believe that this is a unique example of metal/*t*-BuOOH-induced catalytic activation of O_2 for useful chemistry (four 10-mM-*t*-BuOOH increments yield 80 mM PhC(O)Me). Although this appears to be a radical-induced process, the electrochemical results (Figure 3) and the selectivity ($\{R\} = 44$) indicate that the dioxygen adduct of species **1** [**1**(O_2)] is the initiator rather than an oxy-radical.

Note Added in Proof. Closely similar results have been obtained for several iron(II) complexes;[11] e.g., in py/HOAc the 5 mM $Fe^{II}(PA)_2$/100 mM *t*-BuOOH, O_2/1 M c-C_6H_{12} system yields 46 mM c-C_6H_{10}(O) [without O_2, it yields 19 mM (c-C_6H_{11})py, 11 mM c-C_6H_{10}(O), and 7 mM c-C_6H_{11}OOBu-*t*] versus 25 mM c-C_6H_{10}(O) for the comparable $Cu^I(bpy)_2$[7] system (Table IA).

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Origin of the Stability of Carbon Tetrafluoride: Negative Hyperconjugation Reexamined

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Abstract: The energetic preference for multiple fluorine substitution at carbon has been examined theoretically. Both the stabilization and bond shortening with increasing fluorine substitution may be attributed to Coulombic interactions between the negatively charged fluorines and the increasingly more positively charged carbon. This conclusion leads to the prediction that multiple silyl substitution should also lead to stabilization, and it was confirmed by calculations. Conversely, FCH_2SiH_3, in which the carbon will be close to neutral because of the opposing electron demand of the substituents, has negligible stabilization. Multiple cyano substitution leads to destabilization, and this may be attributed to Coulombic interactions between the positively charged carbons of the cyano groups and the increasingly more positively charged central carbon. The same is found with multiple nitro substitution. Multiple chlorine substitution has little effect, in accord with the smaller difference in electronegativity between carbon and chlorine. The question of negative hyperconjugation in carbon tetrafluoride was explored by the calculation of delocalization indices for the fluorine lone pairs, and no significant interactions were found. Deformation density plots also were examined and showed that increasing fluorine substitution led to reduction in charge density only at the backside of the C–F bonds, as expected for electron polarization due to the increasing positive charge at carbon. A case in which negative hyperconjugation is more likely to be important ((fluoromethyl)amine) also was examined, and some evidence for nitrogen lone pair donation was found.

Introduction

The thermochemical stability of carbon tetrafluoride has been the subject of considerable discussion.[1-11] The basic observation is that the isodesmic reaction

$$CF_4 + 3CH_4 \rightarrow 4CH_3F$$

is endothermic by 53 kcal/mol, indicating that carbon prefers to be multiply substituted by fluorine. A similar preference is found in the corresponding fluoromethyl radicals and anions, in which multiple fluorine substitution also leads to a synergistic stabilization.[9] The stability of carbon tetrafluoride as compared to methyl fluoride has commonly been discussed in terms of negative hyperconjugation, using no bond–double bond resonance structures,[1,3,9] or in MO terms via delocalization of the fluorine lone pairs into adjacent C–F-bond σ^* orbitals.[4] Recently Salzner and Schleyer[12] have presented a detailed analysis in these terms making use of the Weinhold–Reed NBO formalism.[13] Here the molecular orbitals are localized, and it is found that there are significant off-diagonal elements between the lone pairs and the partially occupied C–F σ^* localized orbitals. These terms are attributed to negative hyperconjugation. Their effect was estimated by removing the off-diagonal elements and performing one SCF cycle to evaluate the energy of the altered Fock matrix. The stabilization energy thus calculated was 15.7 kcal/mol per F lone pair–σ^* CF interaction. There are 12 such interactions leading to a total stabilization of 188 kcal/mol!

Hyperconjugation is a well-established phenomenon.[14] In the *tert*-butyl carbocation the C–H bond orbitals may interact with the empty p orbital, transferring some charge density to the latter. The electrons find themselves in a region of lower potential energy,

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Table I. Observed and Calculated Energies

