for bond angle bending as well as for bond stretchings. In both MM3 and MM4, there is a serious limitation which we imposed long ago, in the atom type numbers. We recognized long ago that in some cases we could use general parameters for a group of atoms, rather than specifically parametrizing them one by one. Hydrogen was a special case from the start, but other first row atoms were frequently lumped together, and assigned identical parameters. Thus, we had type 1, type 2, and type 3 atoms, where a carbon atom was attached to zero, one, or two hydrogens. With a hydrocarbon force field, the non-hydrogens are carbons. When MM2 was developed, we simply carried over these atom types to include other first row (and later second row) atoms. Accordingly, the substitution pattern on the fluorides as we use it here does not differentiate carbon and fluorine for many of these parameters. This is clearly a limitation and may in fact be the most serious limitation with respect to the accuracy of the vibrational frequencies calculated by MM4. This limitation could, of course, be removed. However, it is a defined limitation in MM4, and we do not wish to make such a fundamental change in the force field at this point. It is accordingly retained.

Perfluorocarbons. The simplest perfluorocarbons would be perfluoromethane (carbon tetrafluoride) and perfluoroethane (hexafluoroethane). These two compounds have been discussed earlier in some detail. They have no structural features that require comment, other than to note the anomously low C−C stretching vibrational frequency calculated by MM4 for perfluoroethane.

For our discussion of the higher perfluoro molecules, we will proceed as follows. First, we will discuss perfluoropropane, where various bond angles come into importance. Subsequently, we will discuss perfluorobutane, wherein conformational problems arise. Finally, we will discuss Teflon. In each case, we will proceed by starting with the molecule as calculated with the present parameter set developed to this point. In each case, the results are not satisfactory. We will then discuss why we think this is the case and how the situation may be improved. We will simultaneously derive a revised parameter set for perfluoro compounds, which will attempt to account for the major parts of these errors, and produce acceptable MM4 structures and properties for these compounds.

Perfluoropropane. Perfluoropropane seems like it would be a straightforward molecule for molecular mechanics; however, the structure that is calculated using the MM4 force field developed to this point is not in good agreement with the BC structure (Supporting Information Table S26). Those portions of the structure that could be determined experimentally[94] are also listed in Supporting Information Table S26, and they are in satisfactory agreement with the BC structure. However, the structure of perfluoropropane as calculated by MM4 at this point shows some major discrepancies when compared with the BC structure, and these discrepancies can be divided into two groups. First, there are angular errors, and second, there are bond length errors. Taking these in order, the C−C−C bond angle from MM4 is too large by 2.9°. Second, the $-CF_3$ groups are tilted in toward each other by 1.6−3.0° too much, increasing the bond angle of the $C_2-C_1-F_a$ angle, and decreasing the $C_2-C_1-F_g$ angles.

TABLE 25: Molecular Structure of Perfluoropropane (Special Parameters)

	ED (r_a)[88]	MM3 (r_g)	MM4 (r_a)	MP2/BC (r_e)	MM4 (r_e)
$C-F_{av}$	1.330(2)	1.332	1.334	1.329	1.328
C_1F_a		1.329	1.330	1.325	1.325
C_1F_g		1.326	1.328	1.325	1.324
C_2F		1.346	1.342	1.339	1.338
$C-C$	1.546(4)	1.536	1.539	1.540	1.534
$C_1C_2C_3$	115.9(7)	116.8	116.0	115.7	116.0
C_1C_2F	108.4(7)	108.4	107.9	107.9	107.9
FC_2F	107.0(13)	106.1	109.2	109.6	109.1
FC_1F_{av}	109.3(2)	107.4	109.6	109.1	109.5
$F_gC_1F_g$		107.3	109.5	109.2	109.4
$F_gC_1F_a$		107.5	109.7	109.0	109.6
$C_2\ C_1F_a$		112.3	108.2	108.6	108.4
$C_2\ C_1F_g$		111.0	109.9	110.5	109.9

The special parameter set for perfluoro compounds must deal with these angular errors. We know that fluorination causes stretching force constant increases, so the C−C−C bond angle would reasonably be expected to have its force constant increased somewhat in this molecule. The bending frequency calculated with the regular MM4 parameters for this molecule is 123 cm^{-1}, whereas the BC value is 151 cm^{-1}. While this error is not alarmingly large, if the bending constant were increased from the present value of 0.74 to a trial value of 1.25, the calculated frequency would be increased to 138 cm^{-1}, a considerable improvement. Also, the C−C−C angle would close down to approximately the correct value. However, this change is of negligible help with respect to the CF_3 tilt problem. Apparently, the latter can be improved only with a torsion−bend interaction, and such an interaction for the torsion angle C−C−C−F was therefore tried. It was also noticed that the θ_0 values for the C−C−F and F−C−F angles had to be changed somewhat simultaneously. When these two things are changed in the calculation (Supporting Information Table S29), the tilt became acceptable (Table 25). It was also noted that the C−C−C angle was adequately corrected during the process. Hence, it was decided not to change the C−C−C bending constant. In view of the quality of the data that we have for perfluoro compounds, anything more than a rather approximate fit is probably not meaningful.

After these changes were made in the parameters, the C−C bond lengths were found to be reasonable, but the C−F bond lengths were systematically too long by some 0.008 Å. Accordingly, the value for l_0 for the C−F bond was correspondingly reduced (Supporting Information Table S29). The structure then found for perfluoropropane using the complete set of special parameters (given in Supporting Information Table S29) is given in Table 25. We feel that the MM4 structure here fits to within the accuracy of the available data. Accordingly, the perfluoroalkanes (special parameters) as described above were used for compounds of this group. However, more is still needed here.

Perfluorobutane. Using the regular parameters in Supporting Information Table S1, the trifluoromethyl groups on butane tended to tilt incorrectly, as they did with perfluoropropane (Supporting Information Table S27). When using the parameters developed for perfluoropropane (Supporting Information Table S29), however, that tilt and the C−C−C bond angles were corrected, as shown in Table 26, so the perfluoropropane parameters are transferable to perfluorobutane, as expected.

