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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force field (UFF). The force field functional forms and parameters are described in detail in the first paper of this series.[18] In the previous paper[19] of the series we applied the force field to the structures and energetics of organic molecules. 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 to within 0.02 Å. The structures of four- and five-membered rings, congested hydrocarbons, and aromatic ethers are only fairly well described with distance errors of up to 0.033 Å and angle errors of up to 10°. The Si–Si bond lengths of disilanes are poorly reproduced with errors of up to 0.1 Å. UFF predicts the structures of secondary halides reasonably well, but is only fair at reproducing the C–X bond lengths of tertiary halides (errors up to 0.08 Å). UFF also cannot reproduce the carbon–halide bond lengths in vinyl and aromatic halides, with overestimations as large as 0.1 Å. Geometries of N, O, and S heteroaromatics are also not well described by UFF. This force field is also not adequate to predict the structures of conjugated multiple bond containing molecules such as oximes and nitro compounds. Here calculated bond length errors are as large as 0.08 Å, and bond angle errors are as large as 5°.

In the present paper we apply UFF to reproduce the experimental geometries of a series of main group molecules.

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. The structures of most of the larger compounds were minimized starting with the X-ray structure coordinates obtained from the Cambridge data base. Additional minima on the potential surface were not sought in this study.

III. Structural Results

The ability of UFF to correctly reproduce experimental geometries of a variety of main group molecules was investigated. The structural results calculated with UFF, along with the experimental values, are presented in Tables I through IV.

Before we discuss the structural results for main group molecules, we must provide a working definition of acceptable error. Comparison with alternative theoretical methodologies will be used to assess the terms: good, fair, and poor agreement with experiment. For small organic molecules (H_mABH_n), average absolute errors have been reported[20] using an ab initio Hartree–Fock wave function with the 6-31G* basis: 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). For hypervalent compounds, calculations with an ab initio Hartree–Fock wave function and the 3-21G basis gave a mean absolute error of 0.125 Å. Addition of d polarization functions dropped the error to 0.015 Å.[20] For complexes containing dative bonds, calculations with an ab initio Hartree–Fock wave function and the 6-31G* basis gave errors of more than 0.1 Å.[20] Addition of electron correlation at the MP2 level lowered the error to 0.01 Å for BH_3CO and to ~0.07 Å for BH_3NH_3.[20] As defined previously for organic compounds, errors of less than 0.02 Å in bond distances and bond angle errors of less than 2° will still be considered in "good agreement with experiment". It seems reasonable, however, that larger errors might be acceptable in defining fair and poor for main group compounds. Bond distance errors of less than 0.08 Å and bond angle errors of less than 5° will be described as being in "fair agreement with experiment"; structures with larger errors will be considered to be in "poor agreement with experiment".

Table I. Calculated and Experimental Structures of Selected Main Group Molecules

compound	bond or angle	Universal	exp	ref[a]
BF_3	B–F	1.411	1.313	p 23
BCl_3	B–Cl	1.814	1.742	p 22
BBr_3	B–Br	1.973	1.893	p 21
BI_3	B–I	2.178	2.118	p 29
AsH_3	As–H	1.564	1.511	p 20
	H–As–H	92.1	92.1	
AsF_3	As–F	1.817	1.710	p 19
	F–As–F	92.1	96.0	
$AsCl_3$	As–Cl	2.220	2.165	p 19
	Cl–As–Cl	92.1	98.6	
$AsBr_3$	As–Br	2.379	2.329	p 18
	Br–As–Br	92.1	99.7	
AsI_3	As–I	2.581	2.557	p 20
	I–As–I	92.1	100.2	
$H_3C-O-CH_3$	C–O	1.410	1.410	p 204
	C–O–C	109.2	111.7	
$H_3C-S-CH_3$	C–S	1.821	1.802	p 205
	C–S–C	94.6	98.9	
$H_3C-Se-CH_3$	C–Se	1.947	1.943	p 206
	C–Se–C	92.2	96.2	
$H_3Si-O-SiH_3$	Si–O	1.591	1.634	p 90
	Si–O–Si	145.4	144.1	
$H_3Si-S-SiH_3$	Si–S	2.148	2.136	p 93
	Si–S–Si	92.6	97.4	
$H_3Si-Se-SiH_3$	Si–Se	2.281	2.274	p 94
	Si–Se–Si	90.7	96.6	
$H_3Ge-O-GeH_3$[b]	Ge–O	1.665	1.766	p 81
	Ge–O–Ge	145.4	126.5	
$H_3Ge-O-GeH_3$[c]	Ge–O	1.791	1.766	p 81
	Ge–O–Ge	105.0	126.5	
$H_3Ge-S-GeH_3$	Ge–S	2.221	2.209	p 81
	Ge–S–Ge	92.2	98.9	
$H_3Ge-Se-GeH_3$	Ge–Se	2.355	2.344	p 82
	Ge–Se–Ge	90.5	94.6	

[a] Hellwege, K.-H. *Landolt-Boernstein Numerical Data and Functional Relationships in Science and Technology*; Springer Verlag: Berlin, 1976; Vol. 7. [b] O_3_z atom type. [c] O_3 atom type.

The initial observation and subsequent understanding of many important structural effects in main group chemistry arose by comparing "standard" bond distances (from a summation of covalent radii) with experimental bond distances.[21] These structural-electronic effects include dative bonding and hypervalent bonding. A force field capable of fully predicting the structure of main group complexes must systematically reproduce these effects.

Dative bonding is the electronic interaction wherein both electrons of a bond pair are donated by one atom of the bonding pair; as a result this bonding interaction does not represent a full covalent bond. For the present work we take dative bonds to have a bond order of $^1/_2$. As discussed below, there are additional, angular complications in predicting the structures of datively bonded compounds.

Hypervalent bonding is an additional area of complication. Hypervalent multiple bonds are typically drawn as a double bond even though the bonding interaction is not that of a simple covalent bond.[22] In addition to this multiple bonding, there typically is a significant electrostatic contribution. For the present work we take hypervalent bonds to have a bond order of 3. This effect is discussed below for a set of five hypervalent molecules.

