Ab Initio Study of the Structures, Properties, and Heats of Formation of Fluorochloromethanes and -silanes, $CH_{4-m-n}F_mCl_n$ and $SiH_{4-m-n}F_mCl_n$ ($m + n = 0-4$)

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Equilibrium geometries and vibrational frequencies for $CH_{4-m-n}F_mCl_n$ and $SiH_{4-m-n}F_mCl_n$ ($m + n = 0-4$) were computed at the HF/6-31G* levels; electron correlation contributions were calculated at the MP4/6-31G** level. Heats of formation were obtained from isodesmic reactions using the experimental $\Delta H_f°$ for AH_4, AF_4, and ACl_4 (A = C, Si). Good agreement between theory and experiment is found for $CH_{4-m-n}F_mCl_n$. For the mixed fluorochlorosilanes, the calculations predict the following heats of formation (in kcal/mol at 298 K and 1 atm): SiH_2FCl, -129.3 ± 3; $SiHF_2Cl$, -230.3 ± 3; $SiHFCl_2$, -171.6 ± 3; SiF_3Cl, -329.5 ± 3; SiF_2Cl_2, -272.9 ± 3; $SiFCl_3$, -215.8. Trends in the bond lengths, AH vibrational frequencies, and stabilization energies can be explained as a balance between electrostatic effects due to the electronegative substituents and negative hyperconjugation from the halogen lone pairs to adjacent σ^* orbitals.

Introduction

Halogenated silanes are key intermediates in silicon chemistry[1,2] as well as important reactants in chemical vapor deposition (CVD) of silicon.[3–5] Considerable experimental and theoretical information is available on the thermochemistry of the fluorosilanes,[6–13] $SiH_{4-n}F_n$, and the chlorosilanes,[6–9,14] $SiH_{4-n}Cl_n$, but much less has been published on the mixed fluorochlorosilanes.[6–9] The structures and thermochemistry of the mixed fluorochloromethanes, by comparison, are relatively well-known[6,15–17] because of their commercial importance. The properties and energetics of fluorine substituted compounds are often quite different from other halogenated species. As a first approximation, the properties and energetics of these molecules might be expected to vary linearly with the number of substituents of a given type and with the electronegativity of the substituents. Deviations from linearity in the heats of formation of some of these compounds have already been pointed out.[7,10–14] Nonlinearities in the Si–H stretching frequencies have also been noted for halosilanes with increasing numbers of fluorine substituents.[18–21] The purpose of this paper is to examine the trends in the thermodynamics and a number of related properties for the mixed fluorine and chlorine substituted methanes and silanes using ab initio molecular orbital methods.

Conformational, structural, and energetic effects of substituents on a central atom have been discussed widely within the context of the anomeric effect.[22–30] Numerous theoretical studies over the past 20 years have culminated in an explanation of the anomeric effect that balances electrostatic effects against negative hyperconjugation. As shown in Figure 1, electrostatic effects resulting from electronegative substituents shorten and strengthen all bonds attached to the central atom. On the other hand, hyperconjugation, i.e. stabilizing orbital interactions between the halogen lone pairs donating into the neighboring σ^* orbitals (partially offset by destabilizing four electron interactions between the lone pairs and the occupied σ orbitals), has a net effect of shortening the bond of the donor and lengthening the bond of the acceptor, as well as lowering the energy of the molecule. We use these two effects to interpret the variations in the structures and energetics of the fluorochloromethanes and -silanes.

Computational Method

Ab initio molecular orbital (MO) calculations were carried out with the GAUSSIAN series of programs[31] using split valence and polarization basis sets (3-21G, 6-31G*, 6-31G**).[32,33] All geometries were fully optimized at the Hartree–Fock level with the 3-21G and 6-31G* basis sets using analytical gradient methods.[34]

Figure 1. Bond length changes (open arrows) accompanying halogen substitution. (a) The electrostatic effect shortens all bonds attached to the central atom. (b) Negative hyperconjugation from a halogen lone pair on X to an adjacent A–H or A–Y σ^* orbital shortens the A–X bond and lengthens the acceptor bond.
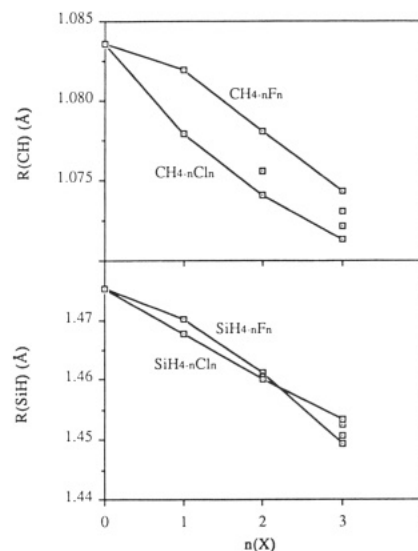
Figure 2. Variation of the C–H and Si–H bond lengths (computed at the HF/6-31G* level) with the number of halogen substituents, $n(X)$.

Vibrational frequencies, zero point energies, and thermal corrections were obtained at the HF/6-31G* level using analytical second derivatives.[35] Fourth-order Møller–Plesset perturbation theory[36] in the space of single, double, triplet, and quadruple excitations (MP4SDTQ, frozen core) was used to estimate electron correlation. For a fair number of these halogenated compounds, it was possible to obtain the structural and energetic information from previous publications[10–14] and from the Carnegie-Mellon Quantum Chemistry Archive.[37]

Results and Discussion

Geometries. The optimized geometrical parameters are presented in Table I. The 3-21G data have been included for comparison with calculations on larger halogenated alkanes and silanes, for which HF/6-31G* calculations may be less practical. The

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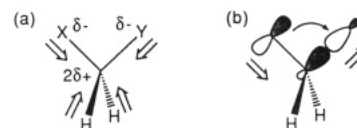† Present address: Department of Chemistry, MSU-Iligan Institute of Technology, Iligan City, 9200, Philippines.