In addition to the structural features found in perfluoropropane, the butane analogue also has a torsion potential (C−C−C−C) which is of considerable interest. A few quantum mechanical studies have been published previously on perfluorobutane,[95−98] and there are a number of interesting features. One is that the anti conformer has a C−C−C−C torsional angle of about 165° instead of 180°. Another is that a third unexpected stable conformer was found in addition to the gauche and anti forms. It has been called ortho and has a C−C−C−C torsional angle of about 95°. The existence of this form was confirmed experimentally by nitrogen matrix-isolation IR spectroscopy.[95] From the temperature-dependent gauche−anti relative infrared intensities analysis, it was found that the gauche form is about 0.9 kcal/mol higher in enthalpy than the anti form, in a frozen nitrogen matrix. Quantum mechanical calculations by Michl at the MP2/6-311G*//MP2/6-31G* level agreed and showed that the anti form is more stable (ΔE) by 0.85 and 2.12 kcal/mol than the gauche and ortho conformers, respectively.[98] We repeated these calculations in the present work with geometry optimization at the MP2/B level and found a similar result, with ΔE values of 0.37 and 1.71 kcal/mol. The MM3 and MM4 calculated structures for these three conformers are summarized in Table 26, along with the most recent ab initio (BC) results. In Table 27 are given the conformational energies at all of the stationary points by MP2B, MM3, and MM4. MM3 gives the anti form at a C−C−C−C torsional angle of 180°. Earlier workers have suggested[95−98] the van der Waals interactions between fluorine are responsible for the actual distortion. This problem might be corrected in molecular mechanics by adding a small V_6 term in the torsional parameters (which option is included in MM4 but not in MM3). The molecular structures in general are not very well calculated by MM3 either. Both C−C and C−F bond lengths are calculated too short, and the C−C−C and F−C−F angles are too big. The relative MM3 energies of the gauche and ortho forms are too high, but the MM3 calculation did find that the ortho form is a stable conformer with a C−C−C−C torsional angle of 85°. Note that this stable ortho result was not put into the calculation with the aid of parametrization. It came out of the calculation automatically, mainly due to the van der Waals characteristics assigned to fluorine in the original version of MM3 (1989), which were based on scattering data for neon.

If we compare the MM4 structure of *anti*-perfluorobutane given in Supporting Information Table S27 from the regular parameters with that in Table 26 from the special perfluoro parameters, we note that the significant angular errors analogous to those which occurred in perfluoropropane have been removed, and the bond lengths have also been improved. In Supporting Information Table S27, with the bond angles opened much too widely. The BC calculations indicate that the C−C−C−C torsional angle is 165.4° at the energy minimum, but the barrier at 180° is only 0.1 kcal/mol. Niether the BC nor MM4 calculations are expected to be accurate to 0.1 kcal/mol, so our interpretation is that they agree that the potential surface is flat in the 160−180° range.

TABLE 26: Molecular Structure (r_e) of Perfluorobutane (Special Parameters)

	MP2/BC	MM3 (r_g)	MM4
		Anti	
C−F_3 av	1.325	1.327	1.324
C_1−F_a	1.325	1.328	1.325
C_1−F_g	1.326	1.326	1.324
C_1−$F_{g'}$	1.323	1.326	1.324
C−F_2 av	1.343	1.346	1.343
C_2−F_g	1.344	1.346	1.343
C_2−$F_{g'}$	1.341	1.346	1.343
C_1−C_2	1.544	1.540	1.536
C_2−C_3	1.544	1.531	1.541
CCC	114.2	117.4	114.8
FC_1F av	109.1	107.4	109.5
FgC_1Fg'	109.3	107.3	109.4
FaC_1Fg'	108.8	107.4	109.5
FaC_1Fg	109.1	107.4	109.5
FC_2F	109.3	106.0	108.4
C_2C_1F av	110.0	111.5	109.5
C_2C_1Fa	108.6	111.8	108.3
C_2C_1Fg	110.3	111.4	110.1
C_2C_1Fg'	110.7	111.4	110.1
C_1C_2F av	107.6	108.3	107.0
C_1C_2Fg	107.5	108.3	107.0
C_1C_2Fg'	107.7	108.3	107.0
ωCCCC	165.4	180	180.0
		Gauche	
C_1−F_3 av	1.325	1.327	1.324
C_1−F_a	1.324	1.329	1.326
C_1−F_g	1.325	1.326	1.324
C_1−$F_{g'}$	1.326	1.325	1.322
C−F_2 av	1.340	1.348	1.344
C_2−F_t	1.341	1.350	1.345
C_2−$F_{g'}$	1.340	1.346	1.342
C_1−C_2	1.540	1.539	1.540
C_2−C_3	1.548	1.539	1.552
CCC	117.6	118.7	117.1
FC_1F av	109.1	107.3	109.6
FgC_1Fa	109.1	107.3	109.8
$Fg'C_1Fa$	108.7	107.2	109.5
FgC_1Fg'	109.4	107.3	109.5
FC_2F	109.2	106.0	108.7
C_2C_1F av	109.9	111.4	109.3
C_2C_1Fa	108.7	112.3	108.4
C_2C_1Fg	110.7	110.9	110.5
C_2C_1Fg'	110.2	110.9	109.1
C_1C_2F av	107.5	107.7	106.9
C_1C_2Ft	107.5	107.9	107.0
C_1C_2Fg'	107.5	107.4	106.8
ωCCCC	53.5	62.1	56.1
		Ortho	
C_1−F_3 av	1.327	1.327	1.331
C_1−F_a	1.326	1.329	1.324
C_1−F_g	1.330	1.327	1.331
C_1−$F_{g'}$	1.325	1.324	1.324
C−F_2 av	1.340	1.347	1.344
C_2−F_t	1.337	1.349	1.342
C_2−$F_{g'}$	1.342	1.345	1.345
C_1−C_2	1.544	1.519	1.545
C_2−C_3	1.559	1.540	1.568
CCC	115.3	118.6	114.8
FC_1F av	109.0	107.3	109.6
FgC_1Fg'	109.4	107.3	109.6
FaC_1Fg	108.8	107.3	109.6
FaC_1Fg'	108.9	107.3	109.7
FC_2F	108.9	106.0	108.6
C_2C_1F av	109.9	111.6	109.3
C_2C_1Fa	108.4	112.0	108.4
C_2C_1Fg	110.5	111.6	110.1
C_2C_1Fg'	110.8	111.1	109.4
C_1C_2F av	107.2	107.7	106.4
C_1C_2Ft	106.8	107.0	106.1
C_1C_2Fg'	107.7	108.3	106.7
ωCCCC	97.7	84.5	103.2