Boron Halides. Experimental gas-phase as well as calculated geometric results for the series BX_3, X = F through I, are collected in Table I. The error in calculated B–X bond distance ranges from 0.06 Å for boron triiodide to 0.098 Å for boron trifluoride.

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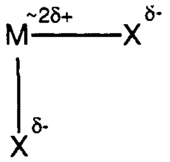
The error in B–X bond distance is nearly linear with electronegativity difference (a slope of 0.6 and an intercept of 0.04 Å). This correlation suggests that the O'Keefe and Brese[23] electronegativity correction used in UFF (eq 4 of paper 1) is insufficient.[24] The O'Keefe–Brese correction accounts for partial ionicity in covalent bonds:

$$\overset{\delta+}{\mathrm{M}}\text{———}\overset{\delta-}{\mathrm{X}}$$

it does not account for more than one electronegative substituent being present. If two electronegative substituents are present, the partial positive charge on the electropositive center will be nearly twice as large:



$$\overset{\sim 2\delta+}{\mathrm{M}}\text{———}\overset{\delta-}{\mathrm{X}}, \quad \mathrm{M}\text{—}\overset{\delta-}{\mathrm{X}}$$

which will in turn nearly double the favorable interaction between the electropositive and electronegative centers. Bond length contraction by adjacent electronegative groups has been noted before[24] and an alternative explanation and correction has been discussed previously.[5] Because of this multiple electronegative substituent effect, the experimental M–X bond distances are shorter than predicted by the present UFF force field. The interplay between multiple electronegative substituents at an electropositive center must be taken into account in a future force field in order to obtain good structural predictions for main group compounds. In addition, the nonzero intercept in a plot of bond length error versus electronegativity difference suggests that Bπ–Xπ bonding[21] is indeed significant.

Arsenic Halides. Experimental gas-phase as well as calculated geometric results for the series AsX_3, X = H, and F through I, are presented in Table I. The error in the calculated As–X bond distance ranges from 0.024 Å for arsenic triiodide to 0.107 Å for arsenic trifluoride. As above, the error in As–X bond distance is also nearly linear with electronegativity difference if AsH_3 is ignored. The slope for the series AsX_3 is 1.6, whereas the slope for the series BX_3 is 0.6, suggesting that the error in the O'Keefe and Brese equation[23] is not a simple multiplicative constant. It is interesting to note that in contrast to the series BX_3, the intercept is nearly zero (0.005 Å) for the series AsX_3, suggesting no additional 1,2 interactions. The data in Table I show an experimental monotonic increase in X–As–X angle as the size of the substituent X increases. UFF cannot reproduce this trend, indicating a need to include a 1,3 interaction term in the force field.

Ether Analogues. Experimental gas-phase as well as calculated geometric results for the series $Y(XH_3)_2$, Y = O, S, and Se, and X = C, Si, and Ge, are collected in Table I. The geometries of the series $Y(CH_3)_2$ are well described with the largest error being for Y = S (0.019 Å). This is not surprising considering the fundamental Y radii were obtained from Y–C bonds. The C–Y–C angles are calculated to be too small by 2.5° to 4°, again suggesting that the inclusion of a 1,3 interaction term in the force field would increase the quality of geometric prediction from fair to good. The series $Y(SiH_3)_2$ is also described well, with the exception of Y = O where the Si–O distance is in error by 0.043 Å. This compound, along with the related Si–O–Si molecules illustrated in Figure 1, provides additional evidence for the importance of considering adjacent substituents when assigning electronegativity corrections and force field parameters. The experimental Si–O bond distances range from 1.580 Å for $O(SiF_3)_2$ to 1.634 Å for $O(SiH_3)_2$. The computed distances are all nearly 1.592 Å, where the fundamental Si–O distance was obtained by fitting the O_3_z radius to the structure for $O(SiCl_3)_2$.

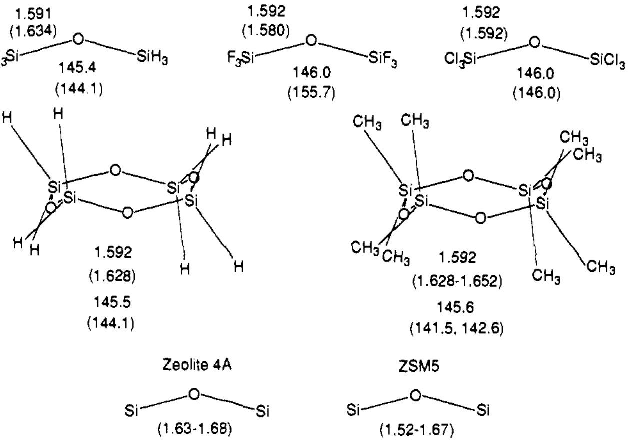


Figure 1. Comparison of experimental and calculated structures for a series of Si–O–Si compounds.

It is interesting to note that Si(Al)–O distances in zeolites such as ZSM5[25] range from 1.52 to 1.67 Å; the long distances are certainly due to partial Al occupancy, but the average distance of 1.59 Å is reflective of Si–O distances. The computed Si–O–Si angles of the siloxanes are all nearly 146°, where the fundamental O_3_z angle of 146° was obtained by fitting to the structure for $O(SiCl_3)_2$. In contrast to the similarity of calculated angles in Figure 1, the experimental angles range from 141.5° to 155.7°. The series $Y(GeH_3)_2$ is also described well by UFF, again with the exception of Y = O. If the O_3_z oxygen is used, the Ge–O distance is short by 0.1 Å and the Ge–O–Ge angle is too large by 19°. If the O_3 oxygen is used, the Ge–O distance is long by only 0.025 Å, but the Ge–O–Ge angle is too small by 21°. An important interplay between degree of ionicity, bond lengths, and X–O–X bond angles cannot be reproduced by the force field.