TABLE I: Geometrical Parameters for $CH_{4-m-n}F_mCl_n$ and $SiH_{4-m-n}F_mCl_n$[a]

molecule	A–H	A–F	A–Cl	HAH	HAF	HACl	FAF	FACl	ClACl
				HF/3-21G					
CH_4	1.0829			109.47					
CH_3F	1.0796	1.4035		109.53	109.41				
CH_3Cl	1.0736		1.8919	112.49		106.25			
CH_2F_2	1.0733	1.3723		111.85	109.01		108.91		
CH_2FCl	1.0696	1.3691	1.8851	113.99	111.33	105.47		108.78	
CH_2Cl_2	1.0688		1.8527	114.47		107.90			110.81
CHF_3	1.0661	1.3452			110.63		108.29		
CHF_2Cl	1.0662	1.3447	1.8670		111.90	106.54	109.77	108.28	
$CHFCl_2$	1.0663	1.3533	1.8457		112.44	108.07		109.02	110.19
$CHCl_3$	1.0670		1.8350			108.38			110.54
CF_4		1.3250					109.47		
CF_3Cl		1.3290	1.8335				109.54	109.40	
CF_2Cl_2		1.3352	1.8359				109.95	109.10	110.51
$CFCl_3$		1.3465	1.8332					108.58	110.35
CCl_4			1.8324						109.47
				HF/6-31G*					
CH_4	1.0836			109.47					
CH_3F	1.0819	1.3647		109.84	109.09				
CH_3Cl	1.0779		1.7848	110.47		108.45			
CH_2F_2	1.0781	1.3382		112.47	108.93		108.60		
CH_2FCl	1.0756	1.3419	1.7718	112.03	109.43	108.01		109.89	
CH_2Cl_2	1.0741		1.7682	111.08		108.24			112.85
CHF_3	1.0743	1.3166			110.44		108.49		
CHF_2Cl	1.0731	1.3205	1.7589		110.10	109.26	108.30	109.53	
$CHFCl_2$	1.0722	1.3287	1.7585		109.59	108.54		109.03	112.08
$CHCl_3$	1.0713		1.7627			107.58			111.30
CF_4		1.3018					109.47		
CF_3Cl		1.3063	1.7467				108.67	110.26	
CF_2Cl_2		1.3128	1.7518				107.89	109.15	112.22
$CFCl_3$		1.3220	1.7579					108.00	110.90
CCl_4			1.7664						109.47
				HF/3-21G					
SiH_4	1.4866			109.47					
SiH_3F	1.4780	1.6350		109.74	109.20				
SiH_3Cl	1.4676		2.1904	111.78		107.05			
SiH_2F_2	1.4644	1.6186		113.2			105.4		
SiH_2FCl	1.4634	1.6226	2.1601	115.70	109.74	106.40		108.55	
SiH_2Cl_2	1.4646		2.1607	115.99		107.73			109.84
$SiHF_3$	1.4454	1.6013			112.07		106.75		
$SiHF_2Cl$	1.4491	1.6073	2.1247		112.20	108.82	105.78	108.87	
$SiHFCl_2$	1.4541	1.6144	2.1302		111.27	109.78		108.34	109.28
$SiHCl_3$	1.4581		2.1384			109.78			109.16
SiF_4		1.5843					109.47		
SiF_3Cl		1.5924	2.0898				108.17	110.74	
SiF_2Cl_2		1.6014	2.1000				106.42	109.95	110.55
$SiFCl_3$		1.6102	2.1115					108.76	110.17
$SiCl_4$			2.1233						109.47
				HF/6-31G*					
SiH_4	1.4753			109.47					
SiH_3F	1.4701	1.5941		110.17	108.76				
SiH_3Cl	1.4676		2.0666	110.62		108.30			
SiH_2F_2	1.4613	1.5810		113.41	108.93		107.56		
SiH_2FCl	1.4605	1.5834	2.0479	113.26	109.03	108.48		108.46	
SiH_2Cl_2	1.4602		2.0504	112.92		108.45			110.16
$SiHF_3$	1.4494	1.5687			110.86		108.04		
$SiHF_2Cl$	1.4507	1.5714	2.0269		110.41	110.89	107.68	108.68	
$SiHFCl_2$	1.4525	1.5756	2.0314		109.93	110.17		108.89	110.35
$SiHCl_3$	1.4534		2.0376			109.36			109.58
SiF_4		1.5570					109.47		
SiF_3Cl		1.5605	2.0072				108.76	110.17	
SiF_2Cl_2		1.5649	2.0132				108.07	109.21	111.86
$SiFCl_3$		1.5701	2.0205					108.26	110.66
$SiCl_4$			2.0290						109.47

[a] Bond lengths in Å, angles in deg. Experimental data can be found in refs 6 and 15–17.

changes in the geometries are the same for both basis sets, but the range is 20–40% too large for the smaller basis set. The experimental and theoretical bond lengths show the same trends, i.e. shortening on increasing substitution. Because of the difficulty in obtaining uniformly accurate experimental geometries for the entire set of molecules, the theoretical geometries will be used to discuss the trends.

The HF/6-31G* optimized bond lengths for C–H and Si–H are summarized in Figure 2. From the analysis of the anomeric effect,[22-30] it is known that bond lengths in these systems are affected by two competing factors, as shown in Figure 1. Electrostatic effects arising from electron withdrawing substituents shorten all bonds attached to the central atom. As expected, Figure 2 shows that increasing halogen substitution decreases the

TABLE II: Vibrational Frequencies for CH$_{4-m-n}$F$_m$Cl$_n$ and SiH$_{4-m-n}$F$_m$Cl$_n$[a]