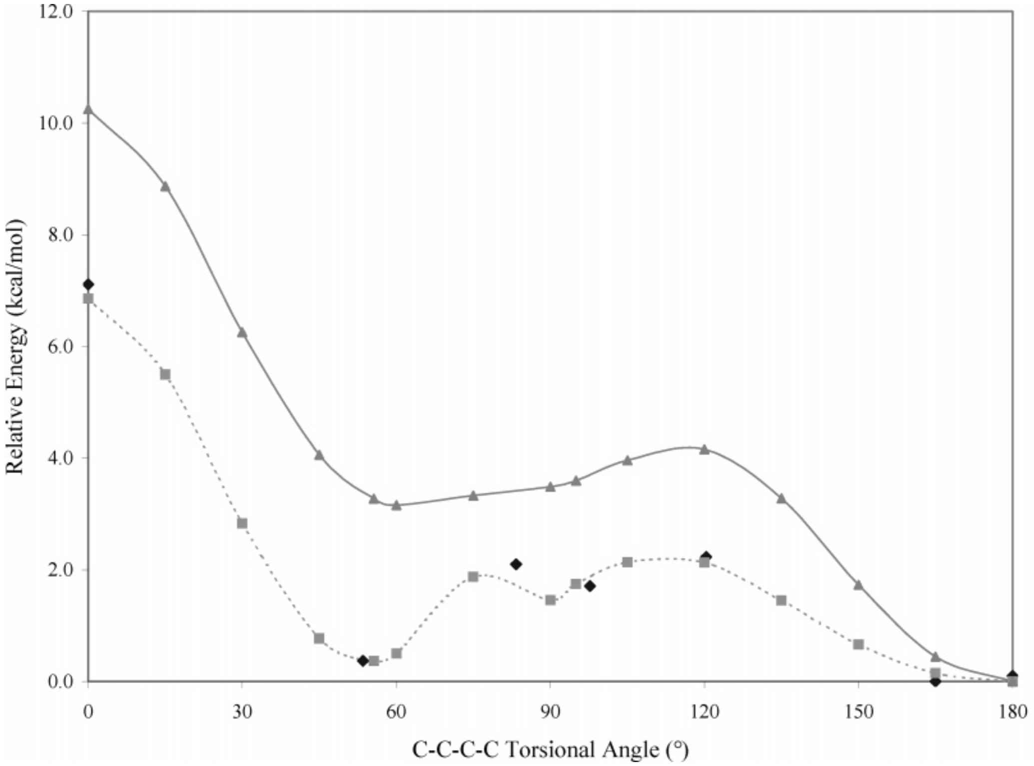


Figure 8. C−C−C−C torsion potential of perfluorobutane (MM3 and MM4 perfluoro parameters vs MP2/B).

TABLE 27: Conformational Energies for Perfluorobutane (kcal/mol)

conformation	MM3	MM4	MP2B
Ecl (0°)	10.26	6.85	7.11
gauche	3.14	0.26	0.37
ortho	3.44	1.94	1.71
120°	4.16	2.13	2.23
165° [a]	0.45	0.15	0.00
180°	0.00	0.00	0.10

[a] See footnote *b* of Table 28 and discussion.

TABLE 28: Structure of Teflon (Poly(tetrafluoroethylene) C_{18}) (Special Parameters)

	r_e	r_g	r_α
C−C	1.554	1.562	1.559
C−F	1.349	1.354	1.350
C−C−C	113.6	112.9	113.2

	exptl[a]		MM3[b]	MM4[b]
*ω*CCCC°	168.0	C10	179.5	158.6
		C12	178.6	158.6
		C18	176.8	158.6
		C24	174.8	158.6
pitch[c]	30		30	17

[a] At 25 °C. [b] C10 to C18 are *C*2 symmetry and C24 is *C*1 symmetry by MM3 and MM4. It is of interest that although the MM4 value puts the anti conformation of perfluorobutane with a 180° torsion angle about 0.1 kcal/mol more stable than one twisted to 165°, the Teflon segment (C_{10}) is calculated to be more stable at 158.6° than at 180° by 1.1 kcal/mol, or by about 0.1 kcal/mol per CF_2 group. [c] The number of CF_2 units per turn of the helix.

In Figure 8 is shown the MM4 potential for rotation about the central C−C bond in perfluorobutane. Also shown are the MP2/B calculated stationary point energies. (The MM4 geometries can be converted to the corresponding MP2/B values with the aid of vibrational corrections that are only valid at stationary points.) The agreement is satisfactory. It is noted, however, that the ortho conformation with MM4 results purely from the induced dipole interactions in the molecule. If those are omitted in the calculation, there would be no energy minimum at that point in the MM4 calculation. The MM3 curve is also shown. It is qualitatively similar to the others, but 2−3 kcal/mol higher relative to the others, which was in reasonably good agreement with the best quantum mechanical calculations available[96] at the time it was developed.

