imato Co–N distances are 0.043 Å long on average. The calculated pyridine Co–N distance is 0.119 Å short, consistent with a significant trans influence from the alkyl group (if a bond order of $^{1}/_{2}$ is used, the calculated pyridine Co–N distance is 0.047 Å long). The Co–C distance is only 0.023 Å long.

1,2-Bis(dimethylphosphino)ethane(neopentylidyne)(neopentylidene)(neopentyl)tungsten(VI).[47] X-ray studies have shown that the coordination environment of the W is a distorted square pyramid. The experimental distortion of the square pyramid plane away from tungsten is not accounted for in the present force field because an octahedral atom type is used for tungsten (W_6+6). Large angular errors at W result: the UFF C1–W–C3 angle is too small by 8°, the C1–W–C5 is too small by 20°. The experimental M–C single, double, and triple bond distances are well reproduced for this unique complex. This is a remarkable result considering a single covalent W radius is used in the UFF force field; the bond order correction can correctly account for the change in bond distance as a function of bond order. The W–C single bond is 0.05 Å short, the W–C double bond is 0.027 Å long, and the W–C triple bond is 0.029 Å long. The electronic effect at metal alkylidene centers whereby the M–C–C angle is enlarged as a result of a electronic donation from the α C–H bond to the metal center is not accounted for in the UFF force field, and hence the W–C_6–C_7 bond angle is 17° too small. The W–C–C angles for the W–C single and triple bonds are in error by less than 1°.

Chloromethyl[(+)-(2*S*,3*S*)-*O*-isopropylidene-2,3-dihydroxy-1,4-bis(diphenylphosphino)butane]platinum(II).[48] The structure of this complex has been analyzed crystallographically and the coordination of the platinum is essentially square planar. The two Pt–P bond distances are significantly different, consistent with trans-influence arguments. The Pt–P1 (trans to Cl) is 0.007 Å short, bond order 2. The computed Pt–P2 (trans to carbon) distance is only 0.005 Å short, bond order $1^{1}/_{2}$. The calculated Pt–C and Pt–Cl distances are only 0.04 Å short and long, respectively.

IV. Conclusions

It is possible to construct a force field from simple rules and atomic parameters that is capable of reproducing most structural features across the periodic table with errors less than 0.1 Å in bond distances and 5° to 10° in angle bend. Further applications of UFF to organic, main group, and metal compounds are described in the following papers. Enhancements to UFF to decrease structural and energetic errors are underway.

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Registry No. Octamethylcyclotetrasiloxane, 556-67-2; 1,3,5,7-tetrakis(trifluoromethyl)-2,4,6,8,9,10-hexathia-1,3,5,7-tetragermaadamantane, 108009-38-7; dodecaphenylcyclohexastannane, 1066-22-4; tris(hexamethyldisilylamide)scandium(III), 37512-28-0; (L- or D-alanine-*N*-acetato)(L-histidinato)chromium(III), 96126-28-2; bis(*N*-allylsalicylidineiminato)nickel(II), 55292-18-7; 1,2-bis(dimethylphosphino)ethane(neopentylidyne)(neopentylidene)(neopentyl)tungsten(VI), 70878-65-8.

Supplementary Material Available: Tables of reference compounds used to obtain covalent radii for main group and transition elements (8 pages). Ordering information is given on any current masthead page.

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Application of a Universal Force Field to Organic Molecules

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Abstract: The application of a Universal force field (UFF) to the treatment of organic molecules is described. The ability of the force field to predict the structures of a variety of organic molecules is examined, and the results are compared with the MM2 or MM3 force fields. UFF correctly predicts the structures of unstrained and uncongested hydrocarbons, silanes, alkenes, saturated amines, saturated ethers and phosphines, aromatic systems, and simple unconjugated multiple bond containing compounds such as nitriles, ketones, and imines well. Bond angles are usually correct to within 3°, and bond lengths usually to within 0.02 Å. Specifically, the rms error in the UFF predicted C–C bond distances is 0.021 Å, with a maximum of 0.067 Å for a set of 65 distances. For comparison, the MM2/3 RMS error in C–C distances is 0.012 Å with a maximum of 0.029 for the same set of molecules. The UFF rms error in C–N bond distances is 0.024 Å, with a maximum of 0.041 Å for a set of 13 distances. For the same set of molecules, the MM2/3 rms error in C–N distances is 0.013 Å with a maximum of 0.031. The UFF rms error in C–O bond distances is 0.025 Å, with a maximum of 0.05 Å for a set of seven distances. For the same set of molecules the MM2/3 rms error in C–O distances is 0.007 Å with a maximum of 0.015. The ability of UFF to calculate conformational energy differences in simple organic molecules is also examined.

I. Introduction

Over the last two decades, molecular mechanics has developed into a powerful and standard method for studying the molecular structure and related properties of organic molecules. The MM2,[1] MMP2,[2] MM3[3] force fields, developed by Allinger and his group, are the premier force fields for the prediction of organic structures and energies; the molecular mechanics results are usually of experimental accuracy. However, as pointed out in the first paper of this series,[4] standard force fields such as MM2 are limited to

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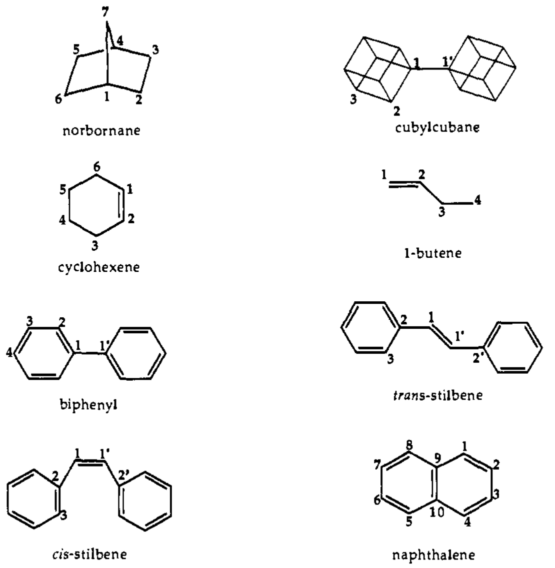

Figure 1. Structural formulas and numbering of atoms for a set of hydrocarbons.

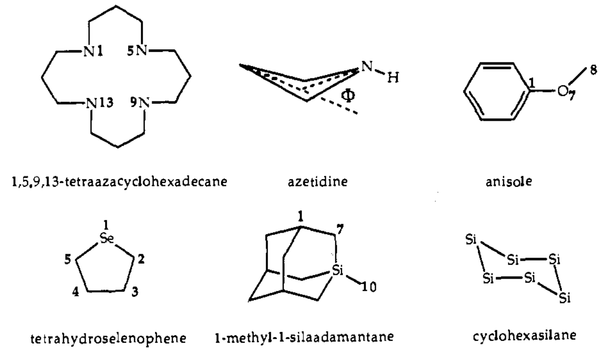

Figure 2. Structural formulas and numbering of atoms for a set of organic molecules.

particular combinations of atoms, in this case to organics, owing to the large number of parameters needed to define a particular atomic association (atom type). In order to facilitate studies of a variety of atomic associations, we have developed a new force field using general rules for estimating force field parameters based on simple relations from the literature. We refer to this new force field as a Universal force field (UFF). The force field is described in detail in the first paper of this series.[4]

In this paper we apply UFF to predict the geometries of a variety of organic molecules. The results are compared with the experimental structures and the published results of the Allinger force fields. The ability of UFF to calculate experimental conformational energy differences in simple organic molecules is also investigated and compared with published MM2 results.