Dative Complexes. Experimental gas-phase as well as calculated geometric results for a set of Lewis acid–base adducts are given in Table II. Covalent bonds within the molecules are well described by UFF, but the dative bonds are problematic. Using a bond order of 1 for the dative bonds overestimates the degree of bonding, and hence the calculated bond distances are too short. Using a bond order of $^1/_2$ for the dative bonds underestimates the degree of bonding resulting in the calculated bond distances being too long. In addition, because the Lewis acid and Lewis base centers are assumed to be tetrahedral (appropriate for a bond order of 1), the valence bond angles are substantially in error. The Lewis acid bond angles are too small; a decrease in bond order should result in a systematic decrease in pyramidalization back toward the 120° bond angles of the free Lewis acid. The Lewis base bond angles are too large; a decrease in bond order should result in a systematic increase in pyramidalization back toward the <109.5° bond angles of the free Lewis base. Considering the effect of multiple electronegative substituents as discussed above, it appears empirically that use of a $^1/_2$ bond order for dative bonds is preferred, though future efforts need to be directed toward improved descriptions of dative bonding. The calculations reported below for larger molecules utilize a bond order of $^1/_2$ for dative bonds.

Hypervalent Complexes. Experimental gas-phase as well as calculated geometric results for a set of hypervalent sulfur complexes are given in Table III. The calculated covalent single bond distances are in good agreement with experiment. The hypervalent S–X (O or N) bond lengths are difficult to accurately predict owing to the unknown degree of multiple/hypervalent bonding. If a bond order of 2 is used, the degree of bonding is underestimated and hence the bond distances are on the order of 0.09 Å too long. If a bond order of 3 is used, the degree of bonding is slightly overestimated for many compounds, and hence the bond distances are somewhat too short. Recent generalized valence bond calculations by Patterson and Messmer[22] are suggestive of

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Table II. Calculated and Experimental Structures of Selected Main Group Molecules with Dative Bonds

		Universal[a]			
compound	bond or angle	B.O. = 1	B.O. = $^1/_2$	exp	ref[b]
H_3BPH_3	B–P	1.884	2.058	1.937	p 28
	B–H	1.191	1.191	1.212	
	P–H	1.408	1.408	1.399	
	B–P–H	109.4	109.4	116.9	
	P–B–H	109.4	109.4	103.6	
H_3BPF_3	B–P	1.884	2.058	1.836	p 25
	B–H	1.191	1.191	1.207	
	P–F	1.674	1.674	1.538	
	F–P–F	109.5	109.5	99.8	
	H–B–H	109.5	109.5	115.1	
$H_3BN(CH_3)_3$	B–N	1.544	1.681	1.637	p 260
	N–C	1.480	1.477	1.495	
	B–N–C	109.6	109.2	109.6	
$F_3BN(CH_3)_3$	B–N	1.555	1.690	1.636	p 254
$H_3BP(CH_3)_3$	B–P	1.885	2.058	1.901	p 261
	B–H	1.191	1.191	1.212	
	P–C	1.814	1.813	1.819	
	C–P–C	109.5	109.6	105.0	
	H–B–H	109.5	109.6	113.5	
$H_3AlN(CH_3)_3$	Al–N	1.904	2.074	2.063	p 260
	Al–H	1.586	1.585	1.560	
	N–C	1.478	1.474	1.476	
	H–Al–N	109.5	109.3	104.3	
	Al–N–C	109.5	109.1	109.0	
Cl_3AlNH_3	Al–N	1.865	2.043	1.996	p 16
	Al–Cl	2.145	2.145	2.100	
	Cl–Al–Cl	109.5	109.5	116.4	
$Cl_3AlN(CH_3)_3$	Al–N	1.911	2.079	1.945	p 253
	N–C	1.478	1.475	1.516	
	Cl–Al–N	110.1	109.7	104.9	
	Al–N–C	109.7	109.2	112.6	
$(CH_3)_3AlN(CH_3)_3$	Al–N	1.914	2.080	2.099	p 349
	N–C	1.478	1.475	1.474	
	Al–C	1.964	1.961	1.987	
	C–Al–N	110.5	109.9	102.3	
	Al–N–C	109.8	109.3	109.3	

[a] B.O. = bond order. [b] Hellwege, K.-H. *Landolt-Boernstein Numerical Data and Functional Relationships in Science and Technology*; Springer Verlag: Berlin, 1976; Vol. 7.

Table III. Calculated and Experimental Structures of Selected Main Group Molecules with Hypervalent Multiple Bonds

		Universal			
compound	bond or angle	B.O. = 2	B.O. = 3	exp	ref[a]
thionyl chloride	S–O	1.522	1.431	1.443	p 50
	Cl–S	2.087	2.087	2.076	
	Cl–S–Cl	103.2	103.2	96.1	
	Cl–S–O	103.2	103.2	106.3	
sulfuryl chloride	S–O	1.502	1.413	1.404	p 50
	Cl–S	2.065	2.065	2.011	
	Cl–S–Cl	109.5	109.5	100.0	
	Cl–S–O	109.5	109.5	107.7	
	O–S–O	109.5	109.5	123.5	
dimethyl sulfoxide	S–O	1.523	1.432	1.485	p 204
	C–S	1.802	1.802	1.799	
	C–S–C	104.1	104.1	96.6	
	C–S–O	103.6	103.6	106.5	
dimethyl sulfone	S–O	1.503	1.413	1.431	p 204
	C–S	1.779	1.779	1.777	
	C–S–C	109.6	109.5	103.3	
	O–S–O	109.4	109.4	121.0	
N-chloro-*S*,*S*-difluorosulfoximine	S–O	1.502	1.412	1.394	p 38
	S–N	1.556	1.464	1.484	
	S–F	1.675	1.675	1.548	
	Cl–N	1.726	1.727	1.715	
	Cl–N–S	111.9	112.2	114.7	
	N–S–F	109.5	109.6	111.8	
	F–S–F	106.6	105.5	92.6	

[a] Hellwege, K.-H. *Landolt-Boernstein Numerical Data and Functional Relationships in Science and Technology*; Springer Verlag: Berlin, 1976; Vol. 7.

a bond order of at least 2 for the hypervalent bonds of H_2SO_4 with ionicity contributing additional bonding.[26] It appears that use of a bond order of 3 for hypervalent bonds might be appropriate, although future work in improving a Universal force field description of hypervalent bonding must be carried out. The calculations reported below for larger molecules utilize a bond order of 3 for hypervalent bonds.