Teflon. The crystal structure of poly(tetrafluoroethylene) (Teflon) has long been known from X-ray diffraction studies.[99] This polymer has a double helix conformation with a 168.0° C−C−C−C torsional angle (at 25 °C). The X-ray structure also showed that there is a twist of 360° per 30 CF_2 groups with a repeat distance of 39.0 Å per turn.[99] A series of compounds has been studied with MM3 and MM4 ($C_{10}F_{22}$, $C_{12}F_{26}$, $C_{18}F_{36}$, and $C_{24}F_{50}$), to mimic the structure of Teflon. With MM3 studies, it was found that the central C−C−C−C torsion angle is twisted more away from 180° (see Table 28) with increasing chain length, but with MM4, the limiting torsion angle (158.6°) was already reached with the C_{10} analogue. (We will only discuss here the structure obtained with the special perfluoro parameters. The structure of teflon obtained with the regular MM4 fluorine parameters is poor, and shows the same errors as were seen earlier in perfluoropropane and perfluorobutane. That structure is given in S28 for reference, but will not be discussed.)

With perfluorobutane, the most stable conformation by all quantum mechanical calculations is anti, but twisted somewhat away from the 180° torsion angle found in simple systems. This twisted form should naturally lead to a helix in Teflon. The MM4 calculated energies in the perfluorobutane have a structure at 180° more stable (by 0.1 kcal/mol) than the twisted one. Accordingly, one wonders if MM4 then would make the prediction that the Teflon conformation would be preferentially zigzag (C_s symmetry), rather than helical (C_2). It turns out that the MM4 calculation still predicts the helical conformation to be more stable. It might be thought that the reason is that, with the isolated Teflon molecule, the helical conformation is more compact. The ends of the molecule are much closer together than in the zigzag conformation. The compact molecule would have higher van der Waals attractions, and these might outweigh the small energy required to twist the anti conformation from 180 to 167° in torsion angle. For our $C_{10}F_{22}$ model molecule, the steric energies are respectively calculated by MM4 to be 112.16 kcal/mol for the zigzag conformation and 111.04 kcal/mol for the helical. This amounts to an energy difference of 0.16 kcal/mol per CF_2 unit. However, closer examination of the model shows that the van der Waals attraction between the adjacent loops of the helix cannot stabilize the helix in a significant way. The intracoil distance is 19.5 Å, and the coil is only about 5.1 Å thick (from the van der Waals surfaces). Thus, the helix is not tightly twisted like a protein but slowly twisted. Why? The small observed twist in Teflon is quite similar to the twist in isolated molecules of polyperfluoroethylene units. Thus, the twist is already present in the single molecule, and these pack to form a double helix without much distortion in the crystal. The perfluorobutane itself is a borderline case, and the MM4 energy difference between the 180 and 167° conformations is only about 0.1 kcal/mol. However, the perfluorobutane differs from Teflon in that the "end effects" present in the former are absent in the latter. Of course, these are expected to be quite small, and they are. However, they tend to stabilize very slightly the 180° anti conformation in perfluorobutane itself, and their absence stabilizes the slightly twisted conformation in Teflon. It should be pointed out that there is an additional small complication here. When MM4 was being developed, many years ago, the induced dipoles were not originally included. When it was decided to add them a few years later, sample calculations on a variety of molecules of the sort that we normally study (up to about eight carbons, and two or three dipoles in the total molecule) showed that the total change in the induced dipole energy was usually of the order of 1 or 2 kcal/mol, and the difference in energies between different conformations of the molecule were generally changed by a few tenths of a kilocalorie per mole. Hence, it was decided that, instead of trying to include these induced dipoles in the energy optimization scheme, we would simply calculate the induced dipole energies after the rest of the computation was finished and add those energies to the total energy to obtain the conformational energies. (This corresponds to the scheme often used in quantum mechanics, where the molecular structure is optimized with a particular basis set, and the energy is then calculated at that point using a larger basis, the so-called single-point calculation.) This means that the structure which is actually optimized does not contain the induced dipole energies, which are added later. We have applied this method to many calculations over the years, with no obvious problem to this point. These perfluoro compounds, however, are something of a special case, compared with our usual studies. Here, there are many dipoles in the molecule, and the total induced dipole energies become quite large. The difference between them in different conformations is usually pretty small. However, in the case of perfluorobutane, the most stable conformation before the induced dipole energies are added has a torsion angle of 167°. After the relative induced dipole energy is added, the energy at 167° goes up so that it is now slightly higher than the energy at 180°. Hence, as in Figure 8, the energy calculated at 167° by MM4 is actually higher than the energy at 180°, although the former is the position to which the calculation optimized the geometry. This can only be viewed as a glitch in the calculation, which is beyond the accuracy (less than 0.2 kcal/mol) of the MM4 calculation. This situation leads to the apparent inconsistency in the discussion and tables, where perfluorobutane is given as having different geometries for the anti conformation.

Looking at the twist of Teflon in Table 28, one might conclude that the MM4 and experimental torsion angles do not agree very well. However, the MM4 structure is an isolated molecule, while the experimental structure is a double helix, with hexagonal packing into a crystal lattice. To twist the MM4 model from a torsion angle of 158.6 to 180° requires only 0.16 kcal/mol per CF_2 group. Thus, the energy difference between 158.6 and 168.0° would be very small, and beyond the accuracy that one tries to achieve with molecular mechanics.

Conclusions

Fluorinated alkanes have been studied with the MM4 molecular mechanics program with respect to structure, including conformations, and some physical properties, including vibrational spectra. The earlier use of a secondary electronegativity correction factor in MM3 improved the calculated C−F bond lengths over those produced by MM2 or other simple force field calculations. Further improvements were obtained with MM4 by adding the secondary electronegativity correction to bond angles. The vibrational results obtained with MM3 also indicated that further significant improvements were needed. There appear to be several reasons why the MM3 calculated frequencies were markedly poorer for fluorocarbons than for hydrocarbons. Because the masses of carbon and fluorine are similar, the C−H and C−C sretch−stretch interactions that are rather unimportant in hydrocarbons become C−F and C−C stretch interactions, and these are important here. For the same reason, couplings between C−C stretchings and hydrogen bendings that are important in hydrocarbons are less important here. Hyperconjugation and electronegativity of the fluorine lead to force constants for stretching (and probably also for bending) that are not really constants but are functions of both of these quantities. Thus, to obtain rms errors for fluorocarbon frequency calculations that are comparable in accuracy to the hydrocarbon counterparts, the inclusion of additional cross-terms proved to be essential. This also meant that additional parameters were needed. Another source of error in the calculated frequencies arises from the fact that the bending parameters are taken to be the same for what are actually different angle types in MM4. Since electronegative substituents have noticeable effects on bond lengths and stretching frequencies, lumping carbon and fluorine together and assigning them common parameters is not a very good approximation. It is, however, the way that MM4 works.