II. Calculations

Minimizations were carried out on a IRIS 4D20 using a Newton–Raphson minimization scheme with a norm of the gradient convergence criteria of 1×10^{-10} (kcal/mol)/Å and were verified as minima by the absence of negative eigenvalues in the force constant matrix. Saddle points were obtained using a hill-climbing algorithm and were verified by the presence of a single negative eigenvalue in the force constant matrix. The structures of 1,5,9,13-tetraazacyclohexadecane and 1,10-cyclooctadecanedione were minimized starting with the X-ray structure coordinates obtained from the Cambridge data base.

III. Structural Results

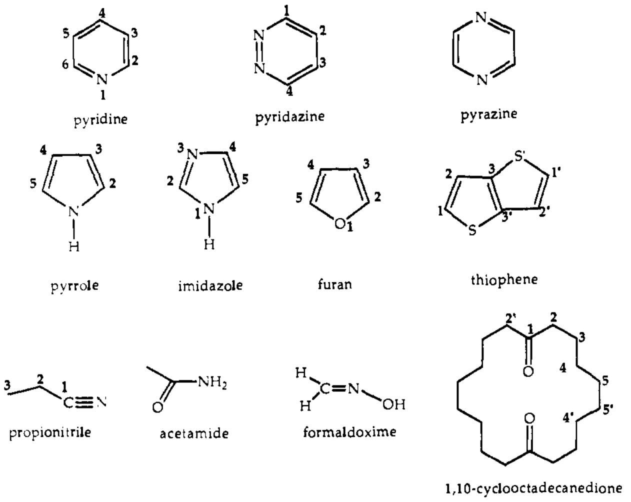

Figure 3. Structural formulas and numbering of atoms for a set of aromatic molecules.

The ability of UFF to correctly reproduce experimental geometries of a variety of organic molecules was investigated. The structural formulas and the numbering of atoms are given in Figures 1 through 3. Selected structural parameters calculated with UFF, along with the experimental values, are listed in Tables I through III. In addition, the structural predictions by the most recent of the published Allinger force fields are presented.

Prior to a discussion of the structural results we must define what we mean by acceptable error. Clearly, exact reproduction of experimental results would be desirable, but this is not feasible owing to both uncertainties in the experimental measurements (discussed below) and errors inherent in any theoretical model. Comparison with alternative theoretical methodologies and definitions of acceptability from the literature will be used to define the terms: good, fair, and poor. For small organic molecules (H_mABH_n) average absolute errors have been reported[5a] for an ab initio Hartree–Fock wave function with the 6-31G* basis of 0.030 Å for AB single bonds, 0.018 Å for AB multiple bonds, 0.014 Å for AH bonds, and 1.5° for bond angles (smaller basis sets gave correspondingly larger errors and inclusion of electron correlation decreased the error). Average absolute errors in distance of 0.054 Å, 0.050 Å, and 0.036 Å have been reported[5b] for MNDO, AM1, and PM3, respectively, for the atomic associations that have been parameterized. Bond angle errors of 4.3°, 3.3°, and 3.9° have also been reported for MNDO, AM1, and PM3, respectively. Reported dihedral angle absolute average errors are 21.6°, 12.5°, and 14.9° for MNDO, AM1, and PM3, respectively. Based on these numerical results[6] we will describe (for organic molecules) bond distance errors of less than 0.02 Å and bond angle errors of less than 2° as being in "good agreement with experiment" and bond distance errors of less than 0.04 Å and bond angle errors of less than 5° as being in "fair agreement with experiment"; structures with larger errors will be considered to be in "poor agreement with experiment".

There are three generally available experimental techniques for determining accurate molecular structure: X-ray diffraction, electron diffraction, and microwave spectroscopy. X-ray diffraction is carried out on crystalline samples of a material and has a well-defined estimation of error. The effect of crystal packing forces on the three-dimensional structure of a molecule is always an issue for structures derived from X-ray diffraction.[7] Further, since X-rays are scattered by electron densities, X-ray diffraction determines the position of electron densities rather than nuclei. For elements other than hydrogen or helium this is not an issue, but X–H bond distances obtained by X-ray diffraction are problematic.[8]

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Table I. Calculated and Experimental Structures of Saturated and Unsaturated Hydrocarbons

compound	bond or angle	exp	Universal	MM3
isobutane	C–C	1.535^{a}	1.532	1.538^{b}
	C(central)–H	1.122	1.112	1.118
	C–C–C	110.8	110.6	110.4
cyclohexane	C–C	1.536^{c}	1.534	1.536^{b}
	C–H	1.121	1.113	1.115
	C–C–C	111.4	110.5	111.3
	H–C–H	107.5 ± 1.5	107.7	106.7
	C–C–C–C	54.9 ± 0.4	57.3	55.3
hexamethylethane	C–C(central)	1.582^{d}	1.606	1.577^{b}
	C–Me	1.542	1.552	1.548
	Me–C–C	110.0	111.8	111.7
	Me–C–C–Me	65 ± 4	72.7	66.6
norbornane	C1–C2	1.536^{e}	1.539	1.548^{f}
	C1–C7	1.544	1.511	1.540
	C2–C3	1.573	1.538	1.557
	C1–C2–C3	102.7	102.7	103.3
	C2–C1–C6	109.0	108.6	107.9
	C2–C1–C7	102.0	101.8	101.3
	C1–C7–C4	93.4	94.4	95.0
	C6–C1–C2–C3	71.6	71.6	71.0
	C2–C1–C7–C4	56.3	56.1	55.5
	C7–C1–C2–C3	35.8	35.3	34.9
	C1–C2–C3–C4	0.0	0.0	0.0
cubylcubane	C1–C1′	1.458^{g}	1.518	1.486^{g,h}
	C1–C2	1.568	1.535	1.550
	C2–C3	1.553	1.545	1.558
cyclohexene	C1–C2	1.335^{i}	1.344	1.342^{j}
	C2–C3	1.504	1.509	1.508
	C3–C4	1.515	1.534	1.537
	C4–C5	1.550	1.529	1.533
	C1–C2–C3	123.5	122.9	123.3
	C3–C2–C1–C6	0.0	1.8	0.8
	C3–C4–C5–C6	60.2	60.8	62.8
skew-1-butene	C1–C2	1.340^{k}	1.336	1.339^{j}
	C3–C2	1.502	1.504	1.506
	C3–C4	1.535	1.524	1.534
	C4–H	1.114	1.111	1.113
	C2–H	1.104	1.086	1.104
	C1–C2–C3	125.6	122.0	124.4
	C2–C3–C4	111.7	110.5	111.9
	C1–C2–C3–C4	119.9	118.5	114.5
2,3-dimethyl-2-butene	C=C	1.353^{l}	1.364	1.353^{j}
	C–C	1.511	1.514	1.513
	C–H	1.118	1.110	1.113
	C–C=C	123.9	120.9	123.8
	C–C=C–C	0.0	0.0	
biphenyl	C1–C1′	1.507^{m}	1.485	1.484^{n,o}
	C1–C2	1.404	1.407	1.403
	C2–C3	1.395	1.399	1.396
	C3–C4	1.396	1.397	1.396
	C–H	1.102	1.083	
	C2–C1–C6	119.4	118.9	
	C2–C1–C1′–C2′	44.4 ± 1.2	42.7	36.7
trans-stilbene	C1–C1′	1.329^{p}	1.343	1.355^{n,o}
	C1–C2	1.481	1.483	1.473
	C–H	1.095	1.082	
	C2–C1–C1′	127.7	123.4	
	C1′–C1–C2–C3	32.5	25.0	0.2
cis-stilbene	C1–C1′	1.334^{q}	1.343	1.351^{n,o}
	C1–C2	1.489	1.480	1.476
	C–H	1.095	1.083	
	C2–C1–C1′	129.5	125.4	126.6
	C1′–C1–C2–C3	33.2	43.4	33.8
naphthalene	C1–C2	1.381^{r}	1.398	1.375^{s}
	C2–C3	1.417	1.398	1.421
	C1–C9	1.422	1.404	1.428
	C9–C10	1.412	1.417	1.408
	C–H	1.092	1.084	
	C10–C9–C1	119.5	119.6	

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Electron diffraction measures the average distances between nuclear positions in the gas phase; as such, electron diffraction is quite subject to vibrational effects such as shrinkage from bond angle bending and bond elongation due to anharmonicity in the bond stretch.[9] The bond distances directly obtained from the electron diffraction experiment are r_a's when vibrationally corrected r_g's result. The distances between the mean positions of the atoms are derived from additional vibrational corrections and the resulting distances are r_α's. These distances with the corresponding error estimates are the distances that should be compared with isolated molecule theoretical studies; they are unfortunately not generally available for the molecules of interest.