Compd	ΔH_f (298 K)	ΔH_f (0 K)	ref[a]	ZPE[b]	HF 6-31G*	MP2[c] 6-31G*	MP2/ex[d] 6-311++G**	MP3/ex[d] 6-311++G**	$\langle s^2\rangle$[e]
CH_4	-17.8 ± 0.1	-15.9	P	26.8	-40.195 17	-40.337 04	-40.380 88	-40.399 69	
C_2H_6	-20.0 ± 0.1	-16.3	P	44.7	-79.228 76	-79.503 97	-79.574 18	-79.604 03	
CH_3F	-55.9 ± 2?	-54.0	est S	23.8	-139.034 62	-139.342 66	-139.454 07	-139.464 34	
CH_2F_2	-108.1 ± 0.2	-106.3	P	20.2	-237.896 35	-238.373 31	-238.546 76	-238.547 46	
CHF_3	-166.2 ± 0.7	-164.5	P	15.8	-336.771 64	-337.418 98	-337.649 33	-337.640 68	
CF_4	-223.1 ± 0.3	-221.7	P	10.7	-435.645 21	-436.462 23	-436.747 18	-436.730 31	
CH_3Cl	-19.6 ± 0.1	-17.7	P	22.8	-499.093 15	-499.369 08	-499.431 35	-499.457 04	
CH_2Cl_2	-22.8 ± 0.3	-21.2	P	18.0	-957.985 18	-958.400 72	-958.483 06	-958.513 98	
$CHCl_3$	-24.8 ± 0.3	-23.6	P	12.3	-1416.869 71	-1417.429 45	-1417.533 10	-1417.567 36	
CCl_4	-22.9 ± 0.3	-22.4	P	6.1	-1875.744 84	-1876.452 80	-1876.577 55	-1876.613 11	
Me_4C	-40.2 ± 0.2	-31.8	P	95.7	-196.333 82	-197.023 26	-197.173 90	-197.232 36	
Me_3CF	-82.0 ± 2	-75.4	est S	74.2	-256.159 00	-256.878 56	-257.065 45	-257.106 38	
Me_2CF_2	-131.5 ± 2	-126.7	est W	53.0	-315.989 18	-316.740 36	-316.961 55	-316.983 57	
$MeCF_3$	-178.0 ± 0.4	-175.0	P	32.2	-375.820 37	-376.604 19	-376.857 85	-376.860 38	
CH_3CN	15.4 ± 1.7	17.1	P	27.4	-131.927 53	-132.351 31	-132.416 18	-132.422 36	
$CH_2(CN)_2$				27.3	-223.643 92	-224.353 78	-224.439 41	-224.430 48	
$CH(CN)_3$				26.6	-315.346 97	-316.347 74	-316.454 52	-316.427 24	
$C(CN)_4$	160.8 ± 2.2	160.3	P	25.4	-407.038 42	-408.335 84	-408.463 34	-408.413 67	
CH_3SiH_3	-7.0 ± 2.0	-3.2	D	36.6	-330.272 41	-330.500 40	-330.582 59	-330.616 55	
$CH_2(SiH_3)_2$				46.0	-620.351 66	-620.668 61	-620.788 45	-620.836 87	
$CH(SiH_3)_3$				55.7	-910.432 28	-910.841 89	-910.998 73	-911.060 69	
$C(SiH_3)_4$				65.6	-1200.514 44	-1201.020 82	-1201.214 26	-1201.288 59	
FCH_2SiH_3				32.8	-429.501 85	-429.501 85	-429.642 22	-429.668 62	
$CH_3^{\bullet}$	-39.4 ± 0.2	-35.7	J	17.4	-39.558 99	-39.673 03	-39.711 79	-39.729 07	0.761
$H^{\bullet}$	52.1 ± 0.0	51.6	J	0.0	-0.498 23	-0.498 23	-0.499 82	-0.499 82	0.750
$F^{\bullet}$	18.5 ± 0.1	19.0	J	0.0	-99.364 96	-99.487 27	-99.566 47	-99.573 36	0.753
$Cl^{\bullet}$	28.6 ± 0.0	29.0	J	0.0	-459.447 96	-459.552 43	-459.588 53	-459.602 58	0.755
$H_2CF^{\bullet}$				15.1	-138.402 11	-138.685 95	-138.790 05	-138.797 63	0.760
$HCF_2^{\bullet}$				11.8	-237.263 13	-237.717 64	-237.882 09	-237.879 53	0.756
$CF_3^{\bullet}$	-112.4 ± 1.0	-111.7	J	7.6	-336.131 18	-336.755 76	-336.976 98	-336.964 93	0.754
$H_2CCl^{\bullet}$				13.9	-498.461 08	-498.712 39	-498.769 32	-498.792 91	0.765
$HCCl_2^{\bullet}$				9.6	-957.358 05	-957.750 34	-957.826 25	-957.854 98	0.766
$CCl_3^{\bullet}$				4.5	-1416.248 16	-1416.784 30	-1416.880 47	-1416.912 96	0.767
CN	104.5 ± 0.5	104.1	H	2.5	-92.204 83	-92.441 96	-92.490 28	-92.490 87	1.033
CH_2CN				18.1	-131.306 89	-131.685 32	-131.754 52	-131.765 74	0.897
$CH(CN)_2$				17.8	-223.037 87	-223.684 78	-223.783 45	-223.787 72	1.035
$C(CN)_3$				16.8	-314.755 89	-315.674 81	-315.802 43	-315.798 44	1.168
SiH_3	46.6 ± 1.5	47.9	D	12.8	-290.606 12	-290.684 16	-290.729 29	-290.748 51	0.754
CH_2SiH_3[f]				28.1	-329.643 74	-329.842 70	-329.918 25	-329.951 65	0.761
$CH(SiH_3)_2$				38.3	-619.728 26	-620.015 00	-620.127 38	-620.176 26	0.761
$C(SiH_3)_3$				48.5	-909.813 42	-910.191 32	-910.340 37	-910.403 88	0.761