Larger Molecules. Selected structural parameters for an additional set of molecules with main group–main group bonds are collected in Table IV. The structural formulas and the numbering of atoms are given in Figure 2. Note that the dative bonds of molecules in Table IV were calculated using a bond order of $^1/_2$, and the hypervalent bonds were calculated using a bond order of 3.

***N*,*N*-Dimethylaminodiborane.**[27] The agreement between the gas-phase experimental and UFF computed structures is fair to good. The calculated B–B distance is overestimated by 0.050 Å. The calculated terminal B–H bonds are only 0.007 Å too long, but the bridging B–H bonds are 0.059 Å long. The calculated B–N bond is 0.001 Å too short. A bond order of $^3/_4$ was used for the B–N bonds since these bonds are a mixture of covalent bonding (bond order 1) and dative bonding (bond order $^1/_2$). The C–N bond is 0.015 Å short. The terminal H–B–H angle is 9.8° small but the bridging B–H–B angle is only 1.9° small. The B–N–B angle is 2.3° large and the C–N–C angle is 3.9° large.

Triphenylboroxin.[28] As discussed above for the silyl ethers, UFF has difficulty describing the bridging oxygens correctly. We provide two computed structures for triphenylboroxin, one where it is assumed that there is π bonding between the boron and the oxygen centers (O_R atom type is used), and a second structure where O_3_z atom type is used. The agreement with experiment for both calculated structures is fair. For the O_R structure the B–O–B angle is underestimated by 4.3°, and for the O_3_z structure the B–O–B angle is overestimated by 6.7°. The B–O bond distances are 0.078 Å long for O_R and 0.054 Å short for O_3_z. For both representations the B–C distances are well described; they are 0.028 Å (O_R) and 0.024 Å (O_3_z) short. For the O_R structure the O–B–O angle is 4.6° large, and for the O_3_z structure the O–B–O angle is 6.4° small.

Dichloro-1,2,4-trithia-3,5-diborolane.[29] This molecule has been shown by X-ray crystallography to be approximately planar. The calculated bond distances are in fair agreement with experiment. The B–S bond distances are overestimated by 0.077 Å, and the S–S bond distances by 0.094 Å. The UFF predicted B–Cl distance is overestimated by 0.057 Å. The electronegativity effect of adjacent substituents unaccounted for by the force field is likely responsible. The bond angles in this compound are well described by the force field. The B–S–B angle is 1.6° small; the S–B–S angle is on average only 1.5° large. The average B–S–S angle is 0.7° small and the S2–B–Cl angle is 2.4° small.

Hexa[methyl(isopropylimido)aluminum].[30] Overall the three-dimensional structure of this prismatic hexagonal cluster is well reproduced by UFF. The calculated Al–C and N–C bond distances are in good agreement with the corresponding experimental values; they are in error by only 0.009 Å and 0.025 Å, respectively. The intra-six-membered ring Al–N distances (bond order 1) are in good agreement with experiment, on average 0.017 Å short. The distances for the Al–N bonds that connect the two six-membered rings (Al1–N2) are poorly described; they are over-

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Table IV. Calculated and Experimental Structures of Selected Main Group Molecules

bond/angle	Universal	exp	bond/angle	Universal	exp
N,N-Dimethylaminodiborane					
B–B	1.964	1.916[a]	H1–B–H1	109.8	119.6
B–H1	1.198	1.191	B–H2–B	87.2	89.1
B–H2	1.424	1.365	B–N–B	79.1	76.8
B–N	1.543	1.544	C–N–C	113.9	110.0
C–N	1.473	1.488			
Triphenylboroxin					
O_R B–O (av)	1.464	1.386[b]	O_3_z B–O (av)	1.332	1.386
B–C (av)	1.569	1.541	B–C (av)	1.565	1.541
B–O–B (av)	117.4	121.7	B–O–B (av)	128.4	121.7
O–B–O (av)	122.6	118.0	O–B–O (av)	111.6	118.0
Dichloro-1,2,4-trithia-3,5-diborolane					
S–B (av)	1.871	1.794[c]	S–B–S (av)	123.2	121.7
S–S	2.163	2.069	B–S–S (av)	99.2	99.9
B–Cl	1.813	1.756	S2–B–Cl	118.4	120.8
B–S–B	95.3	96.9			
Hexa[methyl(isopropylimido)aluminum]					
Al–C2	1.986	1.977[d]	N1–Al1–N1	115.6	115.7
Al1–N1	1.900	1.917	N1–Al1–N2	98.2	91.4
Al1–N2	2.070	1.964	Al1–N1–Al1	119.9	123.9
N–C1	1.489	1.514	Al1–N1–Al2	81.8	88.6
Bis[dibromo(pyridine)gallium]					
Ga–Br	2.321	2.350[e]	Br–Ga–Br	109.5	105.8
Ga–N	2.067	2.024	Ga–Ga–Br	108.8	116.3
Ga–Ga	2.521	2.421			
Dodecamethylcyclo-2,4,6-triinda-1,3,5-triarsane					
In–As (av)	2.707	2.670[f]	C–As–C (av)	101.0	126
C–In–C (av)	110.8	99			
Diethyldithiocarbamatodiphenylthallium(III)					
Tl–C (av)	2.210	2.159[g]	C–N	1.386	1.403
Tl–S (av)	2.611	2.720	C–Tl–C	114.0	148.4
S1–C	1.647	1.626	S–Tl–S	68.0	65.3
S2–C	1.807	1.732	S–C–S	115.6	121.8
S–C (av)	1.728	1.679			
Octamethylcyclotetrasiloxane					
Si–O (av)	1.592	1.65[h]	O–Si–O (av)	109.5	109
Si–C (av)	1.866	1.92	C–Si–C (av)	109.6	106
Si–O–Si (av)	145.6	142.5			
1,3,5,7-Tetrakis(trifluoromethyl)-2,4,6,8,9,10-hexathia-1,3,5,7-tetragermaadamantane					
Ge–S (av)	2.221	2.210[i]	S–Ge–S (av)	114.7	113.8
Ge–C (av)	1.946	1.996	Ge–S–Ge (av)	97.5	99.9
F–C (av)	1.382	1.312			
Dodecaphenylcyclohexastannane					
Sn–Sn (av)	2.779	2.780[j]	C–Sn–C (av)	110.3	106.7
Sn–C (av)	2.114	2.150	Sn–Sn–Sn–Sn (av)	56.9	51.6
Sn–Sn–Sn (av)	110.7	112.5			
(Benzenethiolato)triphenyllead					
Pb–C (av)	2.176	2.203[k]	Pb–S	2.493	2.515
Phosphorus(III,V) Oxide					
P2–O2	1.738	1.68[l]	O2–P1–O2	112.5	103
P2–O3	1.751	1.64	O2–P2–O3	104.0	99
P1–O2	1.673	1.59	P1–O2–P2	110.9	124
P1–O1	1.420	1.44	P2–O3–P2	119.9	128
O1–P1–O2	106.2	115			
Tris(*o*-ethylxanthato)arsenic(III)					
As–S1	2.288	2.307[m]	C–O	1.410	1.320
As–S2	3.330	2.956	S1–As–S1	92.2	91.4
S1–C	1.812	1.744	As–S1–C	96.9	93.9
S2–C	1.444	1.641			
Tris[bis(pentafluorophenyl)germa]dibismuth					
Bi–Ge (av)	2.699	2.739[n]	Ge–Bi–Ge (av)	81.2	72.4
Ge–C (av)	1.925	1.97	Bi–Ge–Bi (av)	82.6	93.9
Bis(triphenyltin)tellurium					
Te–Sn (av)	2.762	2.727[o]	Sn–Te–Sn	92.5	103.7
Sn–C (av)	2.120	2.138			
Dichlorobis(7-azaindole)zinc(II)					
Zn–Cl (av)	2.201	2.222[p]	Cl–Zn–Cl	109.2	117.5
Zn–N (av)	2.058	2.051	N–Zn–N	109.6	100.7
Tetrakis(thiophenolato)zinc(II)					
Zn–S (av)	2.384	2.357[q]	Zn–S–C (av)	102.4	109.3
S–C (av)	1.809	1.760	S–Zn–S (range)	109.4–109.5	99.9–117.2
Tetrakis(thiophenolato)cadmium(II)					
Cd–S (av)	2.585	2.541[q]	Cd–S–C (av)	99.0	107.8
S–C (av)	1.807	1.755	S–Cd–S (range)	109.4–109.5	98.9–116.6