Microwave spectroscopy directly determines molecular moments of inertia from which (for simple molecules) r_0 distances are derived.[9] When a detailed isotopic substitution study is carried out, substitution distances (r_s's) result. When a vibrational correction is applied to a microwave study, r_z distances are obtained with which isolated molecule theoretical studies can be compared. The structures discussed below come from a variety of sources, and when appropriate the experimental technique used will be described.

1. Saturated Hydrocarbons. Geometric results for several saturated hydrocarbons are collected in Table I. UFF correctly predicts the structures of unstrained hydrocarbons but is in only on fair agreement with experiment for strained systems (errors as large as 0.033 Å). The central C–C bond length in highly substituted ethanes is overestimated, and the bond distances in angle strained molecules are underestimated by UFF.

Isobutane.[10] The UFF geometry for this molecule is in very good agreement with the experimental structure obtained with a combination of electron diffraction and microwave spectroscopy.

Cyclohexane.[11] The calculated and gas electron diffraction values of this molecule are in very good agreement. The calculated geometry has C–C 1.534 Å, C–C–C 110.5°, C–H 1.113 Å, with H–C–H 107.7° and a dihedral angle of 57.3°. The corresponding experimental values are 1.536, 111.4, 1.121, 107.5, and 54.9.

Hexamethylethane.[12] UFF predicts substantial elongation of the central carbon–carbon bond distance for this congested[13]

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Table II. Calculated and Experimental Structures of Simple Heteroatom Containing Molecules

compound	bond or angle	exp	Universal	MM2
1,5,9,13-tetraazacyclohexadecane	N–C (av)	1.457[a]	1.470	1.462[b]
	C–C (av)	1.511	1.537	1.540
	N1···N5	2.92	3.24	2.96
	N1···N9	4.14	4.50	4.18
	C–C–C(av)	116.0	113.5	115.5
	C–C–N(av)	112.4	111.8	113.2
azetidine	C–N	1.482[c]	1.463	1.471[b]
	C–C	1.553	1.514	1.549
	C–H	1.107	1.112	1.116
	N–H	1.022	1.048	1.014
	C–C–C	86.9	84.9	86.6
	C–C–N	85.8	93.2	86.4
	Φ	33.1 ± 2.4	0.1	36.2
methyl ethyl ether	C–O(Me)	1.415[d]	1.411	1.414[e]
	C–O(Et)	1.404	1.415	1.419
	C–C	1.520	1.525	
	C–C–O	108.2	110.3	108.6
	C–O–C	111.8	110.4	112.5
anisole	C8–O7	1.423 ± 0.015[f]	1.427	1.419[g]
	C1–O7	1.361 ± 0.015	1.411	1.372
	C1–O7–C8	120.0 ± 2.0	118.3	118.4
trimethylphosphine	P–C	1.846[h]	1.867	1.854[i]
	C–P–C	98.6	96.0	99.0
	P–C–H	110.7	110.0	110.3
triphenylphosphine	P–C(av)	1.828[j]	1.857	1.828[i]
	C–P–C(av)	103.0	99.1	101.4
	P–C–C(int)	124.0	122.4	124.0
	P–C–C(ext)	116.1	118.3	117.3
tetrahydroselenophene	Se–C2	1.975[k]	1.945	1.971[l]
	C2–C3	1.537	1.521	1.537
	C2–Se–C5	89.1	89.0	89.3
	C3–C2–Se	105.8	108.1	106.6
	C2–C3–C4	106.0	108.1	107.2
	Se–C2–C3–C4	42.7 ± 1.4	36.1	
	C2–C3–C4–C5	56.9 ± 1.7	47.4	
	C3–C2–Se–C5	15.4	13.0	
eq-chlorocyclohexane	C–Cl	1.793[m]	1.785	
	C–C–C	111.2	111.0	
2-bromopropane	C–Br	1.957[n]	1.941	
	C–C	1.508	1.527	
	C–C–Br	110.0	109.7	
	C–C–C	114.2	111.1	
tert-butyl fluoride	C–F	1.425[o]	1.385	1.393[p,q]
	C–C	1.520	1.533	1.533
	C–C–F	107.9	108.6	
	C–C–C	111.0	110.3	
tert-butyl chloride	C–Cl	1.827[r]	1.789	1.80[p,q]
	C–C	1.525	1.535	1.538
	C–C–Cl	107.3	108.8	
	C–C–C	111.6	110.2	
cis-1,2-dichloroethylene	C–Cl	1.718[s]	1.760	1.722[t]
	C–C	1.354	1.337	
	C–H	1.075	1.085	
	C–C–Cl	123.8	122.3	124.9
	C–C–H	132 ± 3	119.4	
	Cl–C–C–Cl		0.0	
cis-1,2-dibromoethylene	C–Br	1.871[u]	1.917	1.885[t]
	C–C	1.360	1.337	
	H–C	1.10	1.085	
	C–C–Br	124.1	122.9	126.4
	Br–C–C–Br		0.0	
1,4-dichlorobenzene	C–Cl	1.69[v]	1.754	1.725[t]
1,4-dibromobenzene	C–Br	1.88[w]	1.910	1.890[t]
1-fluoro-3-chlorobenzene	C–F	1.329[x]	1.356	1.323[t]
	C–Cl	1.699	1.754	1.726
triethylsilane	Si–C	1.886[y]	1.878	1.889[z]
	C–C	1.547	1.523	1.548
	C–Si–C	108.7	110.2	108.7
	Si–C–C	114.2	111.4	114.3
1-methyl-1-silaadamantane	Si–C (av)	1.879[aa]	1.863	1.879[z]
	C–C (av)	1.548	1.548	1.548
	C10–Si–C7	115.2	115.4	115.0
	Si–C7–C1	107.4	108.0	107.0
vinylsilane	Si–C	1.853[bb]	1.847	1.868[z]
	C–C	1.347	1.333	1.339
	Si–H	1.475	1.470	1.489
	Si–C–C	122.9	121.1	123.0
	H–Si–H	108.7	109.5	108.9

Table II (Continued)

compound	bond or angle	exp	Universal	MM2
hexamethyldisilane	Si–Si	2.340[cc]	2.229	2.344[z]
	C–Si	1.877	1.866	1.880
	C–Si–C	110.5	109.6	109.9
	Si–Si–C	108.4	109.3	109.0
	H–C–H	110.3	109.5	110.5
cyclohexasilane	Si–Si	2.342[dd]	2.232	2.334[z]
	Si–H	1.484	1.470	1.489
	Si–Si–Si	110.3	109.1	109.1
	Si–Si–Si–Si	57.8 ± 0.9	60.8	60.8
trimethylgermane	Ge–H	1.532[ee]	1.550	1.530[ff]
	Ge–C	1.947	1.944	1.949
	C–Ge–C		109.4	109.6
methylstannane	Sn–H	1.708[gg]	1.751	1.696[ff]
	Sn–C	2.140	2.144	2.148
	H–Sn–C	109.4	109.4	110.0
	H–C–Sn	110.4	109.4	110.9

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molecule. The calculated distance is 1.606 Å, 0.024 Å longer than the gas-phase electron diffraction value of 1.582 Å. UFF also predicts a distortion of the geometry from normal 60° torsion angles, giving a twist about the central bond of 13°. The corresponding experimental twist is 5 ± 4°.