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and as a result the energy of the ion is significantly lower than that of the hypothetical non-delocalized ion. Negative hyperconjugation[1,2,4] is often quite different. As noted above, in the case of carbon tetrafluoride it is postulated that the lone pair electrons are delocalized into the C–F σ^* orbitals.[4] Whereas the physics of ordinary hyperconjugation is readily apparent, it is not as clear that negative hyperconjugation would have a similar effect in this case. Since each fluorine is both a donor and an acceptor, it is not obvious why the energy should decrease.

We have carried out a theoretical study of the fluoromethanes in an attempt to find a simpler explanation for the well-established energy changes. In order to have good agreement with the available experimental data, we have carried out geometry optimizations and single-point energy calculations at a significantly higher theoretical level than used previously. We also have examined other related cases of multiple substitution onto methane in order to gain further information on the factors responsible for changes in energies.

Calculations

The structures of the fluoromethanes were calculated at the MP2/6-31G* level, which usually gives good agreement with experimental structural data.[15] The energies are given in Table I, and the calculated and observed structural parameters[16] are compared in Table II. Our studies of 1,2-difluoroethane and 1,2-difluoroethene showed that diffuse functions were important in obtaining the correct relative energies.[17] Therefore, the energies were calculated at the MP3/6-311++G** level using the MP2 structures. In addition, corrections for differences in zero-point energies are needed, and the vibrational frequencies were calculated at the HF/6-31G* level and were scaled by the factor 0.893.[18] These data are included in Table I.

It was possible that the changes in energy resulted from some special feature of replacing a hydrogen in methane by a first-row atom. A suggestion that this might be the case is found in the observation that neopentane is the most stable of the C_5H_{12} isomers.[19] Therefore, we have also examined the series of compounds formed by replacing methyl groups of neopentane with fluorines. These data are included in Table