Table IV (Continued)

bond/angle	Universal	exp	bond/angle	Universal	exp
Bis(2,4,6-triisopropylbenzenethiolato)bis(1-methylimidazole)cadmium(II)					
Cd-S (av)	2.458	2.463[r]	N-Cd-N	106.7	93.7
Cd-N (av)	2.282	2.281	S-Cd-N (av)	109.7	107.9
S-Cd-S	111.1	126.3			
Bis(2-furyl)mercury					
Hg-C	2.064	2.059[s]	O-C1	1.321	1.388
C1-C2	1.375	1.336	O-C4	1.321	1.377
C2-C3	1.363	1.409	Hg-C1-O	123.5	117.1
C3-C4	1.375	1.347			
Bis(di(*tert*-butyl)phosphino)mercury					
P-C (av)	1.902	1.89[r]	Hg-P-C (av)	97.6	101.8
Hg-P (av)	2.456	2.446	P-Hg-P	170.4	177.5
Bis(acetylacetonato)beryllium(II)					
Be-O (av)	1.703	1.618[u]	O-Be-O (range)	108.3-111.9	106.9-112.6
O-C (av)	1.315	1.282	O-Be-O (av)	110.1	107.5
[Bis(dimethylsilylmethylimido)methyl]beryllium dimer					
Be-N1 (av)	1.773	1.752[v]	Be-N1-Be (av)	82.7	80.2
Be-N2 (av)	1.776	1.722	N1-Be-N1 (av)	97.3	99.8
(Acetonitrilo)(pentafluorophenyl)xenon(II)					
Xe-C	2.005	2.092[w]	Xe-N	2.096	2.681

[a] Hellwege, K.-H. *Landolt-Boernstein Numerical Data and Functional Relationships in Science and Technology*; Springer Verlag: Berlin, 1976; Vol. 7, p 215. [b] Brock, C. P.; Minton, R. P.; Niedenzu, K. *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **1987**, *C43*, 1775. [c] Almenningen, A.; Seip, H. M.; Vassbotn, P. *Acta Chem. Scand.* **1973**, *27*, 21. [d] Del Piero, G.; Perego, G.; Cucinella, S.; Cesari, M.; Mazzei, A. *J. Organomet. Chem.* **1977**, *136*, 13. [e] Small, R. W. H.; Worrall, I. J. *Acta Crystallogr., Sect. B: Struct. Sci.* **1982**, *B38*, 86. [f] Cowley, A. H.; Jones, R. A.; Kidd, K. B.; Nunn, C. M. *J. Organomet. Chem.* **1988**, *341*, C1. [g] Griffin, R. T.; Henrick, K.; Matthews, R. W.; McPartlin, M. *J. Chem. Soc., Dalton Trans.* **1978**, 1550. [h] Steinfink, H.; Post, B.; Fankuchen, I. *Acta Crystallogr.* **1955**, *8*, 420. [i] Haas, A.; Kutsch, H. J.; Krüger, C. *Chem. Ber.* **1987**, *120*, 1045. [j] Dräger, V. M.; Mathiasch, B.; Ross, L.; Ross, M. *Z. Anorg. Allg. Chem.* **1983**, *506*, 99. [k] Begley, M. G.; Gaffney, C.; Harrison, P. G.; Steel, A. *J. Organomet. Chem.* **1985**, *289*, 281. [l] Jost, K. H.; Schneider, M. *Acta Crystallogr., Sect. B: Struct. Sci.* **1981**, *B37*, 222. [m] Hoskins, B. F.; Piko, P. M.; Tiekink, E. R. T.; Winter, G. *Inorg. Chim. Acta* **1983**, *84*, L13. [n] Bochkarev, M. N.; Razuvaev, G. A. *J. Organomet. Chem.* **1980**, *199*, 205. [o] Einstein, F. W.; Jones, C. H.; Jones, T.; Sharma, R. D. *Can. J. Chem.* **1983**, *61*, 2611. [p] Sheldrick, W. S. *Z. Naturforsch.* **1981**, *37b*, 653. [q] Ueyama, N.; Sugawara, T.; Sasaki, K.; Nakamura, A.; Yamashita, S.; Wakatsuki, Y.; Yamazaki, H.; Yasuoka, N. *Inorg. Chem.* **1988**, *27*, 741. [r] Corwin, D. T., Jr.; Gruff, E. S.; Koch, S. A. *J. Chem. Soc., Chem. Commun.* **1987**, 966. [s] Sikirica, M.; Grdenic', D.; Cimas, S. *Acta Crystallogr., Sect. B: Struct. Sci.* **1982**, *B38*, 926. [t] Benac, B. L.; Cowley, A. H.; Jones, R. A.; Nunn, C. M.; Wright, T. C. *J. Am. Chem. Soc.* **1989**, *111*, 4986. [u] Onuma, S.; Shibata, S. *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **1985**, *C41*, 1181. [v] Brauer, D. J.; Burger, H.; Moretto, H. H.; Wannagat, U.; Wiegel, K. *J. Organomet. Chem.* **1979**, *170*, 161. [w] Frohn, H. J.; Jakobs, S.; Henkel, G. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 1506.