molecule	frequencies								
				HF/3-21G					
CH$_4$	1520	1520	1520	1740	1740	3187	3280	3280	3280
CH$_3$F	1143	1278	1278	1663	1686	1686	3227	3293	3293
CH$_3$Cl	662	1095	1095	1500	1638	1638	3280	3399	3399
CH$_2$F$_2$	534	1182	1250	1261	1401	1639	1733	3300	3363
CH$_2$FCl	355	688	1066	1200	1349	1489	1672	3341	3435
CH$_2$Cl$_2$	278	674	731	935	1257	1386	1588	3361	3466
CHF$_3$	523	523	716	1218	1331	1331	1590	1590	3423
CHF$_2$Cl	351	383	594	762	1210	1328	1433	1545	3431
CHFCl$_2$	271	352	421	704	773	1234	1348	1443	3429
CHCl$_3$	260	260	353	637	778	778	1322	1322	3437
CF$_4$	454	454	654	654	654	971	1513	1513	1513
CF$_3$Cl	342	342	442	569	569	780	1176	1451	1451
CF$_2$Cl$_2$	257	317	408	414	527	649	885	1231	1395
CFCl$_3$	242	242	335	380	380	486	846	846	1253
CCl$_4$	221	221	311	311	311	435	816	816	816
				HF/6-31G*					
CH$_4$	1488	1488	1488	1703	1703	3197	3302	3302	3302
CH$_3$F	1186	1312	1312	1652	1653	1653	3232	3313	3313
CH$_3$Cl	782	1138	1138	1538	1629	1629	3267	3370	3370
CH$_2$F$_2$	571	1238	1257	1304	1410	1639	1713	3295	3367
CH$_2$FCl	418	825	1118	1226	1388	1539	1669	3319	3400
CH$_2$Cl$_2$	312	774	842	995	1315	1451	1619	3336	3418
CHF$_3$	551	551	762	1262	1328	1328	1583	1583	3401
CHF$_2$Cl	399	449	647	893	1256	1311	1497	1550	3400
CHFCl$_2$	305	404	498	810	908	1253	1424	1495	3402
CHCl$_3$	289	289	404	731	874	874	1399	1399	3408
CF$_4$	473	473	683	683	683	1004	1473	1473	1473
CF$_3$Cl	381	381	520	609	609	860	1256	1419	1419
CF$_2$Cl$_2$	289	356	473	478	499	729	1036	1274	1364
CFCl$_3$	272	272	385	437	437	584	966	966	1270
CCl$_4$	244	244	348	348	348	503	902	902	902
				HF/3-21G					
SiH$_4$	973	973	973	1046	1046	2286	2286	2286	2295
SiH$_3$F	799	799	943	990	990	1132	2338	2338	2352
SiH$_3$Cl	475	684	684	999	1009	1009	2346	2357	2357
SiH$_2$F$_2$	341	782	805	934	996	1041	1127	2430	2435
SiH$_2$FCl	241	502	651	808	963	971	1073	2422	2435
SiH$_2$Cl$_2$	177	471	528	592	757	923	990	2397	2421
SiHF$_3$	315	315	430	922	946	946	1119	1119	2556
SiHF$_2$Cl	215	272	373	536	872	937	979	1099	2523
SiHFCl$_2$	172	237	292	491	567	809	908	1021	2482
SiHCl$_3$	168	168	229	449	554	554	823	823	2446
SiF$_4$	270	270	392	392	392	844	1156	1156	1156
SiF$_3$Cl	211	211	339	349	349	568	945	1131	1131
SiF$_2$Cl$_2$	166	193	271	297	324	491	632	1001	1103
SiFCl$_3$	155	155	227	268	268	425	608	608	1032
SiCl$_4$	143	143	205	205	205	381	583	583	583
				HF/6-31G*					
SiH$_4$	1016	1016	1016	1051	1051	2385	2385	2385	2393
SiH$_3$F	795	795	943	1051	1051	1111	2421	2421	2429
SiH$_3$Cl	571	719	719	1043	1043	1049	2429	2433	2433
SiH$_2$F$_2$	342	780	808	932	983	1083	1093	2480	2481
SiH$_2$FCl	266	589	701	806	960	1025	1069	2476	2483
SiH$_2$Cl$_2$	201	553	617	648	782	971	1046	2468	2480
SiHF$_3$	320	320	448	913	932	932	1083	1083	2556
SiHF$_2$Cl	244	294	391	609	916	925	973	1070	2543
SiHFCl$_2$	196	292	326	562	646	901	913	1008	2526
SiHCl$_3$	189	189	270	521	634	634	888	888	2513
SiF$_4$	274	274	406	406	406	848	1107	1107	1107
SiF$_3$Cl	233	233	363	363	368	625	938	1093	1093
SiF$_2$Cl$_2$	186	220	294	332	341	549	699	984	1076
SiFCl$_3$	176	176	254	297	297	489	677	677	1015
SiCl$_4$	159	159	238	238	238	446	656	656	656

[a] Calculated harmonic frequencies in cm^{-1}. Experimental data can be found in refs 6 and 15–17.

C–H and Si–H bond lengths. However, if only electrostatic effects were operative, one would have expected a greater shortening from the more electronegative fluorine than from chlorine. The electrostatic effect is partially offset by negative hyperconjugation, i.e. mixing of a π-type long pair on a halogen with the σ and σ^* orbitals on an adjacent bond, which shortens the bond of the donor and lengthens the bond of the acceptor. Analysis of the bond

separation energies (see below and more extensive compilations in refs 23–27) and natural bond orbital (NBO) decompositions of the orbital interactions[26-28] have shown that negative hyperconjugation is larger for fluorine than for chlorine. Thus the greater electrostatic C–H shortening on F substitution is balanced by a greater lengthening due to hyperconjugation, resulting in a smaller net shortening of the C–H bond for F substitution than
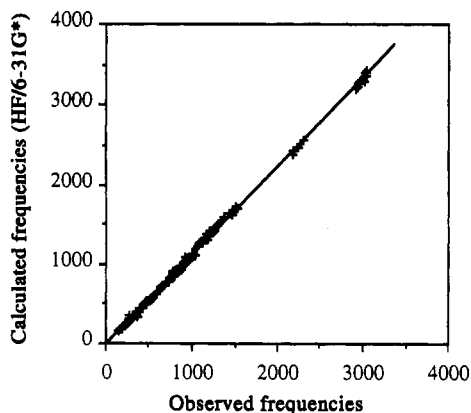
Figure 3. Comparison of the harmonic frequencies calculated at the HF/6-31G* level with the observed anharmonic frequencies of the fluorochloromethanes and -silanes.
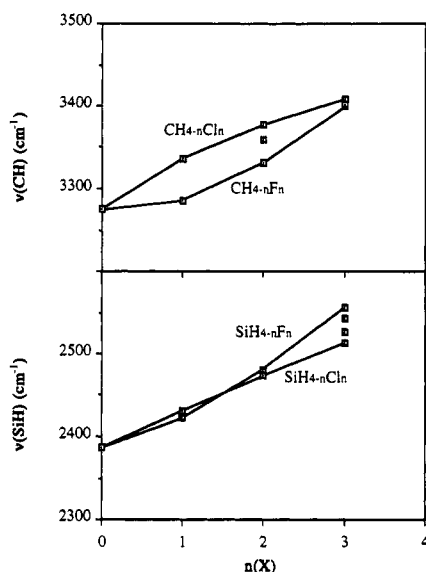

Figure 4. Variation of the average C–H and Si–H stretching frequencies (computed at the HF/6-31G* level) with the number of halogen substituents, $n(X)$.

TABLE III: Dipole Moments and Charges for $CH_{4-m-n}F_mCl_n$ and $SiH_{4-m-n}F_mCl_n{}^a$