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Table II. Structural Data

compound	unit[a]	RHF/ 6-31G*	MP2/ 6-31G*	obsd[b]
methane	*r*CH	1.084	1.090	
fluoromethane	*r*CF	1.365	1.390	1.383
	*r*CH	1.082	1.092	1.100
	∠HCF	109.1	109.1	108.3
difluoromethane	*r*CF	1.338	1.364	1.357
	*r*CH	1.078	1.091	1.093
	∠HCF	108.9	108.8	108.7
	∠FCF	108.6	108.8	108.3
trifluoromethane	*r*CF	1.317	1.343	1.332
	*r*CH	1.074	1.089	1.098
	∠HCF	110.4	110.5	110.1
	∠FCF	108.5	108.5	108.8
tetrafluoromethane	*r*CF	1.302	1.329	1.320
chloromethane	*r*CCl	1.785	1.777	1.776
	*r*CH	1.078	1.088	1.085
	∠HCCl	108.5	108.9	
	∠HCH	110.5	110.0	110.4
dichloromethane	*r*CCl	1.768	1.767	1.765
	*r*CH	1.074	1.087	1.087
	∠HCCl	108.2	108.3	
	∠ClCCl	112.9	113.0	112.0
	∠HCH	111.1	110.9	111.5
trichloromethane	*r*CCl	1.763	1.765	1.758
	*r*CH	1.071	1.086	1.100
	∠HCCl	107.6	107.6	
	∠ClCCl	111.3	111.2	111.3
tetrachloromethane	*r*CCl	1.766	1.769	1.767
neopentane	*r*CC	1.535	1.528	1.537
	*r*CH	1.087	1.095	1.114
	∠HCC	110.9	111.1	112.2
tert-butylfluoride	*r*CF	1.390	1.418	
	*r*CC	1.521	1.516	
	*r*CH	1.085	1.093	
	∠CCF	106.6	106.4	
2,2-difluoropropane	*r*CF	1.354	1.382	1.353
	*r*CC	1.509	1.505	1.532
	*r*CHa	1.083	1.091	[1.090]
	*r*CHb	1.083	1.091	[1.090]
	∠CCF	108.6	108.4	
	∠FCF	105.9	106.0	106.0
	∠CCC	116.1	116.7	112.5
	∠CCHa	109.1	108.7	110.0 (av)
	∠CCHb	110.3	110.1	
1,1,1-trifluoroethane	*r*CF	1.325	1.353	1.340
	*r*CC	1.499	1.496	1.494
	*r*CH	1.082	1.090	1.081
	∠CCF	111.6	111.6	111.9
	∠CCH	109.4	109.2	
acetonitrile	*r*CC	1.468	1.461	1.462
	*r*CH	1.082	1.091	1.095
	*r*CN	1.135	1.178	1.157
	∠CCH	109.8	110.1	109.9
dicyanomethane	*r*CC	1.472	1.466	1.468
	*r*CH	1.083	1.095	1.088
	*r*CN	1.133	1.179	1.167
	∠CCH	109.1	109.4	
	∠CCC	112.2	111.9	109.4
	∠HCH	108.0	107.4	108.7
tricyanomethane	*r*CC	1.477	1.473	
	*r*CH	1.085	1.100	
	*r*CN	1.132	1.180	
	∠CCH	107.9	108.1	
	∠CCC	111.0	110.8	
tetracyanomethane	*r*CC	1.484	1.479	
	*r*CN	1.131	1.181	
methylsilane	*r*CSi	1.888	1.880	1.864
	*r*CH	1.086	1.093	1.095
	∠HCSi	111.1	111.0	
	∠HCH	107.8	107.9	108.0
	∠HSiH	108.3	108.8	108.8
	∠CSiH	110.6	110.6	110.4
disilylmethane	*r*CSi	1.888	1.880	1.874
	*r*CH	1.089	1.096	1.091
	∠HCSi	108.4	108.8	108.8
	∠SiCSi	116.5	114.7	114.1
trisilylmethane	*r*CSi	1.891	1.880	
	*r*CH	1.092	1.098	
	∠HCSi	106.3	107.7	
	∠SiCSi	112.4	111.2	
tetrasilylmethane	*r*CSi	1.895	1.879	

[a] Bond lengths are given in angstroms and bond angles in degrees. [b] The data were taken from ref 16.

Table III. Energy Changes for Isodesmic Reactions[a]