estimated by 0.106 Å using an Al-N bond order of $^1/_2$. The calculated bond angles within the four-membered ring are also overestimated, by an average of 6.8°. The other six-membered ring angles are in fairly good agreement with experiment; the N-Al-N angle is 0.1° small and the Al-N-Al angle is 4° small.

Bis[dibromo(pyridine)gallium].[31] The structure of this molecule has been determined by X-ray diffraction and shown to have a Ga-Ga bond with a trans configuration of the pyridines. The Ga-Br bond distances are well reproduced by UFF (in error by only 0.029 Å). The Ga-N dative bonds are too long by 0.043 Å, and the Ga-Ga bond is 0.1 Å long. The Br-Ga-Br angle is 3.7° large and the Ga-Ga-Br bond angle is 7.5° too small.

Dodecamethylcyclo-2,4,6-triinda-1,3,5-triarsane.[32] X-ray studies have shown that this indium-arsenic compound possesses a puckered In_3As_3 ring. Three In atoms and one As atom are virtually coplanar, and the other two As atoms lie above and below this plane, respectively. Although the gross conformation of this ring is reproduced by UFF, the quantitative agreement between UFF and experiment is only fair. The average calculated In-As distance is 0.037 Å long. Because this bonding is a combination of both polar covalent bonding and a III-V dative interaction a bond order of $^3/_4$ was used. The calculated C-In-C angles are 11.8° large on average and the C-As-C angles are 25° small on average.

Diethyldithiocarbamatodiphenylthallium(III).[33] The experimental coordination geometry around Tl is a highly distorted tetrahedron with a large C-Tl-C angle (148°) and small S-Tl-S angle (65°). The tetrahedral atom type Tl3_3 is inadequate to describe the central coordination of this molecule, giving a calculated C-Tl-C bond angle too small by 44°. The Tl in the $Tl(Ph)_2^+$ unit is isoelectronic with Hg in the linear $Hg(CH_3)_2$, and thus this complex might be more correctly thought of as a linear $Tl(Ph)_2^+$ weakly coordinated by the diethyldithiocarbamate ligand. The calculated Tl-S dative/covalent bonds are 0.109 Å short, even using a bond order of $^1/_2$ for the dative bond. The calculated S-Tl-S angle is 2.7° large and the S-C-S angle is 6.2° small. The covalent bond between S and the tetrahedral Tl center opens up the S-Tl-S angle and thus forces the S-C-S angle to shrink from the experimentally observed angle of 121.8°. The calculated Tl-C bond distances are 0.051 Å long. The calculated C-S double bond is 0.021 Å long and the C-S single bond is 0.075 Å long. The C-N bond is 0.017 Å short.

Octamethylcyclotetrasiloxane.[34] X-ray studies have shown that this eight-membered siloxane ring is puckered, with Si-O-Si angles of 142°. As discussed above, the correct description of Si-O-Si linkages by molecular mechanics is still a matter of concern; the Si-O bond distances and Si-O-Si angles are very sensitive to the nature of the other substituents bound to Si. Agreement between UFF and experiment is fair for this molecule; the calculated Si-O distances are 0.058 Å short and the Si-O-Si bond angle is 3.1° large. The calculated Si-C distances are 0.054 Å short and the C-Si-C angles are 3.6° large. The O-Si-O bond angle is only 0.5° too large.

1,3,5,7-Tetrakis(trifluoromethyl)-2,4,6,8,9,10-hexathia-1,3,5,7-tetragermaadamantane.[35] The three-dimensional structure of this Ge-S analogue of adamantane is well reproduced by UFF. The calculated Ge-S bond distances are only 0.011 Å long. The Ge-C distances are 0.05 Å short and the F-C distances are 0.07 Å long. The calculated S-Ge-S angles are only 0.9° large and the Ge-S-Ge angles are 2.4° small.

Dodecaphenylcyclohexastannane.[36] In contrast to the difficulties encountered in correctly predicting Si-Si bond lengths

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(31) Small, R. W. H.; Worrall, I. J. *Acta Crystallogr., Sect. B: Struct. Sci.* **1982**, *B38*, 86.

(32) Cowley, A. H.; Jones, R. A.; Kidd, K. B.; Nunn, C. M. *J. Organomet. Chem.* **1988**, *341*, C1.

(33) Griffin, R. T.; Henrick, K.; Matthews, R. W.; McPartlin, M. *J. Chem. Soc., Dalton Trans.* **1978**, 1550.