molecule	μ	q_A	q_H	q_F	q_{Cl}
CH_4	0.000	−0.473	0.118		
CH_3F	1.990	−0.063	0.115	−0.401	
CH_3Cl	2.247	−0.536	0.215		−0.109
CH_2F_2	2.049	0.452	0.148	−0.374	
CH_2FCl	2.171	0.126	0.159	−0.360	−0.085
CH_2Cl_2	1.994	−0.452	0.259		−0.032
CHF_3	1.698	0.883	0.154	−0.346	
CHF_2Cl	1.656	0.556	0.155	−0.332	−0.048
$CHFCl_2$	1.540	0.125	0.205	−0.322	−0.004
$CHCl_3$	1.353	−0.400	0.299		0.034
CF_4	0.000	1.313		−0.328	
CF_3Cl	0.271	0.922		−0.308	0.004
CF_2Cl_2	0.395	0.531		0.298	0.033
$CFCl_3$	0.430	0.100		−0.292	0.064
CCl_4	0.000	−0.364			0.091
SiH_4	0.000	0.545	−0.136		
SiH_3F	1.472	0.993	−0.160	−0.514	
SiH_3Cl	2.067	0.727	−0.120		−0.367
SiH_2F_2	1.708	1.326	−0.165	−0.498	
SiH_2FCl	1.936	1.100	−0.134	−0.486	−0.346
SiH_2Cl_2	1.947	0.841	−0.100		−0.320
$SiHF_3$	1.551	1.593	−0.148	−0.482	
$SiHF_2Cl$	1.554	1.384	−0.128	−0.471	−0.313
$SiHFCl_2$	1.486	1.156	−0.104	−0.461	−0.295
$SiHCl_3$	1.362	0.903	−0.076		−0.276
SiF_4	0.000	1.855		−0.464	
SiF_3Cl	0.199	1.642		−0.455	−0.275
SiF_2Cl_2	0.287	1.421		−0.446	−0.265
$SiFCl_3$	0.300	1.188		−0.435	−0.251
$SiCl_4$	0.000	0.931			−0.233

^{a} Computed at the HF/6-31G* level; dipole moments in D; charges by Mulliken population analysis.

for Cl. For the silanes, the contribution from hyperconjugation is smaller, resulting in a very similar Si–H shortening for both F and Cl. The range of bond length changes is considerably larger for Si–H than for C–H, possibly reflecting the more polarizable nature of the Si–H bond.

Except for $SiH_{4-n}Cl_n$, there is significant curvature in the changes in the A–H bond lengths. This appears to be due to saturation of both the electrostatic effect and the hyperconjugation with increasing halogen substitution. Saturation of the electrostatic effect would cause a curve upward, since additional electron substituents would be less effective at withdrawing more charge and further shortening the bond. As noted above, $CH_{4-n}Cl_n$ is dominated by the electrostatic terms; an upward curvature is seen for this series in Figure 2. On the other hand, saturation of the negative hyperconjugation effect would diminish the bond lengthening caused by additional substituents, resulting in a downward curvature. As discussed in the previous paragraph, $CH_{4-n}F_n$ and $SiH_{4-n}F_n$ are dominated by the hyperconjugation terms, and Figure 2 shows a downward curvature for these species. Saturation of hyperconjugation also reduces the contribution of additional substituents to the stabilization energy (see below).

Increasing substitution by electronegative groups causes even larger changes in the halogen bond lengths than in the A–H bond lengths. Table I shows that fluorine substitution has a significantly greater effect on the heavy atom bond lengths than chlorine substitution for both the carbon and the silicon series. Both the electrostatic effect and the hyperconjugation of X = F, Cl with the A–H bonds shorten the A–X bond. The hyperconjugation

of X with an adjacent A–Y (Y = F, Cl) bond is larger than with an A–H bond[26] and contributes substantially to the stabilization energy. However, the bond length changes arising from hyperconjugation between A–X and A–Y approximately cancel because the interactions are bidirectional.

Useful trends in the angles are somewhat more difficult to distinguish. As expected from the steric size of fluorine and chlorine as well as arguments based on negative hyperconjugation,[26-28] the angles between the halogens are consistently FAF < FACl < ClACl for both the methane and silane series. Trends in the HAX angles result from a balance between steric and hyperconjugative effects. Increasing F substitution increases the HAF angle because hyperconjugation prevails over steric effects, whereas increasing Cl substitution decreases the HACl angle because of the dominance of steric effects and four electron repulsions between the lone pairs and σ orbitals of the adjacent A–Cl bonds.

Frequencies. The calculated harmonic vibrational frequencies are collected in Table II and are compared with the observed anharmonic frequencies[6,15-20] in Figure 3. As found in earlier studies,[38] the calculated harmonic frequencies are ca. 11–12% higher than the observed anharmonic frequencies; this is due to basis set effects, lack of electron correlation corrections, and the neglect of anharmonicity in the calculated frequencies. The average C–H and Si–H stretching frequencies are plotted as a function of halogen substitution in Figure 4. For the methane series, direct comparison with experiment is complicated by Fermi resonance between the C–H stretch and overtones of the C–H bends. For Si–H stretches, good agreement between theory (HF/6-31G*) and experiment is found for the slope and the curvature as a function of halogen substitution. The calculated average stretching frequencies for both C–H and Si–H increase with increasing halogen substitution. The trend is linear for ν(Si–H) with chlorine substitution but nonlinear with fluorine substitution; for ν(C–H), both fluorine and chlorine substitutions yield nonlinear trends, but the curves are bent in opposite directions. The trends and the curvatures in the A–H frequencies are nearly the mirror images of the trends in the A–H bond lengths

TABLE IV: Total Energies for $CH_{4-m-n}F_mCl_n$ and $SiH_{4-m-n}F_mCl_n$[a]