reaction	exptl (298 K)	exptl (0 K)	RHF	MP2[b]	MP2/ex[c]	MP3/ex[d]
$CF_4 + 3CH_4 \rightarrow 4CH_3F$	+53.1	+53.4	+62.0	+68.6	+50.2	+49.3
$CMe_4 + 3CH_4 \rightarrow 4C_2H_6$	+13.3	+14.3	+5.4	+14.3	+15.1	+12.3
$C(CN)_4 + 3CH_4 \rightarrow 4CH_3CN$	−45.8	−44.2	−50.3	−32.8	−33.1	−44.3
$C(SiH_3)_4 + 3CH_4 \rightarrow 4CH_3SiH_3$	na[e]		+6.9	+19.4	+17.1	+13.9
$CCl_4 + 3CH_4 \rightarrow 4CH_3Cl$	−2.1	−0.7	−21.8	−3.1	+1.4	−5.4
$CF_4 + CH_4 \rightarrow HCF_3 + CH_3F$	+18.8	+19.1	+23.4	+25.6	+17.6	+17.7
$HCF_3 + CH_4 \rightarrow H_2CF_2 + CH_3F$	+20.0	+20.1	+23.9	+26.5	+19.8	+19.3
$H_2CF_2 + CH_4 \rightarrow 2CH_3F$	+14.1	+14.2	+14.6	+16.3	+12.8	+12.6
$CCl_4 + CH_4 \rightarrow HCCl_3 + CH_3Cl$	−3.7	−3.0	−12.1	−3.3	−1.6	−5.1
$HCCl_3 + CH_4 \rightarrow H_2CCl_2 + CH_3Cl$	+0.2	+0.6	−6.7	−0.4	+1.4	−0.8
$H_2CCl_2 + CH_4 \rightarrow 2CH_3Cl$	+1.4	+1.7	−2.9	+0.5	+1.6	+0.5
$C(CN)_4 + CH_4 \rightarrow HC(CN)_3 + CH_3CN$	na		−23.8	−14.6	−14.8	−20.9
$HC(CN)_3 + CH_4 \rightarrow H_2C(CN)_2 + CH_3CN$	na		−17.0	−11.4	−11.4	−14.9
$H_2C(CN)_2 + CH_4 \rightarrow 2CH_3CN$	na		−9.3	−6.7	−6.9	−8.4
$C(SiH_3)_4 + CH_4 \rightarrow HC(SiH_3)_3 + CH_3SiH_3$	na		+3.0	+9.7	+8.6	+6.8
$HC(SiH_3)_3 + CH_4 \rightarrow H_2C(SiH_3)_2 + CH_3SiH_3$	na		+2.2	+6.3	+5.5	+4.5
$H_2C(SiH_3)_2 + CH_4 \rightarrow 2CH_3SiH_3$	na		+1.7	+3.4	+3.0	+2.6
$CF_4 + C_2H_6 \rightarrow CH_3CF_3 + CH_3F$	+9.2	+9.0	+12.5	+12.7	+6.5	+6.6
$CH_3CF_3 + C_2H_6 \rightarrow (CH_3)_2CF_2 + CH_3F$	+10.6	+10.4	+15.8	+15.7	+10.2	+10.3
$(CH_3)_2CF_2 + C_2H_6 \rightarrow (CH_3)_3CF + CH_3F$	+13.6	+13.6	+15.6	+14.8	+10.5	+10.9
$(CH_3)_3CF + C_2H_6 \rightarrow (CH_3)_4C + CH_3F$	+5.9	+5.9	+12.7	+11.0	+7.9	+9.2

[a] The calculated reaction energies include the zero-point energy correction. [b] MP2/6-31G* energy at MP2/6-31G* optimized geometry. All electrons were included in the correlation calculation (MP2(fu)/6-31G* optimization). [c] MP2/6-311++G**(6d) energies at the MP2/6-31G* geometry. Core electrons were excluded from the correlation calculation (MP2(fc)/6-311++G**(6d)//MP2(fu)/6-31G*). [d] MP3/6-311++G**(6d) energies at the MP2/6-31G* geometry. Core electrons were excluded from the correlation calculation (MP3(fc)/6-311++G**(6d)//MP2(fu)/6-31G*). [e] na = not available.

Table IV. Atomic Charges Derived by Charge Density Integrations, HF/6-311++G**(6d)//MP2(fu)/6-31G*

compd	atoms					total
	C	H				
CH_4	0.127	–0.031				0.001
	C	H	F			
CH_3F	0.682	0.008	–0.706			0.000
CH_2F_2	1.297	0.056	–0.705			–0.001
CHF_3	1.998	0.119	–0.704			0.005
CF_4	2.776		–0.694			0.002
	C	H	C(N)	N		
CH_3CN	0.260	0.046	0.907	–1.305		0.001
$CH_2(CN)_2$	0.350	0.109	0.947	–1.231		0.001
$CH(CN)_3$	0.421	0.161	0.973	–1.166		0.004
$C(CN)_4$	0.474		0.990	–1.108		0.001
	C	H	Cl			
CH_3Cl	0.231	0.029	–0.322			–0.003
CH_2Cl_2	0.337	0.083	–0.252			0.000
$CHCl_3$	0.426	0.129	–0.185			–0.001
CCl_4	0.502		–0.125			0.002
	C	H	Si	H (av)		
CH_3SiH_3	–0.683	–0.018	2.984	–0.748		0.003
$CH_2(SiH_3)_2$	–1.468	–0.006	2.984	–0.747		0.005
$CH(SiH_3)_3$	–2.241	0.006	2.983	–0.746		0.000
$C(SiH_3)_4$	–3.008		2.987	–0.745		0.002
	C	H	F	Si	H (av)	
FCH_2SiH_3	–0.084	0.012	–0.704	2.978	–0.736	0.000
	C	H (av)	F	N	H (av)	
FCH_2NH_2	1.114	0.024	–0.713	–1.214	0.381	–0.003
FCH_2NH_2 rot[a]	1.075	0.006	–0.708	–1.137	0.377	–0.001

[a] The "lone pair" axis is rotated 80° from the anti position, which is the highest energy conformer. This is at the maximum in the torsional potential for the C–N bond.