Norbornane.[14] The electron diffraction bond angles and dihedrals are very well reproduced by the Universal force field, but the bridgehead bond distances (C1–C7) and the C2–C3 bond distances are not. The compressed bridgehead bond angle (93.4°) is experimentally accompanied by bond stretching; UFF underestimates the bridgehead distance by 0.033 Å. Allinger[15] has reproduced this effect by including a stretch–bend cross term in the MM2 and MM3 force fields. The calculated C2–C3 distance is underestimated by about 0.03 Å. Allinger and others have been able to correctly reproduce the stretching of an eclipsing bond by including a torsion–stretch interaction term.[3]

Cubylcubane.[17] The X-ray structure of this molecule shows a very short cage–cage bond length of 1.458 Å. UFF predicts a much longer bond distance of 1.518 Å, overestimating the steric repulsion between the cubanes, much in the same way UFF overestimated the central C–C bond length in hexamethylethane. The especially short experimental cage–cage bond of cubylcubane is thought to be a result of enriched s character in the exocyclic orbitals, due to increased p character in the highly angle strained endocyclic orbitals.[18] Without special parameters to mimic this electronic effect, the force field describes this molecule only fairly well. Not surprisingly, the UFF cubane edge bond length is too short by 0.033 Å, a consequence of an inadequate description of the strained endocyclic p enriched bonds by a Universal force field. The MM2 force field can partially reproduce the long cubane bond lengths by employing a stretch–bend cross term and specific parameters for four-membered rings.

2. Unsaturated and Aromatic Hydrocarbons. Geometric results for unsaturated and aromatic hydrocarbons are also collected in Table I. UFF reproduces the structures of alkenes and aromatic systems well. Bond angles are correct to within 3°, and bond lengths to within 0.02 Å. Because UFF uses only a single resonating carbon atom type, modified only by a predetermined simple bond order rather than by bond order derived from a SCF π calculation, the bond distance error by UFF here can be ascribed to an inadequate description of π delocalization.

Cyclohexane.[19] The calculated and gas electron diffraction structure of cyclohexene are in good agreement.

***skew*-1-Betane.**[20] The calculated C–C distances for this alkene are in good agreement with the experimental distances obtained by molecular orbital constrained electron diffraction. The calculated C1–C2–C3 bond angle is underestimated by about 3°.

2,3-Dimethyl-2-butene.[21] The experimental gas electron diffraction C–C distances for this tetrasubstituted ethylene are well reproduced by UFF. As observed with 1-butene, the calculated C1–C2–C3 bond angle is underestimated by about 3°.

Biphenyl.[22] The gas-phase structure of this molecule had been determined by electron diffraction. It is nonplanar with a torsional angle about the central bond of 44.4 ± 1.2°. The UFF calculated value is 41.7°. The bond distances of the ring carbons are in good agreement with the experimental electron diffraction distances;

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Table III. Calculated and Experimental Structures of Multiply Bonded Heteroatom Containing Molecules

compound	bond or angle	exp	Universal	MM2
pyridine	C2–N	1.338[a]	1.361	1.340[b]
	C2–C3	1.394	1.398	1.398
	C3–C4	1.392	1.397	1.397
	C2–H	1.086	1.082	1.103
	C2–C3–C4	118.5	119.3	118.5
	C3–C4–C5	118.4	119.8	118.3
	C2–N–C6	116.9	121.6	117.3
	C3–C2–N	123.8	120.0	123.8
pyridazine	N–N	1.332[c]	1.336	1.340[b]
	C1–N	1.341	1.360	1.310
	C1–C2	1.393	1.394	1.415
	C2–C3	1.375	1.393	1.374
	C–H	1.064 ± 0.016	1.083	
	C–C–C	117.0	119.1	116.2
	N–C–C	123.7	119.6	124.5
	C–N–N	119.3	121.3	119.3
pyrazine	N–C	1.339[d]	1.359	1.335[b]
	C–C	1.393	1.397	1.402
	C–N–C	116.3	121.1	115.5
	N–C–C	121.8	119.4	122.2
pyrrole	C2–N	1.370[e]	1.345	1.371[b]
	C2–C3	1.382	1.380	1.382
	C3–C4	1.417	1.381	1.409
	C–H (av)	1.077	1.082	1.102
	N–H	0.996	1.044	1.046
	C–N–C	109.8	107.1	109.6
	N–C–C	107.7	110.0	107.7
	C–C–C	107.4	106.5	107.5
imidazole	N1–C5	1.381[f]	1.341	1.379[b]
	N1–C2	1.358	1.345	1.353
	C4–C5	1.378	1.376	1.377
	C4–N3	1.389	1.348	1.359
	N3–C2	1.333	1.349	1.328
	N1–H	1.053	1.044	1.044
	C–H (av)	1.087	1.082	1.102
	C5–N1–C2	107.2	105.4	106.9
	N1–C5–C4	106.0	108.2	105.0
	N3–C4–C5	109.8	109.5	111.0
	C2–N3–C4	105.3	104.2	104.9
furan	C2–O	1.362[g]	1.321	1.360[h]
	C2–C3	1.361	1.375	1.364
	C3–C4	1.430	1.363	1.428
	C–H (av)	1.076	1.082	1.102
	C2–O–C5	106.6	104.6	106.3
	H–C2–O	116.0	123.3	117.5
	O–C2–C3	110.6	112.4	111.0
	C2–C3–C4	106.1	105.3	105.9
thiophthene	S–C1	1.72[i]	1.729	1.733[h]
	S–C3′	1.74	1.701	1.722
	C1–C2	1.36	1.388	1.370
	C2–C3	1.41	1.365	1.425
	C3–C3′	1.36	1.342	1.382
	S–C1–C2	116.5	114.9	113.1
	S–C3′–C3	110.2	115.9	111.4
	S–C3′–C2′	135.5	131.1	135.1
	C1–C2–C3	111.7	109.5	110.9
	C1–S–C3′	91.2	86.7	91.1
1,10-cyclooctadecanedione	C1–O	1.211[j]	1.223	1.211[j]
	C1–C2	1.512	1.510	1.522
	C2–C3	1.523	1.538	1.539
	C3–C4	1.520	1.538	1.539
	C4–C5	1.512	1.538	1.537
	C5–C5′	1.529	1.538	1.540
	C1–C2–C3	113.4	113.2	114.2
	C2′–C1–C2	117.0	120.0	117.1
	C2–C3–C4	111.5	112.3	112.0
	C3–C4–C5	113.3	111.0	112.4
	C4–C5–C5′	113.3	113.0	113.6
	O–C1–C2	121.5	119.9	121.5
	O···O	6.65	7.38	6.27
	C1–C2–C3–C4	74.2	69.2	67.2
	C2–C3–C4–C5	179.5	172.7	177.3
	C3–C4–C5–C5′	176.7	172.0	176.1
	C4–C5–C5′–C4′	65.6	67.1	64.2
	C3–C2–C1–C2′	159.1	149.1	161.3
	O–C1–C2–C3	21.6	35.0	18.5