molecule	HF/6-31G*	HF/6-31G**	MP2/6-31G**	MP3/6-31G**	MP4/6-31G**	ZPE	thermal energy
			total energy				
CH₄	-40.195 17	-40.201 70	-40.364 62	-40.382 84	-40.388 61	29.98	1.79
CH₃F	-139.034 61	-139.039 73	-139.359 51	-139.373 06	-139.385 83	26.63	1.80
CH₃Cl	-499.093 15	-499.097 90	-499.378 08	-499.403 85	-499.413 58	25.54	1.86
CH₂F₂	-237.896 35	-237.899 81	-238.378 74	-238.385 98	-238.406 67	22.58	1.92
CH₂FCl	-597.936 72	-597.939 94	-598.380 77	-598.400 64	-598.418 44	21.30	2.04
CH₂Cl₂	-957.985 17	-957.988 21	-958.391 48	-958.423 23	-958.438 32	20.10	2.17
CHF₃	-336.771 64	-336.773 38	-337.412 51	-337.412 91	-337.441 61	17.65	2.10
CHF₂Cl	-696.796 90	-696.798 57	-597.401 64	-697.414 55	-697.441 00	16.30	2.28
CHFCl₂	-1056.829 29	-1056.830 85	-1057.398 06	-1057.422 91	-1057.447 11	15.01	2.47
CHCl₃	-1416.869 71	-1416.871 16	-1417.402 04	-1417.438 01	-1417.460 30	13.82	2.66
CF₄	-435.645 21	-435.645 21	-436.443 74	-436.438 00	-436.473 90	12.03	2.35
CF₃Cl	-795.663 20	-795.663 20	-796.428 31	-796.434 41	-796.469 12	10.65	2.58
CF₂Cl₂	-1155.684 68	-1155.684 68	-1156.416 16	-1156.433 65	-1156.467 09	9.29	2.81
CFCl₃	-1515.711 64	-1515.711 64	-1516.409 01	-1516.437 29	-1516.469 61	7.99	3.07
CCl₄	-1875.744 84	-1875.744 84	-1876.407 13	-1876.445 61	-1876.477 18	6.78	3.32
SiH₄	-291.225 13	-291.230 84	-291.338 99	-291.359 99	-291.365 60	21.02	1.87
SiH₃F	-390.148 40	-390.152 84	-390.424 19	-390.437 23	-390.449 60	18.61	1.95
SiH₃Cl	-750.183 41	-750.187 74	-750.413 07	-750.441 17	-750.449 14	17.78	2.08
SiH₂F₂	-489.081 81	-489.084 83	-489.521 09	-489.526 23	-489.545 48	15.70	2.20
SiH₂FCl	-849.111 00	-849.113 98	-849.504 80	-849.524 58	-849.539 94	14.83	2.36
SiH₂Cl₂	-1209.140 93	-1209.143 83	-1209.489 35	-1209.524 06	-1209.535 04	13.96	2.52
SiHF₃	-588.018 33	-588.019 85	-588.621 00	-588.618 64	-588.644 42	12.27	2.57
SiHF₂Cl	-948.043 82	-948.045 33	-948.602 10	-948.613 91	-948.636 41	11.39	2.76
SiHFCl₂	-1308.069 64	-1308.071 12	-1308.583 64	-1308.609 82	-1308.628 62	10.49	2.96
SiHCl₃	-1668.095 93	-1668.097 37	-1668.565 55	-1668.606 30	-1668.620 94	9.62	3.17
SiF₄	-686.949 84	-686.949 84	-687.714 45	-687.705 28	-687.737 00	8.49	3.00
SiF₃Cl	-1046.974 46	-1046.974 46	-1047.696 06	-1047.700 55	-1047.729 61	7.59	3.22
SiF₂Cl₂	-1406.998 80	-1406.998 80	-1407.677 52	-1407.695 77	-1407.721 86	6.69	3.45
SiFCl₃	-1767.022 90	-1767.022 90	-1767.658 67	-1767.690 82	-1767.713 55	5.80	3.68
SiCl₄	-2127.046 88	-2127.046 88	-2127.639 52	-2127.685 75	-2127.704 61	4.93	3.93

[a] Total energies in au; ZPE and thermal energies in kcal/mol at the HF/6-31G* level.

TABLE V: Isodesmic Reactions Involving $CH_{4-m-n}F_mCl_n$ and $SiH_{4-m-n}F_mCl_n$[a]

reaction	6-31G* HF	6-31G** HF	MP2	MP3	MP4
		$\Delta H_r°(298 \text{ K})$			
$^3/_4CH_4 + ^1/_4CF_4 \rightarrow CH_3F$	15.48	15.34	16.63	15.80	16.13
$^3/_4CH_4 + ^1/_4CCl_4 \rightarrow CH_3Cl$	-5.58	-5.49	-0.73	-2.29	-0.73
$^1/_2CH_4 + ^1/_2CF_4 \rightarrow CH_2F_2$	16.38	16.26	17.39	16.76	16.85
$^1/_2CH_4 + ^1/_4CF_4 + ^1/_4CCl_4 \rightarrow CH_2FCl$	6.59	6.62	10.28	8.67	9.89
$^1/_2CH_4 + ^1/_2CCl_4 \rightarrow CH_2Cl_2$	-8.18	-8.04	-2.18	-4.32	-2.07
$^1/_4CH_4 + ^3/_4CF_4 \rightarrow CHF_3$	7.96	7.90	8.21	8.11	7.90
$^1/_4CH_4 + ^1/_2CF_4 + ^1/_4CCl_4 \rightarrow CHF_2Cl$	7.64	7.62	9.19	8.18	8.70
$^1/_4CH_4 + ^1/_4CF_4 + ^1/_2CCl_4 \rightarrow CHFCl_2$	2.92	2.96	5.66	4.10	5.35
$^1/_4CH_4 + ^3/_4CCl_4 \rightarrow CHCl_3$	-6.75	-6.63	-2.51	-4.17	-2.34
$^3/_4CF_4 + ^1/_4CCl_4 \rightarrow CF_3Cl$	4.26	4.26	3.86	3.37	3.43
$^1/_2CF_4 + ^1/_2CCl_4 \rightarrow CF_2Cl_2$	6.35	6.35	5.68	4.98	5.16
$^1/_4CF_4 + ^3/_4CCl_4 \rightarrow CFCl_3$	5.09	5.09	4.46	3.92	4.13
$^3/_4SiH_4 + ^1/_4SiF_4 \rightarrow SiH_3F$	5.48	5.38	5.96	6.22	6.07
$^3/_4SiH_4 + ^1/_4SiCl_4 \rightarrow SiH_3Cl$	-1.31	-1.34	1.14	0.64	1.24
$^1/_2SiH_4 + ^1/_2SiF_4 \rightarrow SiH_2F_2$	4.27	4.17	4.24	4.73	4.36
$^1/_2SiH_4 + ^1/_4SiF_4 + ^1/_4SiCl_4 \rightarrow SiH_2FCl$	1.12	1.05	2.66	2.65	2.70
$^1/_2SiH_4 + ^1/_2SiCl_4 \rightarrow SiH_2Cl_2$	-2.49	-2.51	0.55	-0.14	0.65
$^1/_4SiH_4 + ^3/_4SiF_4 \rightarrow SiHF_3$	0.71	0.65	0.24	0.70	0.33
$^1/_4SiH_4 + ^1/_2SiF_4 + ^1/_4SiCl_4 \rightarrow SiHF_2Cl$	-0.10	-0.15	0.31	0.57	0.24
$^1/_4SiH_4 + ^1/_4SiF_4 + ^1/_2SiCl_4 \rightarrow SiHFCl_2$	-1.12	-1.15	0.10	0.03	0.01
$^1/_4SiH_4 + ^3/_4SiCl_4 \rightarrow SiHCl_3$	-2.39	-2.40	-0.31	-0.83	-0.26
$^3/_4SiF_4 + ^1/_4SiCl_4 \rightarrow SiF_3Cl$	-0.25	-0.25	-0.24	-0.12	-0.47
$^1/_2SiF_4 + ^1/_2SiCl_4 \rightarrow SiF_2Cl_2$	-0.31	-0.31	-0.37	-0.19	-0.70
$^1/_4SiF_4 + ^3/_4SiCl_4 \rightarrow SiFCl_3$	-0.21	-0.21	-0.30	-0.16	-0.56

[a] $\Delta H_r°(298 \text{ K})$ in kcal/mol.

shown in Figure 2. When one takes into account that shorter bond lengths give rise to higher frequencies,[39] it is apparent that the A–H frequencies are controlled by the same factors as the changes in the bond lengths, i.e. electrostatic effects and negative hyperconjugation.