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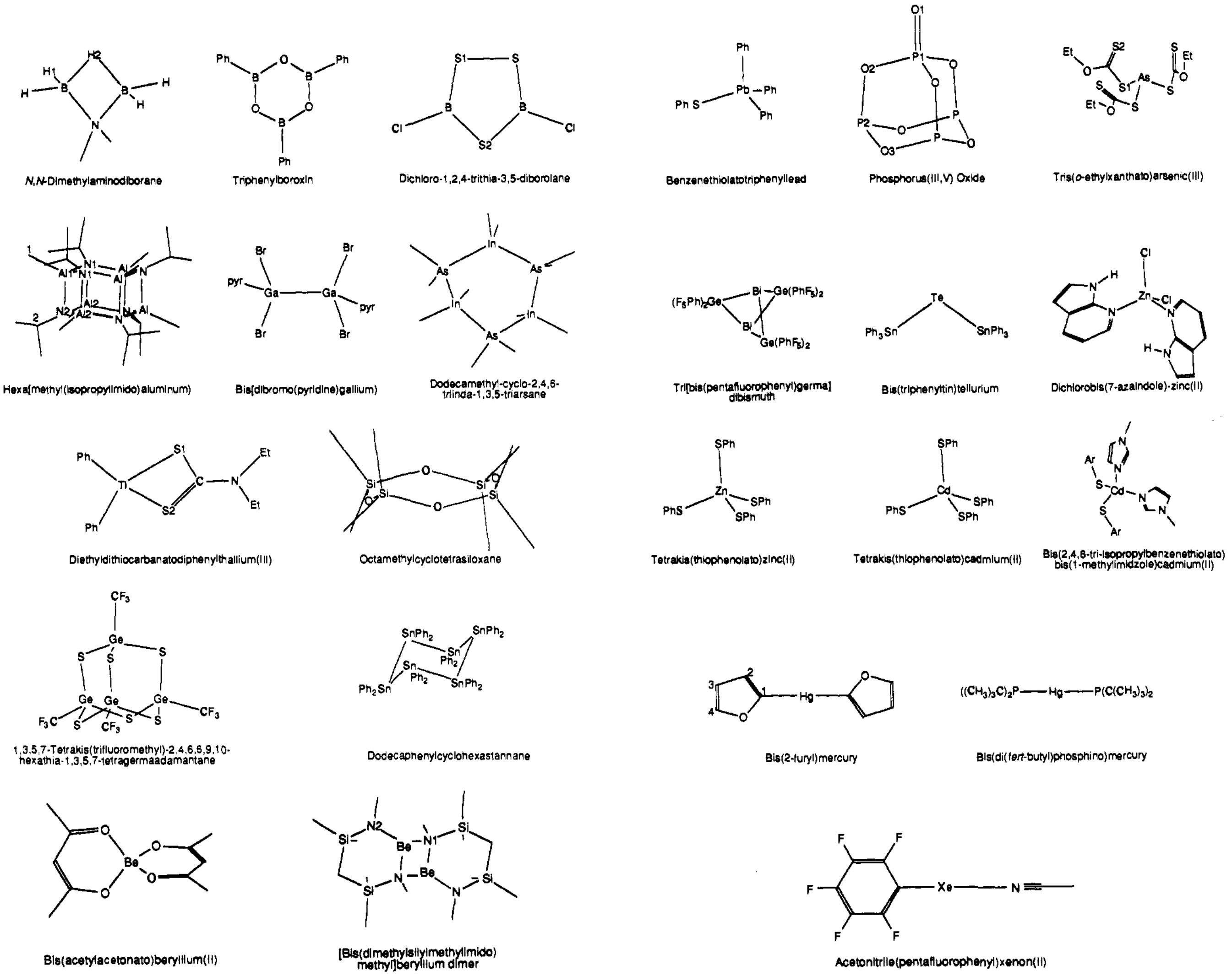

Figure 2. Structural formulas and numbering of atoms for a set of main group molecules.

reported in the second paper of this series, the structure of this Sn ring is well reproduced by UFF. The calculated Sn–Sn bond distances are underestimated by only 0.001 Å, and the Sn–C distances are underestimated by 0.036 Å. The calculated Sn–Sn–Sn angles are 1.8° small and the C–Sn–C angles are 3.6° large. The Sn–Sn–Sn–Sn dihedral angle is 5.3° large.

Benzenethiolatotriphenyllead.[37] The agreement between experiment and UFF is fairly good for this molecule. Calculated Pb–C distances are 0.027 Å short, and the Pb–S distance is only 0.022 Å short.

Phosphorus(III,V) Oxide.[38] The geometry of this molecule has been shown by X-ray crystallography to consist of an adamantane-like P_4O_6 core, with one additional O atom in a terminal position. As would be expected from the discussion of bridging oxides and multiple electronegative substituents above, the structure of P_4O_7 is not well reproduced by UFF. The P–O single bonds are between 0.058 Å and 0.11 Å long, and the P–O hypervalent bond is 0.02 Å short (bond order of 3). The O–P–O bond angles are between 10° small and 10° large. The P–O–P angles are between 8 and 13° small.

Tris(*o*-ethylxanthato)arsenic(III).[39] The structure of this molecule has been determined by X-ray diffraction, and the geometry around the As is shown to be intermediate between trigonal prismatic and octahedral. The xanthate moiety in the molecule bonds asymmetrically, with short (2.307 Å) and long As–S (2.956 Å) bonds. The short As–S covalent bonds are well described by UFF, only underestimated by 0.018 Å. The long As–S bonds are not explicitly included in the force field, and as such are not predicted by UFF; the bond lengths are thus overestimated by 0.374 Å. The calculated S–C single bonds are 0.068 Å long and the S–C double bonds are 0.197 Å short. The C–O bonds are 0.09 Å long. The S–As–S angle is only 0.8 Å in error. The As–S–C angle is 3.0° large.

Tris[bis(pentafluorophenyl)germa]dibismuth.[40] The heteroelemental framework of this compound was found by X-ray crystallography to be trigonal bipyramid, where the two apical Bi atoms are bonded by three bis(pentafluorophenyl)germyl bridges. The experimental Ge–Bi–Ge and Bi–Ge–Bi angles are significantly smaller than the ideal values of 90° and 109.5°, respectively. The bond distances are well described by UFF. The calculated Be–Ge distances are only 0.044 Å short, and the calculated Ge–C distances are 0.045 Å short. The calculated Ge–Bi–Ge bond angles are 8.7° large and the Be–Ge–Bi angles 11.3° small, but both angles are smaller than the ideal values, as in the experimental structure.