Dipole moments were reproduced marginally well by MM3, but moments of inertia, which are key quantities, were not fit very well (rms error 1.11%). This was an indication of significant remaining errors in the structures. Some of these errors come from terms omitted in the MM3 force field already discussed above (sretch−stretch, stretch−bend, and torsion−stretch interactions), and these things were added or improved in MM4. Additional errors are probably present also. The moments of inertia are well reproduced with MM4 (rms error 0.27%), indicating overall better structures than those given by MM3. The dipole moments were also improved somewhat by the inclusion of induced dipoles in the electrostatic calculations.

The MM3 force field was of only marginal accuracy for compounds containing multiple fluorines. The problem was not the parametrization but rather that an accurate treatment of these compounds requires terms in the force field that are not present in MM3. Several of the appropriate terms have been added to

MM4, and indeed, the overall results are improved relative to those from MM3.

It is important to note that in molecular mechanics the assumption is always made that parameters are transferable between structures. It is also normally assumed that these parameters are constants. It is now abundantly clear that some of the parameters are not constants but are functions of other things, such as electronegativities of substituents.

Note that the general force field described herein, which is an addition to the ordinary MM4 hydrocarbon force field, produces the results as indicated, with one special case. That is the case of perfluorocarbons which contain three carbon atoms or more. For that group, a special parameter set (given separately) is required. The difference in these parameter sets is significant, although not terribly large, and in our opinion most likely comes from the neglect of the fact that some of the parameters, especially the bending parameters, should better be treated as functions of the degree of fluorination to properly reproduce the ab initio calculations. Since that has not been done, one can imagine highly fluorinated, but not completely fluorinated, compounds for which neither of these parameter sets may be as good as one would like.

Acknowledgment. The authors are indebted to Professor J. Michl for much useful information concerning perfluorobutane in advance of publication, to Professor Richard Wong for his help on the calculation of the perfluoropropane spectrum, and to Tripos Associates and the Petroleum Research Fund of the American Chemical Society (ACS-PRF 33932-AC4) for their financial support. The authors of MM3 and MM4 are also grateful to Dr. Hedberg for a copy of her program (ASYM20) prior to publication.

Appendix

This paper cuts across several areas of structural chemistry, spectroscopy, and thermodynamics. Therefore, some definitions and an explanation of abbreviations may be helpful. We use the abbreviations ED, MW, and IR frequently, to indicate electron diffraction, microwave spectroscopy, and infrared spectroscopy, and usually in tables to indicate structures determined by those methods. The most fundamental structure would be the equilibrium structure, and bond lengths for that structure are usually written as r_e. This is the structure at the point on a potential surface where the energy is a minimum. It is the structure approximated by most quantum mechanical calculations, and it can be determined accurately by using different basis sets and degrees of electron correlation and extrapolating to complete correlation with an infinite basis set. However, real molecules cannot sit still at this structure; instead, they vibrate in the lowest vibrational level at 0 K, or in a Boltzmann distribution at higher temperatures. Depending on the experimental or calculational technique used to determine the structure, one obtains a structure peculiar to that particular method of measurement. Thus, from electron diffraction, one does not measure a bond length directly. One measures a diffraction pattern in which the vibrational averaging is already built in. From the diffraction pattern by calculation, the structure obtained is referred to as r_g, or prior to about 1970 a slightly different structure, r_a. From microwave spectroscopy, we usually obtain r_z, but sometimes, we obtain slightly different structures, r_o or r_s. From X-ray crystallography, we determined r_α, which may or may not be corrected for rigid body motion. These structures are all somewhat different, and different from the r_e structure, because there is an inherent way of averaging the vibrational motion from the different experiments or calculations. The difference in bond lengths between one kind of structure and another is usually in the range 0.002−0.005 Å but may be as large as 0.015 Å in some cases. To compare structures determined by different methods, one needs to be able to interconvert these different kinds of structures. Because the relationship between the structures and vibrational motions is known in each case, this can be done, and is routinely done in the MM4 program. The latter uses r_g as the standard quantity when no other description is given. The interconversions are somewhat tedious and will not be given here, but they are described and discussed in detail in various places, particularly in the book by Cyvin (ref 46). In the tables of the present manuscript, the headings list exactly what kind of structure was reported in the experimental paper, and the MM4 calculated values that are being compared always refer to that same kind of structure. In the figures, the MM4 plots refer to r_g structures but the quantum mechanical plots are r_e. These cannot be interconverted except at the stationary points.

Supporting Information Available: Tables showing MM4 parameters, bond lengths, molecular structures, and vibrational spectra and figures showing bond length and bond angle variation with torsion angle. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Allinger, N. L.; Yuh, Y. H.; Lii, J.-H. *J. Am. Chem. Soc.* **1989**, *111*, 8551, 8566, 8576.

(2) The MM3 program is available to all users from Tripos Associates, 1699 South Hanley Road, St. Louis, MO 63144, and to nonprofit organizations only from Norman L. Allinger, Center for Computational Chemistry, Chemistry Annex, University of Georgia, Athens, GA 30602-2526. The MM4 program is also available (UNIX version) from Tripos Incorporated. It is also available from N.L.A. to nonprofit organizations only. A Windows version will be available shortly from Wavefunction, 18401 Von Karman Avenue, Suite 370, Irvine, CA 92612. Those interested should contact the appropriate distributor.

(3) Allinger, N. L.; Chen, K.; Lii, J.-H. *J. Comput. Chem.* **1996**, *17*, 642.