Table III (Continued)

compound	bond or angle	exp	Universal	MM2
methylenimine	C-N	1.273[k]	1.283	1.271[b]
	N-H	1.021	1.031	1.023
	C-H (av)	1.09	1.086	1.102
	H-C-N (cis)	125.1	121.0	121.7
	H-C-N (trans)	117.9	119.7	120.4
	C-N-H	110.4	112.6	110.9
	H-C-H	117.0	119.3	117.9
propionitrile	C1-N	1.159[l]	1.157	1.158[m]
	C1-C2	1.459	1.467	1.473
	C2-C3	1.537	1.523	1.532
	C2-H	1.094	1.110	1.115
	C1-C2-C3	112.0	110.5	110.8
	C2-C1-N	178.7	180.0	
	H-C2-H	107.2	108.9	108.3
acetamide	C-C	1.519[n]	1.497	1.520[o,t]
	C-O	1.220	1.219	1.219
	C-N	1.380	1.364	1.377
	C-H (av)	1.124	1.110	
	N-H (av)	1.022	1.045	1.028
	N-C-O	122.0	119.8	122.8
	O-C-C	123.0	119.4	121.9
	N-C-C	115.1 ± 1.6	120.9	115.3
formaldoxime	C-N	1.276[p]	1.285	1.276[q]
	N-O	1.408	1.341	1.408
	C-H (trans)	1.086	1.084	1.085
	C-H (cis)	1.085	1.088	1.086
	O-H	0.956	0.991	0.956
	N-C-H (trans)	115.6	119.6	116.0
	N-C-H (cis)	121.8	121.7	121.2
	C-N-O	110.2	112.5	110.2
	N-O-H	102.7	104.6	102.7
nitromethane	C-N	1.489[r]	1.455	1.502[s,t]
	N-O	1.224	1.300	1.224
	N-C-H (av)	107.2	110.0	110.5
	C-N-O	117.3	120.2	116.5
	O-N-O	125.3	119.7	127.1

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the calculated phenyl–phenyl (C1–C1′) distance is only in fair agreement with experiment; it is underestimated by 0.022 Å.

***trans*-Stilbene.**[23] The gas-phase structure of *trans*-stilbene has been determined by the electron diffraction method and found to be nonplanar. The phenyl groups were found to be rotated 32° about the C-Ph bonds. The calculations show a Ph—C═C—Ph dihedral angle of 25.0°. The remainder of the calculated bond distances and angles are in good agreement with the experimental structure.

***cis*-Stilbene.**[24] The gas-phase *cis*-stilbene molecule is shown experimentally to have C_2 symmetry having a propeller-like conformation with the phenyl groups rotated 43.2° about the C–Ph bonds. The experimental Ph—C═C—Ph dihedral angle and the rest of the structure are accurately reproduced by the UFF force field.

Naphthalene.[25] The calculated geometry for this molecule is in good agreement with the electron diffraction structure, although UFF overestimates the extent of π delocalization. The calculated structure shows a smaller alternation of C–C bond lengths than the experimental structure; the calculated 2–3 and 1–9 bond lengths are too short by a little less than 0.02 Å, and the calculated 1–2 bond length is too long by 0.017 Å.

3. Amines, Ethers, Phosphines, and Selenides. Geometric results for amines, ethers, phosphines, and selenides are collected in Table II. UFF appears to predict the structures of unstrained saturated amines, ethers, and phosphines reasonably well (angles within 2° and bond lengths to within 0.02 Å). This force field, which has no special ring parameters, predicts the structures of four- and five-membered ring saturated heterocycles, and aromatic ethers poorly, with errors in distance of up to 0.05 Å.

1,5,9,13-Tetraazacyclohexadecane.[26] The X-ray structure of this cyclic tetramine shows a highly symmetric structure with nearly D_{2d} symmetry apart from the N–H bonds. The calculated geometry for this molecule is in fair agreement with the experimental structure; UFF overestimates the C–C bond lengths by about 0.026 Å and underestimates the C–C–C angles by 2.5°. The correlation between the experimental and calculated transannular nitrogen–nitrogen distances is very good.

Azetidine.[27] The electron diffraction structure of this four-membered ring shows it is puckered. UFF, which has no special ring parameters, instead predicts a flat structure. The bond angles and bond distances of this strained molecular are also only fairly

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well described by UFF. The calculated C–N distance is too short by 0.019 Å, and the C–C too short by 0.039 Å.

Methyl Ethyl Ether.[28] The calculated geometry for this molecule is in very good agreement with the experimental microwave structure.

Anisole.[29] The gas electron diffraction structure for this aromatic ether is incorrectly predicted by UFF. Although the calculated C–OMe (C8–O7) distance is well reproduced, the calculated C–OAr (C1–O7) distance is overestimated by 0.05 Å.

Trimethylphosphine.[30] The UFF predicted geometry for this phosphine is in good agreement with the gas electron diffraction structure.

Triphenylphosphine.[31] The X-ray structure of this molecule has been determined, and, owing to the unequal rotation of the benzene rings, the molecule has no symmetry. The calculated geometry for this molecule is in fair agreement with the experimental values: the calculated averaged P–C distance is overestimated by 0.03 Å, and the average C–P–C angle is too small by almost 4°.

Tetrahydroselenophene.[32] The UFF geometry for this cyclic selenide is only in fair agreement with the gas electron diffraction structure. The Se–C distance is underestimated by 0.03 Å, and the C–C distance is underestimated by about 0.016 Å. The bond angle at Se is predicted well by a Universal force field, but the other ring angles are too large by about 2°. The UFF calculated dihedral angles are all smaller than the experimental values; UFF predicts the structure of this five-membered ring to be less puckered than the experimental geometry.

4. Halides. Geometric results for saturated and unsaturated halides are collected in Table II. UFF predicts the structures of secondary halides reasonably well but is only fair at reproducing the C–X bond lengths of tertiary halides. UFF underestimates the C–X bond lengths in *tert*-butyl halides by about 0.04 Å. The C–C bond lengths are underestimated by 0.01 to 0.02 Å for both secondary and tertiary halides.

UFF cannot reproduce the carbon–halide bond lengths in vinyl and aromatic halides. Overestimations are as large as 0.1 Å. The halide bond distance parameter in UFF as derived from saturated halides is obviously inadequate to describe unsaturated halides. This failure is not unexpected: because of conjugation between the halide and π electrons of the phenyl ring or alkenyl group, X_R atom types, rather than X atom types, are required to describe the structures of unsaturated halides correctly. The C–C distances are predicted reasonably well by a Universal force field.

***eq*-Chlorocyclohexane.**[33] The calculated geometry for this halide is in good agreement with the microwave structure.

2-Bromopropane.[34] The UFF geometry for this halide is in good agreement with the microwave structure.

***tert*-Butyl Fluoride.**[35] The computed geometry for this halide is in fair agreement with the gas-phase electron diffraction structure. The C–F distance is too small by 0.04 Å.

***tert*-Butyl Chloride.**[36] The UFF geometry for this halide is in fair agreement with the combined gas-phase electron diffraction and microwave structure. The C–Cl distance is too small by 0.038 Å.

***cis*-1,2-Dichloroethylene.**[37] The calculated geometry for this halide is in poor agreement with the gas-phase electron diffraction structure. The calculated C–Cl distance is overestimated by 0.042 Å, and the C–C distance is underestimated by 0.017 Å. The calculated C–C–Cl angle is in good agreement with the experimental value and the calculated C–C–H angle is in error by 10°!

***cis*-1,2-Dibromoethylene.**[38] The calculated C–Br distance is overestimated by 0.10 Å, and the calculated C–C distance is underestimated by 0.023 Å. The C–C–Br angle is in good agreement with the experimental gas electron diffraction value.

1,4-Dichlorobenzene.[39] The UFF predicted C–Cl distance is too long by 0.06 Å compared with the corresponding experimental gas electron diffraction value.

1,4-Dibromobenzene.[40] The UFF geometry for this halide is in fair agreement with the gas-phase electron diffraction structure. The calculated C–Br distance is overestimated by 0.03 Å.