Bis(triphenyltin)tellurium.[41] This ether analogue exhibits a bent structure, and the geometry about the Sn atoms is essentially tetrahedral. The calculated Te–Sn bond distances are 0.035 Å long, and the Sn–C bond distances are 0.018 Å short. The

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[37] Begley, M. G.; Gaffney, C.; Harrison, P. G.; Steel, A. *J. Organomet. Chem.* **1985**, *289*, 281.

[38] Jost, K. H.; Schneider, M. *Acta Crystallogr., Sect. B: Struct. Sci.* **1981**, *B37*, 222.

[39] Hoskins, B. F.; Piko, P. M.; Tiekink, E. R. T.; Winter, G. *Inorg. Chim. Acta* **1983**, *84*, L13.

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[41] Einstein, F. W.; Jones, C. H.; Jones, T.; Sharma, R. D. *Can. J. Chem.* **1983**, *61*, 2611.

calculated Sn–Te–Sn bond angle is 11.2° small. For further discussion of these analogues of dimethyl ether, see above.

Dichlorobis(7-azaindole)zinc(II).[42] The Zn–Cl distances are well described by UFF, only 0.021 Å short. The dative Zn–N distances are calculated to be too long by 0.007 Å. The distortion from pure tetrahedral observed experimentally for this compound is not reproduced by the force field. The Cl–Zn–Cl bond angle is 8.3° small and the N–Zn–N angle is 8.9° too large.

Tetrakis(thiophenolato)zinc(II).[43] The $ZnSn_4$ core of this zinc thiolate complex was found by X-ray crystallography to be distorted tetrahedral; S–Zn–S angles range from 99.9° to 117.2°. The distortion is not reproduced by UFF; computed angles range only from 109.4° to 109.5°. The Zn–S bond is a mixture of both covalent and dative, so a bond order of $^3/_4$ was used and the computed results are in good agreement with experiment; on average, the bond lengths are overestimated by 0.027 Å. The calculated S–C bond distances are 0.05 Å long. The Zn–S–C bond angles are 6.9° small on average.

Tetrakis(thiophenolato)cadmium(II).[44] This molecule has been structurally characterized by X-ray crystallography, and the CdS_4 core was found to be distorted tetrahedral, with S–Cd–S angles ranging from 98.9° to 116.6°. As with the Zn analogue above, the distortion is not reproduced by UFF; computed angles range only from 109.4° to 109.5°. The Cd–S bonds are a mixture of covalent and dative, so a bond order of $^3/_4$ was used and the distances are fairly well described by UFF; the bond lengths are overestimated by 0.044 Å on average (if a bond order of 1 is used the bond lengths are underestimated by 0.043 Å). The calculated S–C bond distances are 0.052 Å long. The Cd–S–C bond angles are 8.8° small on average.

Bis(2,4,6-triisopropylbenzenethiolato)bis(1-methylimidazole)-cadmium(II).[45] The CdS_2N_2 core in this molecule is known to be significantly distorted from tetrahedral symmetry with an S–Cd–S angle of 126.3° and a N–Cd–N angle of 93.7°. The distortion is not predicted by UFF; the S–Cd–S angle is underestimated by 15.2° and the N–Cd–N angle is overestimated by 13°. In contrast to the results for the tetrathiophenolato cadmium complex above, the calculated Cd–S distances in this molecule are in excellent agreement with experiment (short by 0.005 Å). The calculated dative Cd–N distances are 0.001 Å long.

Bis(2-furyl)mercury.[46] X-ray studies have shown that this molecule is linear with an Hg–C bond distance of 2.059 Å. The calculated Hg–C distance is only 0.005 Å too long. The furyl ring distance errors are as expected from the organic benchmark paper results.[19]

Bis(di(*tert*-butyl)phosphino)mercury.[47] The central Hg atom of this molecule has two-coordinate linear geometry. The calculated bond distances are in good agreement with experiment. The calculated Hg–P distances are 0.010 Å long, on average. The calculated P–C distances are 0.015 Å and 0.019 Å long. The calculated P–Hg–P angle is 7.1° smaller than experiment.

Bis(acetylacetonato)beryllium(II).[48] The geometry around the Be has been shown by X-ray studies to be distorted tetrahedral with O–Be–O angles in the range 108.3–111.9°. The O–Be–O angles calculated by UFF are in good agreement with the experimental results, only overestimated by an average of 2.6°. The calculated Be–O distances are 0.085 Å long, and the C–O distances are an average of 0.033 Å long.

[Bis(dimethylsilylmethylimido)methyl]beryllium Dimer.[49] UFF predicts the three-dimensional structure of this molecule well; the calculated Be–N1 distances are 0.021 Å long. The calculated bridging Be–N2 distances are 0.054 Å long. The calculated Be–N1–Be angles are 2.5° large and the N1–Be–N1 angles are 2.5° small.

(Acetonitrilo)(pentafluorophenyl)xenon(II) Cation.[50] The structure of this molecule has been shown by X-ray diffraction to be an C_6H_5Xe cation coordinated by the N of an acetonitrile molecule by a long bond of 2.68 Å. Using an Xe4+4 atom type to approximate Xe(II), and a bond order of $^1/_2$, the calculated dative Xe–N distance is 0.585 Å too short. The calculated Xe–C distance is in fair agreement with experiment, being underestimated by 0.087 Å.

IV. Conclusions

The magnitude of errors for main group compounds are larger than for organic compounds, though X–C bond distances are well reproduced. For X–Y polar covalent bonds the bond distance errors are generally less than 0.05 Å. Several bond types are only fairly well described by UFF: hypervalent X–O, X–N bonds, where bond length errors are on the order of 0.05 Å (bond order 3); dative bonds where bond length errors as large as 0.04 Å are observed (bond order $^1/_2$); compounds with multiple electronegative substituents about an electropositive center where errors can approach 0.1 Å. In addition, there is an important interplay between degree of ionicity, bond lengths, and X–O–X bond angles unaccounted for in a Universal force field.

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 main group compounds such as the C–Tl–C bond in diethyldithiocarbamatodiphenylthallium(III), where the electronic structure is incorrectly described.

Future efforts will be directed toward understanding these very important cases.

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