(4) Nevins, N.; Chen, K.; Allinger, N. L. *J. Comput. Chem.* **1996**, *17*, 669.

(5) Nevins, N.; Allinger, N. L. *J. Comput. Chem.* **1996**, *17*, 730.

(6) Allinger, N. L.; Chen, K.; Katzenellenbogen, J. A.; Wilson, S. R.; Anstead, G. M. *J. Comput. Chem.* **1996**, *17*, 747.

(7) Allinger, N. L.; Fan, Y. *J. Comput. Chem.* **1997**, *18*, 1827.

(8) Allinger, N. L.; Durkin, K. A. *J. Comput. Chem.* **2000**, *21*, 1229.

(9) Langley, C. H.; Lii, J.-H.; Allinger, N. L. *J. Comput. Chem.* **2001**, *22*, 1396.

(10) Mastryukov, V. S.; Chen, K.-H.; Allinger, N. L. *J. Phys. Chem. A* **2001**, *105*, 8562.

(11) Chen, K.-H.; Allinger, N. L. *THEOCHEM* **2002**, *581*, 215.

(12) Langley, C. H.; Allinger, N. L. *J. Phys. Chem. A* **2002**, *106*, 5638.

(13) Lii, J.-H. *J. Phys. Chem. A* **2002**, *106*, 8667.

(14) Langley, C. H.; Allinger, N. L. *J. Phys. Chem. A* **2003**, *107*, 5208.

(15) Allinger, N. L.; Chen, K.-H.; Lii, J.-H.; Durkin, K. *J. Comput. Chem.* **2003**, *24*, 1447.

(16) Sakakibara, K.; Naka, K.; Yamaguchi, Y.; Asami, M.; Chen, K.-H.; Lii, J.-H.; Allinger, N. L. *J. Phys. Chem. A* **2004**, *108*, 3048.

(17) Langley, C. H.; Lii, J.-H.; Allinger, N. L. *J. Comput. Chem.* **2001**, *22*, 1426.

(18) Langley, C. H.; Lii, J.-H.; Allinger, N. L. *J. Comput. Chem.* **2001**, *22*, 1451.

(19) Langley, C. H.; Lii, J.-H.; Allinger, N. L. *J. Comput. Chem.* **2001**, *22*, 1476.

(20) Allinger, N. L.; Chen, K.-H.; Lii, J.-H.; Durkin, K. *J. Comput. Chem.* **2003**, *24*, 1447.

(21) Lii, J.-H.; Chen, K.-H.; Durkin, K.; Allinger, N. L. *J. Comput. Chem.* **2003**, *24*, 1473.

(22) Lii, J.-H.; Chen, K.-H.; Grindley, T. B.; Allinger, N. L. *J. Comput. Chem.* **2003**, *24*, 1490.

(23) Lii, J.-H.; Chen, K.-H.; Allinger, N. L. *J. Comput. Chem.* **2003**, *24*, 1504.

(24) Lii, J.-H.; Chen, K.-H.; Allinger, N. L. *J. Phys. Chem. A* **2004**, *108*, 3006.

(25) Lii, J.-H.; Chen, K.-H.; Johnson, G. P.; French, A.; Allinger, N. L. *Carbohydr. Res.* **2006**, *340*, 853.

(26) The MM4 program is available to all users from Tripos Associates, 1699 South Hanley Road, St. Louis, MO 63144, and to nonprofit organizations only from Norman L. Allinger, Center for Computational Chemistry, Chemistry Annex, University of Georgia, Athens, GA 30602-2526.

(27) Ma, B.; Lii, J.-H.; Schaefer, H. F.; Allinger, N. L. *J. Phys. Chem.* **1996**, *100*, 8763.

(28) Ma, B.; Lii, J.-H.; Chen, K.-H.; Allinger, N. L. *J. Am. Chem. Soc.* **1997**, *119*, 2570.

(29) Meyer, A. Y.; Allinger, N. L. *Tetrahedron* **1975**, *31*, 1971.

(30) Chen, K.-H.; Walker, G. A.; Allinger, N. L. *THEOCHEM* **1999**, *490*, 87.

(31) (a) Bohlmann, F. *Angew Chem.* **1957**, *69*, 641. (b) Bohlmann F. *Chem. Ber.* **1958**, *91*, 2157. (c) Thomas, H.; Chen, K.; Allinger, N. L. *J. Am. Chem. Soc.* **1994**, *116*, 5887.

(32) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Wong, M. W.; Foresman, J. B.; Robb, M. A.; Head-Gordon, M.; Replogle, E. S.; Gomperts, R.; Andres, J. L.; Raghavachari, K.; Binkley, J. S.; Stewart, J. J. P.; Pople, J. A. *Gaussian 94/DFT*, revision E.2; Gaussian, Inc.: Pittsburgh, PA, 1993.

(33) Pulay's method: Baker, J.; Pulay, P. *J. Comput. Chem.* **1998**, *19*, 1187.

(34) Allinger, N. L. *J. Am. Chem. Soc.* **1977**, *99*, 8127.

(35) Allinger, N. L.; Imam, M. R.; Frierson, M. R.; Yuh, Y.; Schafer, L. In *Mathematics and Computational Concepts in Chemistry*; Trinajstic, N., Ed.; E. Horwood, Ltd.: London, 1986; p 8.

(36) Crowder, G. A.; Jackson, D. *Spectrochim. Acta* **1971**, *27A*, 2505.

(37) Crowder, G. A. *J. Fluorine Chem.* **1973**, *3*, 125.

(38) Branch, G. E. K.; Calvin, M. *The Theory of Organic Chemistry*; Prentice-Hall: New York, 1941; p 217.

(39) Egawa, T.; Yamamoto, S.; Nakata, M.; Kuchitsu, K. *J. Mol. Struct.* **1987**, *156*, 213.

(40) Beagley, B.; Jones, M. O.; Yavari, P. *J. Mol. Struct.* **1981**, *71*, 203.

(41) Kakubari, H.; Iijima, T.; Kimura, M. *Bull. Chem. Soc. Jpn.* **1975**, *48*, 1984.