A number of groups have developed linear fits of the number of substituents or electronegativity to experimental Si–H stretching frequencies.[18-21] Fluorine (and likewise oxygen) appears to require quadratic terms in order to obtain good fits to the experimental data. The quadratic terms arise from the curvature in the fre-

quency trends, which can be understood in terms of saturation of the electrostatic and hyperconjugative effects that control both the bond lengths and the A–H frequencies.

Charge Distribution. The dipole moments and atomic charges (by Mulliken population analysis) are collected in Table III. The usual cautions about the basis set sensitivity of Mulliken charges should be kept in mind (e.g., the large difference in the charge on the carbon in CH_3F versus CH_3Cl is an artifact of the basis set employed). Except for the monofluoro case, halogen substitution makes the hydrogens progressively more positive, as

TABLE VI: Heats of Formation for $CH_{4-m-n}F_mCl_n$ and $SiH_{4-m-n}F_mCl_n{}^a$

molecule	present calculations	previous calculations[b]	experimental value[c]
CH_4		$-16.4,^d -18.6^e$	-17.88
CH_3F	-53.0	$-56.4,^d -58.4^e$	-55.9
CH_3Cl	-19.9	$-19.0,^d -20.5^e$	-19.59
CH_2F_2	-103.6		-108.2
CH_2FCl	-60.5		-63.2
CH_2Cl_2	-22.5		-22.8
CHF_3	-163.8		-166.6
CHF_2Cl	-113.0		-115.6
$CHFCl_2$	-70.8		-68.1
$CHCl_3$	-24.0		-24.6
CF_4			-223.3
CF_3Cl	-169.6		-169.2
CF_2Cl_2	-117.8		-117.9
$CFCl_3$	-68.8		-68.1
CCl_4			-22.9
SiH_4		$6.4,^d 6.0,^e 8.0^f$	8.2
SiH_3F	-84.3	$-85.3,^d -85.0,^e -85.5,^g -85.6,^h$ -85.8^i	$-90, -94^k$
SiH_3Cl	-32.2	$-31.1,^d -31.2,^e -32.2^g$	-33.9
SiH_2F_2	-184.5	$-186.4,^g -185.7,^h -186.3^i$	-189.0
SiH_2FCl	-129.3		
SiH_2Cl_2	-74.4	-76.6^g	-76.6
$SiHF_3$	-287.1	$-288.6,^g -287.7,^h -288.2^i$	-287.0
$SiHF_2Cl$	-230.3		
$SiHFCl_2$	-171.6		
$SiHCl_3$	-117.0	-118.6^g	-118.6
SiF_4		$-381.3,^f -379.8^f$	-386.0
SiF_3Cl	-329.5		-315.0
SiF_2Cl_2	-272.9		
$SiFCl_3$	-215.8		-201.0
$SiCl_4$			-158.4

$^a \Delta H_f{}^\circ$(298 K) in kcal/mol. ^{b} Selected calculations for which the accuracy of $\Delta H_f{}^\circ$ is expected to be similar to or better than the present work. ^{c} Unless otherwise noted, experimental $\Delta H_f{}^\circ$ for carbon compounds from ref 17 and silicon compounds from ref 6. ^{d} Reference 44. ^{e} Reference 45. ^{f} Reference 46. ^{g} Reference 14. ^{h} Reference 12. ^{i} Reference 10. ^{k} Reference 42.

expected from the electron withdrawing effect of these electronegative substituents. This supports the electrostatic arguments for the A–H bond shortening and frequency increase. Curiously, for the trisubstituted species chlorine has a larger effect than fluorine on the net charge on the hydrogen. However, this is also an artifact of the population analysis, since the dipole moments for $CHF_{3-n}Cl_n$ and $SiHF_{3-n}Cl_n$ show the expected decrease as fluorines are replaced with chlorines. The trend in the charges on the halogens is also somewhat surprising—with increasing substitution, the halogens become less negative. Instead of remaining relatively constant, the electron withdrawing ability of the halogens is diminished as the number of electronegative substituents is increased; this is because the increasing number of electronegative substituents compete for the electron density in decreasing number of remaining C–H or Si–H bonds. This effect can be readily modeled using the electronegativity equalization approach[40,41] and directly supports the saturation arguments made above.

Energetics. The total energies, zero point energies (ZPE), and thermal corrections to the internal energy (298 K, 1 atm) are listed in Table IV. These are used to compute the heats of reaction for the following isodesmic reactions:

$$\left(\frac{4-m-n}{4}\right)AH_4 + \left(\frac{m}{4}\right)AF_4 + \left(\frac{n}{4}\right)ACl_4 \rightarrow AH_{4-m-n}F_mCl_n \quad (1)$$
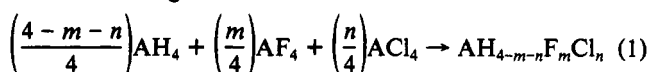
If bond energies were strictly additive, the heats of reaction for eq 1 (and any other isodesmic reaction) would be zero, and the $\Delta H_f{}^\circ$ for the partially substituted compounds could be obtained by linear interpolation from $\Delta H_f{}^\circ$ for methane or silane and the perhalo species. Inspection of Table V reveals large deviations from zero (up to 16 kcal/mol), indicating that linear interpolation of the heats of formation is a poor approximation, especially for the fluoro compounds. The calculated heats of formation reported in Table VI are obtained by combining the calculated heats of reaction for eq 1 with the experimental heats of formation for AX_4 (A = C, Si; X = H, F, Cl). Comparison with experimental results for $CH_{4-m-n}F_mCl_n$ and with higher level calculations on CH_3X and $SiH_{4-n}X_n$ indicates that the present level of theory should be accurate to ± 3 kcal/mol. The 5 kcal/mol discrepancy between theory and experiment for $\Delta H_f{}^\circ(SiH_3F)$ has been discussed be-

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TABLE VII: Bond Separation Reactions Involving $CH_{4-m-n}F_mCl_n$ and $SiH_{4-m-n}F_mCl_n{}^a$