1-Fluoro-3-chlorobenzene.[41] The calculated C–F distance is overestimated by 0.027 Å, the C–Cl distance overestimated by 0.055 Å.

5. Silicon, Germanium, and Tin Compounds. Geometric results for silicon compounds are collected in Table II. UFF correctly predicts the structures of unstrained silanes but does not correctly predict the Si–Si bond distances of hexamethyldisilane and cyclohexasilane. The UFF computed distances in these molecules are underestimated by 0.1 Å. It appears that it is not possible to use the simple covalent bond additivity scheme of a Universal force field to correctly predict *both* Si–Si and Si–C bond lengths within 0.1 Å. Beagley and co-workers[45] noted that using a simple additivity of covalent Si (from disilanes) and C (from ethane) radii leads one to predict an Si–C bond length 0.060 Å too long. (The UFF Si3 covalent radius is derived instead from methylsilane, and thus the predicted Si–C distances are correct but the Si–Si distances are too short.) According to these workers, the experimental Si–C bond is shorter than expected by using covalent bond additivity considerations because of partial double bond character due to a C–Si $p\pi$–$d\pi$ interaction.

Triethylsilane.[42] The experimental geometry of this molecule is well reproduced by a Universal force field. The calculated C–C distance is too small by 0.024 Å, and the skeletal angles are in error by 1–2°.

1-Methyl-1-silaadmantane.[43] The calculated geometry of this moelcule is good agreement with the gas electron diffraction structure. The largest error is in the Si–C bond length, which is underestimated by 0.016 Å.

Vinylsilane.[44] The experimental structure of this molecule has been determined by microwave spectroscopy, and the geometry is well reproduced by UFF.

Hexamethyldisilane.[45] The UFF geometry for this crowded disilane is in poor agreement with the gas electron diffraction structure. The calculated Si–Si bond distance is underestimated by more than 0.1 Å. The calculated angles and the C–Si bond distance for this molecule are in good agreement with the experimental structure.

Cyclohexasilane.[46] The gas electron diffraction geometry of this silicon analogue of cyclohexane is poorly reproduced by a Universal force field. As observed above in hexamethyldisilane, the Si–Si bond distance is underestimated by more than 0.1 Å. The skeletal and dihedral angles are well reproduced.

Trimethylgermane.[47] The calculated geometry of this molecule

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is in good agreement with the experimental microwave structure. The calculated Ge–H distance is overestimated by 0.018 Å.

Methylstannane.[48] The experimental geometry of this molecule has been determined by microwave spectroscopy, and the structure is well reproduced by UFF with the exception of the Sn–H distance. The calculated Sn–H distance is overestimated by 0.043 Å.

6. Heteroaromatics. Geometric results for N, O, and S heteroaromatics are collected in Table III. UFF predicts the bond lengths of six-membered ring nitrogen heteroaromatics such as pyridine well (C–N bond lengths are overestimated by less than 0.02 Å). The angles of six-membered ring heteroaromatics are poorly described by UFF; for example, the C–N–C angle of pyridine is too large by 5°. This Universal force field does not accurately predict the bond lengths of five-membered ring heteroaromatics. The calculated bond lengths are generally too small; for example, the calculated C3–C4 bond distance in furan is underestimated by 0.067 Å, likely a consequence of UFF overestimating the extent of π delocalization. MM2 is able to reproduce the experimental distances in these five-membered rings because the stretching and natural bond length parameters are a function of bond order, and the bond order is determined iteratively from SCF calculation on the π system.

Pyridine.[49] The experimental distances of pyridine determined from microwave spectra are reasonably well described by UFF. The largest bond length error is in the calculated C–N bond distance, too large by 0.023 Å. The error in most of the bond angles is on the order of a few degrees; the largest error is in the C–N–C angle, overestimated by almost 5°.

Pyridazine.[50] The calculated geometry of this heterocycle is in reasonable agreement with the experimental electron diffraction structure. The calculated C–N bond distance is overestimated by 0.019 Å; the C2–C3 distance is overestimated by 0.018 Å. The bond angles are only fairly well predicted by UFF, giving errors as large as 4°.

Pyrazine.[51] The C–C bond length is correctly calculated by UFF, and the C–N bond is 0.02 Å too long. The C–N–C angle is overestimated by almost 5°.

Pyrrole.[52] The microwave geometry of pyrrole is only fairly well described by the UFF force field. The calculated C–N bond distance is underestimated by 0.025 Å, the C3–C4 distance underestimated by 0.036 Å. The error in most of the bond angles is on the order of a few degrees, the largest error being the C–N–C angle, which is underestimated by 2.7°.

Imidazole.[53] Considering the only fair results with pyrrole, it is not surprising that the neutron diffraction structure of imidazole is not well described by the force field. The calculated C–C bond length in this five-membered ring is in agreement with experiment, but the calculated C–N bond distances of this molecule are not. The largest errors are in the calculated N1–C5 and C4–N3 bonds, both too small by about 0.04 Å. The calculated bond angles are in fair agreement with experiment.

Furan.[54] The UFF geometry for this molecule is in poor agreement with the experimental microwave structure. The calculated C3–C4 bond length is underestimated by 0.067 Å, the calculated C–O bond underestimated by 0.04 Å.

Thiophthene.[55] The structure of this fused thiophene has been determined by X-ray analysis. The geometry is poorly reproduced by UFF. The largest bond length error is in the C2–C3 distance, which UFF calculated to be 0.045 Å too small. The angles are also incorrectly calculated; the S–C3′–C2′ and C1–S–C3′ angles are underestimated by almost 5°. The S–C3′–C3 angle is overestimated by 5°.

7. Other Functional Groups. Geometric results for other functional groups are collected in Table III. UFF predicts the structures of simple unconjugated multiple bond containing compounds such as nitriles, ketones, and imines well. Bond length errors are less than 0.02 Å and bond angles are generally in error by less than 3°. However, the force field is not adequate to describe the structures of conjugated multiple bond containing molecules such as oximes and nitro compounds. (Bond length errors are as large as 0.08 Å, and bond angle errors as large as 5°.) The bond lengths of amides are treated reasonably accurately by UFF, but the N_R natural bond radius parameter was fit to *N*-methylformamide.

1,10-Cyclooctadecanedione.[56] The X-ray crystal structure of this 18-membered ring shows a highly symmetric molecule with C_{2h} symmetry. The UFF predicted structure shows instead a molecule of C_2 symmetry; there is a distortion of the carbonyl out of the σ_h plane skewing the ring. Using IR and dipole data, Borgen and Dale[57] have concluded that the related gem-dimethyl substituted 1,10-cyclooctadecanedione consists of several flexible conformers in solution. Calculated average bond distances for this molecule are in reasonable agreement with the experimental X-ray structure. The calculated average bond angles are also in reasonable agreement with experiment, with errors less than 3°. Dihedral angles are poorly predicted by UFF; the largest errors are in the dihedrals about the carbonyl carbon–α-carbon bond (C1–C2) bond, which is the site of the ring distortion away from C_{2h} symmetry. The UFF predicted O–C1–C2–C3 bond dihedrals are 18.1° and 51.8°; the C2′–C1–C2–C3 dihedrals are 166.0° and 132.2°. The corresponding experimental numbers are 21.6° and 159.1°. The correlation between the experimental and calculated tranannular oxygen–oxygen distances is reasonable.

Methylenimine.[58] The experimental microwave bond distances of this molecule are well reproduced by UFF. Errors in the calculated bond angles are somewhat larger; the cis H—C=N angle is underestimated by almost 4°; the C=N—H and H—C—H angles are overestimated by about 2°.

Propionitrile.[59] The calculated distances for this molecule are in good agreement with the experimental values. The bond angles are also reasonably predicted.