(42) Haas, B.; Haas, J.; Zeil, W. *Z. Naturforschg.* **1967**, *22a*, 1646.

(43) Bent, H. *Chem. Rev.* **1961**, *61*, 275.

(44) (a) King, W. C.; Gordy, W. *Phys. Rev.* **1954**, *93*, 407. (b) Lide, D. R., Jr. *J. Am. Chem. Soc.* **1952**, *74*, 3548. (c) Kawashima, Y.; Cox, A. P. *J. Mol. Struct.* **1978**, *72*, 423. (d) Takami, M. *J. Chem. Phys.* **1981**, *74*, 4276. (e) Zeil, W.; Christen, D. *J. Phys. Chem.* **1980**, *84*, 1790. (f) Solimene, N.; Dailey, B. P. *J. Chem. Phys.* **1954**, *22*, 2042. (g) Butcher, S. S. Cohen, R. A.; Rounds, T. C. *J. Chem. Phys.* **1971**, *54*, 4123. (h) Edgell, W. F.; Miller, G. B.; Amy, J. W. *J. Am. Chem. Soc.* **1957**, *79*, 2391. (i) Tipton, A. B.; Britt, C. O.; Boggs, J. E. *J. Chem. Phys.* **1967**, *46*, 1606. (j) Hayashi, M.; Fujitake, M. *J. Mol. Struct.* **1986**, *146*, 9. (k) Griffiths, J. H.; Owen, N. L.; Sheridan, J. *J. Chem. Soc., Faraday Trans. 2* **1973**, *69*, 1359. (l) Durig, J. R.; Guirgis, G. A.; Li, Y. S. *J. Chem. Phys.* **1981**, *74*, 5946. (m) Andersen, F. A.; Bak, B.; Rastrup-Andersen, J. *Acta Chem. Scand.* **1953**, *7*, 643. (n) Pierce, L.; Nelson, R. *J. Am. Chem. Soc.* **1966**, *88*, 216. (o) Pierce, L.; Beecher, J. F. *J. Am. Chem. Soc.* **1966**, *88*, 5406. (p) Damiani, D.; Ferretti, L. *Chem. Phys. Lett.* **1974**, *24*, 357.

(45) (a) Pawlowski, F.; Jorgensen, P.; Olsen, J.; Hegelund, F.; Helgaker, T.; Gauss, J.; Bak, K. L.; Stanton, J. F. *J. Chem. Phys.* **2002**, *116*, 6482. (b) Allen, W. D.; East, A. L. L.; Csaszar, A. G. In *Structures and Conformations of Non-Rigid Molecules*; Laane, J., Kakkouri, M., Van der Veken, B., Oberhammer H., Eds.; Kluwer: Dordrecht, The Netherlands, 1993; p 343.

(46) Kuchitsu, K. In *Molecular Structures and Vibrations*; Cyvin, S. J., Ed.; Elsevier: New York, 1972.

(47) Hedberg, L.; Mills, I. M. *J. Mol. Spectrosc.* **1993**, *160*, 117.

(48) Hayashi, M.; Fujtake, M. *J. Mol. Struct.* **1986**, *146*, 9.

(49) Chu, P.-S.; True, N. S. *J. Phys. Chem.* **1985**, *89*, 5613.

(50) Pierce, L.; Nelson, R. *J. Am. Chem. Soc.* **1966**, *88*, 5406.

(51) Wiberg, K. *J. Org. Chem.* **1999**, *64*, 6387.

(52) Houk, K. N.; Eksterowicz, J. E.; Wu, Y.-D.; Fuglesang, C. D.; Mitchell, D. B. *J. Am. Chem. Soc.* **1993**, *115*, 4170.

(53) Nygaard, L. *Spectrochim. Acta* **1966**, *22*, 1261.

(54) Bak, B.; Detoni, S.; Hansen-Nygaard, L.; Nielson, J.; Rastrup-Andersen, J. *Spectrochim. Acta* **1960**, *16*, 376.

(55) Schwendeman, R. H.; Jacobs, G. D. *J. Chem. Phys.* **1962**, *36*, 1245.

(56) Kraitchman, J.; Dailey, B. P. *J. Chem. Phys.* **1955**, *23*, 184.

(57) Herschbach, D. R. *J. Chem. Phys.* **1956**, *25*, 358.

(58) Lide, D. R., Jr. *J. Chem. Phys.* **1959**, *30*, 37.

(59) Durig, J. R.; Bucy, W. E.; Carreira, L. A.; Wurrey, C. J. *J. Chem. Phys.* **1974**, *60*, 1754.

(60) Sage, G.; Klemperer, W. *J. Chem. Phys.* **1963**, *39*, 371.

(61) Brier, P. N. *J. Mol. Struct.* **1970**, *6*, 23.

(62) Pace, E. L.; Aston, J. G. *J. Am. Chem. Soc.* **1948**, *70*, 566.

(63) Mann, D. E.; Plyler, E. K. *J. Chem. Phys.* **1953**, *21*, 1116.

(64) Eggers, D. F., Jr.; Lord, R. C.; Wickstrom, C. W. *J. Mol. Spectrosc.* **1976**, *59*, 63.

(65) Wolfe, S. *Acc. Chem. Res.* **1972**, *5*, 102.

(66) Radom, L.; Lathan, W. A.; Hehre, W. J.; Pople, J. A. *J. Am. Chem. Soc.* **1973**, *95*, 693.

(67) Durig, J. R.; Liu, J.; Little, T. S.; Kalasinsky, V. F. *J. Phys. Chem.* **1992**, *96*, 8224.

(68) Wiberg, K. B.; Murcko, M. A.; Laidig, K. E.; MacDougall, P. J. *J. Phys. Chem.* **1990**, *94*, 6956.

(69) Butcher, S. S.; Cohen, R. A.; Rounds, T. C. *J. Chem. Phys.* **1971**, *54*, 4123.

(70) Friesen, D.; Hedberg, K. *J. Am. Chem. Soc.* **1980**, *102*, 3987.