	$\Delta H_r{}^\circ$(298 K)				
	6-31G*	6-31G**			
reaction	HF	HF	MP2	MP3	MP4
$CH_2F_2 + CH_4 \rightarrow 2CH_3F$	14.58	14.43	15.86	14.86	15.41
$CH_2FCl + CH_4 \rightarrow CH_3F + CH_3Cl$	3.31	3.24	5.61	4.84	5.51
$CH_2Cl_2 + CH_4 \rightarrow 2CH_3Cl$	-2.98	-2.94	0.72	-0.26	0.62
$CHF_3 + 2CH_4 \rightarrow 3CH_3F$	38.49	38.14	41.67	39.28	40.49
$CHF_2Cl + 2CH_4 \rightarrow 2CH_3F + CH_3Cl$	17.75	17.58	23.34	21.13	22.84
$CHFCl_2 + 2CH_4 \rightarrow CH_3F + 2CH_3Cl$	1.41	1.41	9.51	7.12	9.33
$CHCl_3 + 2CH_4 \rightarrow 3CH_3Cl$	-9.99	-9.83	0.32	-2.70	0.16
$CF_4 + 3CH_4 \rightarrow 4CH_3F$	61.94	61.38	66.50	63.19	64.53
$CF_3Cl + 3CH_4 \rightarrow 3CH_3F + CH_3Cl$	36.61	36.28	45.29	41.74	44.24
$CF_2Cl_2 + 3CH_4 \rightarrow 2CH_3F + 2CH_3Cl$	13.46	13.36	26.11	22.04	25.65
$CFCl_3 + 3CH_4 \rightarrow CH_3F + 3CH_3Cl$	-6.35	-6.21	9.98	5.01	9.82
$CCl_4 + 3CH_4 \rightarrow 4CH_3Cl$	-22.32	-21.95	-2.92	-9.16	-2.91
$SiH_2F_2 + SiH_4 \rightarrow 2SiH_3F$	6.69	6.60	7.67	7.71	7.78
$SiH_2FCl + SiH_4 \rightarrow SiH_3F + SiH_3Cl$	3.05	3.00	4.44	4.21	4.61
$SiH_2Cl_2 + SiH_4 \rightarrow 2SiH_3Cl$	-0.13	-0.16	1.73	1.42	1.83
$SiHF_3 + 2SiH_4 \rightarrow 3SiH_3F$	15.74	15.50	17.63	17.96	17.89
$SiHF_2Cl + 2SiH_4 \rightarrow 2SiH_3F + SiH_3Cl$	9.75	9.58	12.74	12.51	13.14
$SiHFCl_2 + 2SiH_4 \rightarrow SiH_3F + 2SiH_3Cl$	3.99	3.86	8.13	7.47	8.54
$SiHCl_3 + 2SiH_4 \rightarrow 3SiH_3Cl$	-1.53	-1.61	3.72	2.75	3.97
$SiF_4 + 3SiH_4 \rightarrow 4SiH_3F$	21.93	21.53	23.83	24.88	24.29
$SiF_3Cl + 3SiH_4 \rightarrow 3SiH_3F + SiH_3Cl$	15.39	15.06	19.25	19.42	19.93
$SiF_2Cl_2 + 3SiH_4 \rightarrow 2SiH_3F + 2SiH_3Cl$	8.66	8.41	14.56	13.91	15.32
$SiFCl_3 + 3SiH_4 \rightarrow SiH_3F + 3SiH_3Cl$	1.78	1.59	9.67	8.30	10.35
$SiCl_4 + 3SiH_4 \rightarrow 4SiH_3Cl$	-5.22	-5.34	4.55	2.56	4.95

$^a \Delta H_r{}^\circ$(298 K) in kcal/mol.

fore;[7,8,10-13] neither the direct experiment[42] nor linear interpolated value quoted in the JANAF tables[6] is considered reliable. The good agreement between the theoretical numbers suggests that the theoretical values may be more reliable. For the mixed fluorochlorosilanes, the JANAF tables[6] list only two values (both taken from older tabulations and reported without comment). The 14 kcal/mol difference between theory and experiment for SiF$_3$Cl and SiFCl$_3$ is much larger than the deviations for any of the other theoretical $\Delta H_f°$ listed in Table VI. This indicates unequivocally that the experimental values are in error.

One approach to analyzing the nonadditivity in the energetics involves the use of bond separation reactions:[23-28]

$$AH_{4-m-n}F_mCl_n + (m + n - 1)AH_4 \rightarrow mAH_3F + nAH_3Cl \quad (2)$$

If bond energies were strictly additive, the bond separation energies would be zero. The fact that some of the bond separation energies listed in Table VII are quite large indicates that there are strong interactions between some of the bonds. A least squares fit to the data in Table VII yields ca. +12, +4, and −0.4 kcal/mol for individual CF–CF, CF–CCl, and CCl–CCl bond interaction energies,[43] respectively (positive indicates the interaction is stabilizing). For the silicon series the values are +5, +3, and +1 kcal/mol for the SiF–SiF, SiF–SiCl, and SiCl–SiCl interactions, respectively.

The stabilization obtained by multiple halogen substitution on the same center is dominated by the donation from the π-type lone pairs on the halogens into the σ^* acceptor orbitals on adjacent bonds.[22-30] Natural bond orbital analysis shows the stabilization from hyperconjugation is smaller at silicon centers than at carbon because of smaller interaction matrix elements.[26] Calculations also indicates that the net interactions for fluorine are greater than for chlorine, probably because of a closer balance between the stabilizing hyperconjugation and destabilizing four electron repulsions. The bond interaction energies deduced above from the stabilization energies agree with these trends in the orbital interactions.

The data in Table VII also provide evidence for the saturation of hyperconjugation as the number of fluorines is increased. If the AF–AF interactions are computed for individual AH$_{4-n}$F$_n$ species instead of using a least squares fit, one obtains 15.4 kcal/mol for the CF–CF interaction in CH$_2$F$_2$, 13.5 kcal/mol for CHF$_3$, and 10.7 kcal/mol for CF$_4$. The corresponding values for SiH$_{4-n}$F$_n$ are 7.8, 6.0, and 4.0 kcal/mol. Thus, as the number of fluorines increases, the hyperconjugative stabilization of each AF–AF interaction diminishes. These data support the argument made above that the downward curvature in the A–H bond lengths on F substitution is attributable to the saturation of the hyperconjugative interaction. By contrast, the ACl–ACl interactions are small and almost constant (+0.6, +0.1, and −0.5 kcal/mol in CH$_{4-n}$Cl$_n$; +1.8, +1.3 and +0.8 kcal/mol in SiH$_{4-n}$Cl$_n$), showing a near cancelation between the stabilizing hyperconjugative and destabilizing four electron interactions between the chlorine lone pairs and the adjacent σ bonds.

Conclusions

The present study has provided theoretical estimates for the heats of formation of SiH$_2$FCl, SiHF$_2$Cl, SiHFCl$_2$, SiF$_3$Cl, Si-F$_2$Cl$_2$, and SiFCl$_3$ that are expected to be accurate to within ±3 kcal/mol. Nonlinear trends have been observed for the A–H bond lengths, A–H vibrational frequencies, and AH$_{4-m-n}$F$_m$Cl$_n$ heats of formation. The relative slopes of these trends can be interpreted in the same manner as the anomeric effect, i.e. a balance between electrostatic and hyperconjugative effects. The curvature in the trends can be attributed to a saturation of the electrostatic and hyperconjugative effects with increasing halogen substitution.