Acetamide.[60] The electron diffraction bond distances of this molecule are reasonably well reproduced by UFF. The calculated C–C distance is underestimated by 0.022 Å, and the C–N distance is underestimated by 0.016 Å. The experimental bond angles are rather poorly reproduced; the N–C–C angle is too large by 6° and the N–C–O and O–C–C angles are both too small by about 2°.

Formaldoxime.[61] The calculated C–N bond distance for this molecule is in good agreement with the experimental microwave value; the calculated N–O bond distance is underestimated by 0.067 Å. The trans N–C–H bond angle is in error by almost 4°, and the remaining calculated angles are in reasonable agreement with the experimental values.

Nitromethane.[62] The microwave geometry of this molecule is poorly reproduced by the UFF force field. When N_R and O_R atom types are used, the calculated C–N bond length is too small by 0.034 Å, and the N–O bond distance is too large by 0.076 Å. The UFF O–N–O angle is too small by more than 5°; the C–N–O angle is too large by about 3°. Clearly, special nitro group parameters are necessary in order to describe this resonating molecule correctly.

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Table IV. Conformational Energies of Hydrocarbons

compound	conformational energy difference	exp	Universal	MM2
butane	g–a	0.97 ± 0.05[a]	1.15	0.97[b]
2,3-dimethylbutane	g–a	0.05 ± 0.03[a]	0.5	0.38[c]
methylcyclohexane	ax–eq	1.75 ± 0.05[d]	1.87	1.8[b]
1-methyl-1-phenylcyclohexane	$\mathrm{Ph_{ax}}$–$\mathrm{Ph_{eq}}$	0.32 ± 0.04[e]	–0.04	0.9[f]
trans-1,2-dimethylcyclohexane	ax,ax–eq,eq	2.58 ± 0.05[g]	1.94	2.4[b]
trans-1,4-dimethylcyclohexane	ax,ax–eq,eq	3.6[h]	2.8	2.6[b]
1,3,5-trineopentylbenzene	two-syn–all-syn	0.49[i,j]	0.91	0.8[b]
1,3-butadiene	s-cis-s–trans	2.50 ± 0.3[k]	2.46	2.3[b]
cyclohexane	chair	0.0	0.0	0.0
	twist-boat	5.5[l]	8.8	5.4[b]
	boat		9.8	6.5[b]
	half chair	10.8[m]	15.0	10.5[n]

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Table V. Conformational Energies of O- and N-Containing Organics

compound	conformational energy difference	exp	Universal	MM2
methyl ethyl ether	g–a	1.5 ± 0.2[a]	1.8	1.8[b]
2-methoxytetrahydropyran	ax–eq	0.76[c]	−1.41	1.2[b]
2-butanone	ecl	0.0	1.11	0.0
	gauche	2.02 ± 0.10[d]	0.89	1.44[e]
	skew		0.0	1.60
	anti		3.09	2.37
acrolein	s-cis–s-trans	1.6 ± 0.2[f]	0.99	1.6[b]
aminocyclohexane	ax–eq	1.49 ± 0.06[g]	0.83	1.4[b]
N,*N*′-dimethylaminocyclohexane	ax–eq	1.31 ± 0.06[g]	1.95	1.0[b]
N-methylpiperidine	ax–eq	3.15 ± 0.10[h]	3.73	2.5[b]
2-methylpiperidine	ax–eq	2.5[i]	3.0	2.1[b]
4-methylpiperidine	ax–eq	1.93[j]	1.82	1.7[b]

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8. Summary of Structural Results. For most uncongested molecules without special resonance conditions such as those in aromatic heterocycles, or special angle strain such as those in four and five-membered rings, the bond distances are predicted by UFF to within 0.02 Å, and the angles within 3°.

IV. Conformational Energies

The ability of UFF to correctly reproduce the experimental rotational barriers and conformational energies of a variety of organic molecules was investigated. The results are compared with experiment and the published MM2 energies compiled by Pettersson and co-workers.[63] Additional comparison of torsional barriers is provided in the first paper in this series.[4]

Conformational Energies of Hydrocarbons. The ability of UFF to reproduce the experimental conformational energies of a variety of hydrocarbons was examined, and the results are presented in Table IV. In general, the UFF predictions are good; the gauche–anti energy difference in butane,[64] the axial–equatorial energy differences in methylcyclohexane[65] and *trans*-1,4-dimethylcyclohexane[66] are all in excellent agreement with the experimental values.

Reasonable agreement with experiment is obtained for the energy difference between the anti and the two gauche conformations of 2,3-dimethylbutane[64] (0.05 kcal exp; 0.5 kcal UFF), between the two syn–all-syn isomers of 1,3,5-trineopentylbenzene[67] (0.49 kcal exp; 0.91 kcal UFF), and the energy difference between the cis and trans isomers of 1,3-butadiene[68] (2.50 kcal exp; 3.46 kcal UFF).

The experimental axial–equatorial energy difference for 1-phenyl-1-methylcyclohexane[69] is 0.32 kcal; UFF underestimates the axial preference of the phenyl group by 0.36 kcal. UFF predicts the plane of the phenyl group to be perpendicular to the C–methyl bond for both the axial and equatorial conformers, as does MM2.[70]

The experimentally observed axial preference of the methyl groups in *trans*-1,2-dimethylcyclohexane[71] is underestimated by UFF. The experimental ax,ax–eq,eq energy difference is 2.58 kcal, and the corresponding UFF value is 1.94 kcal.

Cyclohexane itself holds an important position in the theory of conformational analysis. Experimentally the chair is known to be the lowest energy conformer, followed by a higher energy twist-boat form.[72] The chair to twist-boat conversion is thought to occur through a "half-chair" transition state.[73] UFF predicts

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Table VI. Conformational Energies of Organic Halides

compound	conformational energy difference	exp	Universal	MM2
fluorocyclohexane	ax–eq	0.16[a]	0.39	0.2[b]
chlorocyclohexane	ax–eq	0.450 ± 0.005[c]	1.19	0.4[b]
bromocyclohexane	ax–eq	0.472 ± 0.005[c]	1.31	0.5[b]
trans-1,2-difluorocyclohexane	ax,ax–eq,eq	1.03 ± 0.06[d]	0.73	0.8[b]
trans-1,2-dichlorocyclohexane	ax,ax–eq,eq	–0.93[e]	1.65	–0.9[b]
trans-1,2-dibromocyclohexane	ax,ax–eq,eq	–1.50[e]	1.62	–0.9[b]
1,2-difluoroethane	g–a	–0.6[f]	0.05	–0.6[b]
1,2-dichloroethane	g–a	1.05 ± 0.10[g]	0.59	1.6[b]
1,2-dibromoethane	g–a	2.2 ± 0.3[h]	0.7	

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the chair form is indeed the lowest energy conformer, and that the twist-boat conformation is 8.8 kcal above the chair. The corresponding experimental value is 5.5 kcal. The experimental barrier to the chair-twist conversion is 10.8 kcal. The UFF calculated barrier is 15.0 kcal. The energies of the higher energy strained conformers of cyclohexane are overestimated by UFF. The inadequacy of the UFF force field in describing the geometries of highly strained hydrocarbons has already been noted.

Conformational Energies of Oxygen- and Nitrogen-Containing Molecules. The ability of UFF to reproduce the experimental conformational energies of a variety of O- and N-containing hydrocarbons was examined, and the results are presented in Table V. The accuracy of the UFF results are mixed: successes include the gauche–anti energy difference in ethyl methyl ether[74] and the axial–equatorial energy differences of methyl-substituted piperidines.[75] Two notable failures are the UFF predictions of the enthalpy changes for the gauche-eclipsed equilibrium in 2-butanone,[76] and the axial–equatorial equilibrium in 2-methoxytetrahydropyran.[77] The failures will be discussed in detail below.