(71) Beagley, B.; Brown, D. E. *J. Mol. Struct.* **1979**, *54*, 175.

(72) Klaboe, P.; Nielsen, J. R. *J. Chem. Phys.* **1960**, *32*, 899.

(73) Brown, D. E.; Beagley, B. *J. Mol. Struct.* **1977**, *38*, 167.

(74) Reeves, R. E. *J. Am. Chem. Soc.* **1950**, *72*, 1499.

(75) Stoddart, J. F. *Stereochemistry of Carbohydrates*; Wiley-Interscience: New York, 1971; p 71.

(76) McClellan, A. L. *Tables of Experimental Dipole Moments*; Rahara Enterprise: E. Cerrito, CA, 1989.

(77) Fateley, W. G.; Miller, F. A. *Spectrochim. Acta* **1961**, *17*, 857.

(78) Brown, F.; Clague, A.; Heitkamp, N.; Koster, D.; Danti, A. *J. Mol. Spectrosc.* **1967**, *24*, 163.

(79) Abraham, R. J.; Kemp, R. H. *J. Chem. Soc. B* **1971**, 1240.

(80) Verdlov, L. M. S., Kovner, M. A., Krainov, E. P., Eds. *Vibrational Spectra of Polyatomic Molecules*; John Wiley and Sons: New York, Toronto, 1974; Moscow, 1970.

(81) Smith, D. C.; Saunders, R. A.; Nielsen, J. R.; Ferguson, E. E. *J. Chem. Phys.* **1952**, *20*, 847.

(82) Durig, J. R.; Craven, S. M.; Hawley, C. W.; Bragin, J. *J. Chem. Phys.* **1972**, *57*, 131.

(83) Durig, J. R.; Liu, J.; Little, T. S.; Kalasinsky, V. F. *J. Phys. Chem.* **1992**, *96*, 8224.

(84) Harris, W. C.; Holtzclaw, J. R.; Kalasinsky, V. F. *J. Chem. Phys.* **1977**, *67*, 3330.

(85) Edgell, W. F.; Riethof, T. R.; Ward, C. *J. Mol. Spectrosc.* **1963**, *11*, 92.

(86) Danti, A.; Wood, J. L. *J. Chem. Phys.* **1959**, *30*, 582.

(87) Kalasinsky, V. F.; Anjaria, H. V.; Little, T. S. *J. Phys. Chem.* **1982**, *86*, 1351.

(88) Klaboe, P.; Nielsen, J. R. *J. Chem. Phys.* **1960**, *32*, 899.

(89) Nielsen, J. R.; Claassen, H. H.; Moran, N. B. *J. Chem. Phys.* **1955**, *23*, 329.

(90) Nielsen, J. R.; Liang, C. Y.; Smith, R. M.; Smith, D. C. *J. Chem. Phys.* **1953**, *21*, 383.

(91) Schachtschneider, J. H.; Snyder, R. G. *Spectrochim. Acta* **1963**, *19*, 117.

(92) There is a small inconsistency here. We expect from our study of the change of C−H bond frequencies due to bond length changes brought about by attached electronegative groups that a similar effect is anticipated for all covalent bonds, and C−C bonds in particular. This fluoride work shows that this is indeed found, but we do not try to calculate vibrational spectra with very high accuracy. The rms error for frequencies in hydrocarbons is about 25 cm^{-1} with MM4, and thus, errors of this order are acceptable. Attaching up to two fluorines to a C−C bond generally leads to errors that are smaller than this, and therefore is not of any present concern. The effect becomes important only when three or more fluorines are attached to the same bond, although it is included for all numbers of fluorines with the equation given. In principle, this effect should also apply for any other electronegative or electropositive substituents added to the hydrocarbon framework. However, since fluorine is the most electronegative atom, presumably adding less than three of some other atom would have a smaller effect than in the case of fluorines, and thus can be ignored at the present level of approximation. In particular, the MM4 force field has already been decided upon for carbohydrates and related compounds, containing C−O bonds. This effect was not included in those structures, but since there are very few carbohydrates that have more than three oxygens attached to the same C−C bond, we do not believe that this constitutes a problem. The program automatically applies this kind of correction to any compound that contains fluorine, and hence, it will apply to compounds that contain both fluorine and oxygen attached to the same bond. This may introduce some inconsistency into the calculations, but we believe that these inconsistencies are negligible for practical purposes.

(93) Schachtschneider, J. H.; Shell Development Co. Technol. Repts., Nos. 231−264 and 57−65, 1965.

(94) Mack, H.-G.; Dakkouri, M.; Oberhammer, H. *J. Phys. Chem.* **1991**, *95*, 3136.

(95) Albinsson, B.; Michl, J. *J. Am. Chem. Soc.* **1995**, *117*, 6378.

(96) Smith, G. D.; Jaffe, R. L.; Yoon, D. Y. *Macromolecules* **1994**, *27*, 3166.

(97) Albinsson, B.; Michl, J. *J. Phys. Chem.* **1996**, *100*, 3418.

(98) Antic, D.; Michl, J. Personal communications to NLA.

(99) Sperati, C. A.; Starkweather, H. W., Jr. *Fortschr. Hochpolym.-Forsch. Bd. S* **1961**, *2*, 465.

(100) Torsional energies are a function of torsion angles (ω), and these can be expressed as a Fourier series expansion, of the form $E = \Sigma V_n/2(1 - \cos n\omega)$. In the simplest case, an infinitely repeating sinusodial curve can be represented by this expression with $n = 1$, the curve has a single minimum (at 0 or 360°) and a single maximum (at 180°). The next case would have $n = 2$, and there are two minima (0 and 180°) and two maxima (90 and 270°). Ethylene can have its torsional energy represented approximately with such a term. Ethane torsion is representing approximately a V_3 curve, with three minima and three maxima. Actually, real molecules can often be better approximated by added small higher-order terms. For ethane, a V_6 term improves the shape of the actual torsion curve as determined experimentally, for example. In the general case, all of these can be used, according to the general equation above.