Registry No. CH$_4$, 74-82-8; CH$_3$F, 593-53-3; CH$_3$Cl, 74-87-3; CH$_2$F$_2$, 75-10-5; CH$_2$FCl, 593-70-4; CH$_2$Cl$_2$, 75-09-2; CHF$_3$, 75-46-7; CHF$_2$Cl, 75-45-6; CHFCl$_2$, 75-43-4; CHCl$_3$, 67-66-3; CF$_4$, 75-73-0; CF$_3$Cl, 75-72-9; CF$_2$Cl$_2$, 75-71-8; CFCl$_3$, 75-69-4; CCl$_4$, 56-23-5; SiH$_4$, 7803-62-5; SiH$_3$F, 13537-33-2; SiH$_3$Cl, 13465-78-6; SiH$_2$F$_2$, 13824-36-7; SiH$_2$FCl, 80003-41-4; SiH$_2$Cl$_2$, 4109-96-0; SiHF$_3$, 13465-71-9; SiHF$_2$Cl, 80003-43-6; SiHFCl$_2$, 19382-74-2; SiHCl$_3$, 10025-78-2; SiF$_4$, 7783-61-1; Si-F$_3$Cl, 14049-36-6; SiF$_2$Cl$_2$, 18356-71-3; SiFCl$_3$, 14965-52-7; SiCl$_4$, 10026-04-7.

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Molecular Structure of 2,6-Difluorobenzenamine and 2-Fluorobenzenamine from Gas-Phase Electron Diffraction

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The molecular structures of 2,6-difluorobenzenamine and 2-fluorobenzenamine have been investigated by gas-phase electron diffraction. The experimental data of the difluoro derivative are consistent with C_s point group the symmetry plane being perpendicular to the ring and bisecting the H–N–H angle. Considerable angular ring deformation has been found for both molecules, dominated by the presence of the F substituents and consistent with additivity of substituent impact. The structure for the monofluorine derivative, with no symmetry, is less precise than for the difluoro derivative. The ring angles at fluorine and NH_2 are 123.6 ± 0.2° and 115.6 ± 0.4° for 2,6-difluorobenzenamine and 123.7 ± 0.8° and 117.6 ± 1.3° for 2-fluorobenzenamine. The C–F bonds are somewhat tilted toward the amino group, 2.1 ± 0.5° and 1.3 ± 0.6° in the difluoro and monofluoro derivatives, respectively. However, there is no other geometrical indication of intramolecular H bond in either molecule. Some further bond lengths (r_g) and angles with estimated total errors for 2,6-difluorobenzenamine are as follows: N–H 1.009 ± 0.007 Å, (C–C)$_{mean}$ 1.391 ± 0.003 Å, F–C 1.356 ● 0.004 Å, C2C3C4 (γ) 118.8 ± 0.2°, C3C4C5 (δ) 119.7 ± 0.4°, dihedral angle HNH/ring 44 ± 6°. 2-Fluorobenzenamine: (C–C)$_{mean}$ 1.394 ± 0.003 Å, F–C 1.365 ± 0.008 Å, C1C6C5 (β') 120.7 ± 0.9°, C2C3C4 (γ) 118.3 ± 0.6°, C4C5C6 (γ') 120.5 ± 0.6°, C3C4C5 (δ) 119.2 ± 0.7°, dihedral angle HNH/ring 26 ± 12°.

Introduction

Ortho-substituted benzene derivatives such as ortho-substituted anilines and phenols have broad ranges of applications. Structural information, however, is scarce on these compounds, especially on their molecular geometry. Recently the structure of a large series of benzene derivatives has been determined primarily to investigate substituent effects on ring deformation.[2] Most of these studies, however have been addressed to non-ortho-substituted benzene derivatives in order to minimize intersubstituent effects.

Recent discussions with Professor R. S. H. Liu, of the University of Hawaii, however, have pointed to the importance of possible structure–activity relationships for ortho-substituted benzene derivatives. These discussions have initiated the present work to probe into possible intersubstituent effects along with ring deformation in ortho-substituted derivatives.

Just as aniline and many halo-substituted anilines, 2-fluorobenzenamine has also been thoroughly investigated by spectroscopic methods.[3–20] The extensive studies involve reinvestigations and new assignments even for aniline itself[3,4,7,20–22] and its derivatives with deuterated amine groups.[6,7,10,17,18] The reinvestigations have been warranted by the difficulties arising in the assignments of the rich spectra. Low-energy vapor-phase spectra are dominated by transition in the inversion vibration of the NH_2 group.[14] Microwave spectroscopic (MW) studies of 2-fluoroaniline[16–18] have been aimed primarily at the determination of the conformation[16] and the amine group geometry[17,18] rather than the complete molecular geometry. The dense and complicated μ_b type rotational spectrum of 2-fluorobenzenamine consists of more than 70 transitions in the 8–40-GHz range and involves assignment difficulties. In addition, accuracy of the calculated substitution coordinates of the NH_2 group is limited by anharmonicity of the inversion motion of hydrogen and deuterium. Furthermore, the attempt to estimate the geometry of the amine group[17] by assuming
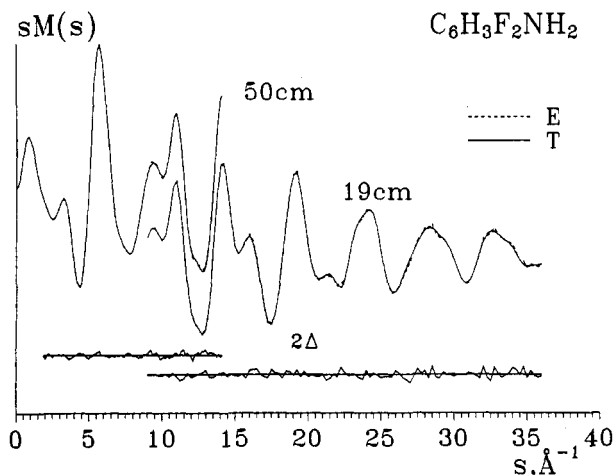

Figure 1. Experimental (*E*) and theoretical (*T*) molecular intensities of 2,6-difluorobenzenamine and the difference curves (Δ = *E* – *T*).

the N–H bond length to be 1.0 Å and calculating the parameters of the C_6H_4NF fragment from those of aniline[22] and fluorobenzene[23] resulted in rather approximate information even for the amine group, and the ring distortion was ignored. Thus, although thoroughly studied, even the most important structural features of 2-fluoroaniline have remained unsolved.

The periodically renewed UV,[3–10] IR,[11–15] MW,[16–18] and theoretical[24,25] studies of haloanilines have been due mainly to interest in the possible hydrogen bonding in these highly reactive molecules, including 2-fluorobenzenamine. At the same time, no direct determination of the complete molecular geometry of 2,6-difluoroaniline and 2-fluorobenzenamine has been attempted yet,