Experimentally[77] the most stable conformer of 2-methoxytetrahydropyran is the one in which the methoxy group adopts an axial position. UFF instead predicts the equatorial conformer is the most stable. The axial preference of polar group on C1 of a pyranose ring is known as the anomeric effect,[78] and the origin of this effect been rationalized in terms of, among others, a dipole–dipole interaction between the substituent and the C–O bond in the ring.[79] UFF does not include such interactions. MM2 correctly reproduces the anomeric effect by including a special 2-fold barrier about the O–C(OCH$_3$) bond in the force field.

Gas-phase electron diffraction studies of 2-butanone[76] show that the ketone prefers a conformer in which the methyl group eclipses the carbonyl bond. Contrary to experiment, UFF calculates that the skew form, in which a hydrogen eclipses the carbonyl bond and the methyl group is rotated about 120° from the carbonyl oxygen, is preferred. In the gas phase another conformer with an energy about 2 kcal higher than the eclipsed form exists, possibly the gauche form, where the methyl group is rotated about 60° from the carbonyl oxygen. UFF calculates the gauche form is about 0.5 kcal higher than the lowest energy conformer (skew, rather than eclipsed).

Fair results are obtained for the axial–equatorial energy differences in amino and *N,N'*-dimethylaminocyclohexanes[80] using UFF. The equatorial conformers are predicted to be more stable, in agreement with experiment, but the UFF axial–equatorial energy difference is underestimated for the amino compound and overestimated for the dimethylamino compound. The cis–trans energy difference for acrolein[81] predicted by UFF is about 0.6 kcal too low.

Conformational Energies of Haloalkanes. The ability of UFF to reproduce the experimental conformational energies in monohalocyclohexanes,[82] *trans*-1,2-dihalocyclohexanes,[83,84] and 1,2-dihaloethanes[85–87] was investigated. The results are presented in Table VI.

In agreement with experimental work on monohalocyclohexanes,[82] UFF predicts the conformer in which the halogen is in the equatorial position is favored. Nonetheless, as the size of the halogen increases, the accuracy of the UFF predicted axial–equatorial energy differences decreases. The fluoro ax–eq energy difference is overestimated by 0.23 kcal, the chloro by about 0.74 kcal, and the bromo by about 0.84 kcal. UFF is likely not including an axial-favoring electrostatic factor between the axial halogen and the axial ring hydrogens which can partially compensate for an equatorial-favoring axial steric interaction.

trans-1,2-Difluorocyclohexane is known[83] to prefer a conformation in which the two fluorines are equatorial. UFF predicts the correct low energy conformer, but underestimates the energy difference between the ax,ax–eq,eq conformers by 0.3 kcal. *trans*-1,2-Dichlorocyclohexane and *trans*-1,2-bromocyclohexane both prefer conformations in which the halides are axial.[84] UFF predicts instead that the eq,eq halide conformers are favored. The energetic predictions by UFF for these two cases are terrible. Both steric and electrostatic dipole–dipole interactions are thought to be important in determining the energy difference between the ax,ax–eq,eq conformers of *trans*-1,2-dihalo-substituted cyclohexanes.[88] The Universal force field as used in these papers uses no charges, and so cannot correctly account for the axial preference in *trans*-1,2-dichloro- and -dibromocyclohexanes.

The vicinal interactions in *trans*-1,2-dihalocyclohexanes and 1,2-dihaloethanes are related; the gauche is analogous to the diequatorial and the anti is analogous to the diaxial. Thus one might expect that, considering how poorly UFF predicts the conformational equilibria of *trans*-1,2-dihalocyclohexanes, UFF also cannot correctly predict the gauche–anti (g–a) energy differences of 1,2-dihalosubstituted ethanes. In fact, UFF does a better job (though still poor) of predicting the g–a energy differences of 1,2-dihaloethanes than the ax,ax–eq,eq energy dif-

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ferences of *trans*-1,2-dihalocyclohexanes. We believe this is due to the complicating factor of 1,3-diaxial electrostatic and steric interactions present in the cyclohexanes not present in the ethanes (see monohalocyclohexanes, above). Experimentally 1,2-difluoroethane[85] prefers a gauche conformation of the two fluorines. The force field predicts instead that the gauche and anti conformers are nearly isoenergetic. The error in the energy difference is about 0.6 kcal. 1,2-Dichloroethane[86] and 1,2-dibromoethane[87] both prefer conformations in which the halides are anti. UFF predicts that the anti conformers are favored, in agreement with experiment, but underestimates the energy difference by 0.46 and 1.5 kcal for 1,2-dichloro- and 1,2-dibromoethane, respectively.

Summary of Conformational Results. Good agreement with experiment is observed when UFF is applied to the conformational equilibria of compounds for which charge apparently does not play an important role, for example, the anti–gauche or ax–eq energy differences for many hydrocarbons. An exception is the calculation of the conformational energetics of cyclohexane. We believe this is a consequence of the inability of UFF to adequately describe highly strained molecules. Good to fair energies are obtained for many monoheteroatom systems such as the ax,eq energy differences in methyl-substituted piperidines. Rather poor results are observed when UFF is applied to *trans*-1,2-dihalocyclohexanes, 1,2-dihaloethanes, butanone, and 2-methoxytetrahydropyran, compounds for which electrostatic interactions are apparently vital in determining conformational energetics.

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Application of a Universal Force Field to Main Group Compounds

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Abstract: The ability of a Universal force field (UFF) to reproduce the structures of a variety of main group molecules is examined. The magnitude of bond distance errors for main group compounds are somewhat larger than for organic compounds, though X–C bond distances are well reproduced. Bond distance errors for X–Y polar covalent bonds are generally less than 0.05 Å. Comparable bond length errors are observed for hypervalent X–O and X–N bonds (errors on the order of 0.05 Å) and dative bonds (errors as large as 0.04 Å). The error in bond length for bonds involving centers with multiple electronegative substituents bound to an electropositive center approaches 0.1 Å. Bond angle errors are generally less than 5°, although larger errors (up to 14°) are frequently observed for hypervalent complexes and in centers with multiple electronegative substituents. UFF gives very large bond angle errors (up to 44°) for some heavy atom maingroup compounds such as the C–Tl–C bond in diethyldithiocarbamatodiphenylthallium(III), where the electronic structure is incorrectly described.

I. Introduction

Application of molecular mechanics to main group chemistry has lagged significantly behind the use of these techniques in organic and biochemistry. Reasons for this disparity include the greater number of elements and the diversity of both geometries and oxidation states. In recent years, the popular MM series of force fields developed by Allinger and co-workers,[1] so successful in describing the structures and other properties of organic molecules, has been extended to selected organo main group compounds, such as silanes,[2] disilanes,[3] polysilanes[4] chlorosilanes,[5] siloxanes,[6a] silicon–sulfur compounds,[6b] phosphines,[7a] phosphine oxides,[7b] phosphoranes,[8] phosphites,[9] sulfides,[10a,b] sulfoxides,[10c] and selenium,[11] tellurium,[11] germanium,[12,13] tin,[12] and lead[12] compounds. Applications of other force field methods to main group molecules include using the MMX force field to study oxaphosphetanes,[14] investigations of conformations of F_3COF and F_3CSF,[15] and using a modified AMBER force field to determine the natural bite angle of chelating phosphines.[16] Nonetheless, even these extended force fields are limited to particular combinations of atoms, in these cases to specific classes of organo main group compounds.

The Dreiding force field[17] parameters for several main group atoms have been published, but to our knowledge this method has only been applied to the structure of diborane.

In order to facilitate studies of a variety of main group atomic associations, we have developed a new force field using general rules for estimating force field parameters based on simple relations from the literature. We refer to this new force field as a Universal

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