I. The energies of isodesmic reactions involving these compounds are summarized in Table III.

Salzner and Schleyer have reported that in the cyanomethane series, unlike the fluoromethanes, multiple cyano substitution is energetically unfavorable.[12] In order to make a comparison with our data for the fluoromethanes, we have carried out geometry optimizations for the cyanomethanes at the MP2/6-31G* level and calculated energies at the MP3/6-311++G** level using the MP2 geometries. The zero-point energies were estimated from HF/6-31G* calculations. The energies are given in Table I, and the structural data are summarized in Table II. In order to have comparisons with other substituents, silyl- and chloro-substituted methanes also were studied at the same level of theory. The energy changes for the associated isodesmic reactions are summarized in Table III.

Charge distributions have been one of our major interests,[20] and therefore the atomic charges were obtained making use of Bader's theory of atoms in molecules.[21] Here one locates the bond critical points (the point of minimum charge density along the bond between a given pair of atoms) and constructs a surface normal to the bond by locating rays starting at the critical point for which the charge density decreases most rapidly. A set of these surfaces serves to separate a molecule into atomic domains, and numerical integration of the charge density within a domain will give the electron population. The charges thus obtained are given in Table IV.

The ab initio calculations were carried out using GAUSSIAN 91,[22] and the charge density analysis was done using PROAIM.[23]

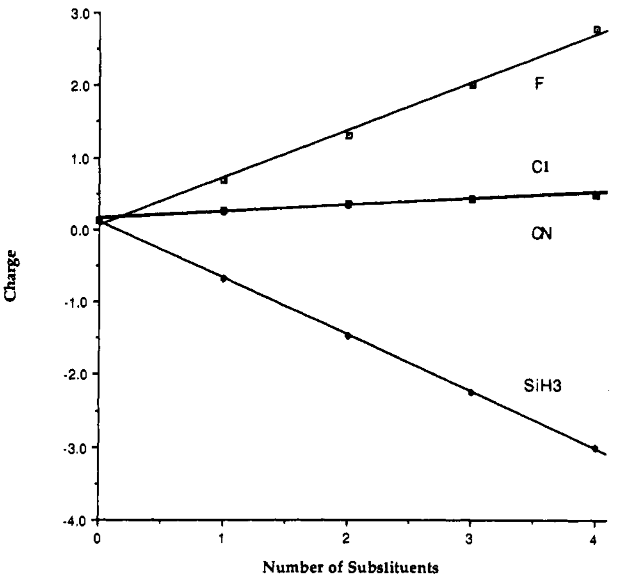

Figure 1. Relationship between the charge at the central carbon and the number of substituents.

Table V. Bond Path Angles (deg) HF/6-311++G**(6d)//MP2(fu)/6-31G*

		X			
compd	angle[a]	F	SiH_3	Cl	CN
CH_4	∠HCH	109.5	109.5	109.5	109.5
CH_3X	∠HCH	112.2	108.5	112.9	110.4
CH_2X_2	∠HCH	120.1	107.7	117.9	110.8
CH_2X_2	∠XCX	104.5	112.2	105.4	108.2
CHX_3	∠XCX	105.4	110.2	106.8	109.0
CX_4	∠XCX	109.5	109.5	109.5	109.5

[a] The bond path angle is defined as the angle between the bond paths (paths of maximum charge density between a pair of bonded atoms) at a given nucleus.

Fluoromethanes

The structural data in Table II show that the C–F bond lengths decrease with increasing fluorine substitution. This structural change has been cited as evidence for negative hyperconjugation.[1,2] However, it may readily be explained in terms of electrostatics.[5,8] We find that the charge at the carbon in this series increases almost linearly with increasing fluorine substitution (Table IV and Figure 1). Contrary to intuition, the small deviation from linearity is in the direction of the carbon charge increasing *more rapidly* as the degree of fluorine substitution increases. Furthermore, the charge of the fluorine atoms remains constant at –0.70 ± 0.01 throughout the entire series. The constancy of the fluorine charge was also observed by Salzner and Schleyer via the use of the Weinhold–Reed natural orbital analysis.[12] In addition, we have calculated the GAPT charges[24] and again found that the charge at fluorine was nearly the same in all the fluoromethanes. The GAPT charges are available as supplementary material. Since the use of three quite different approaches to calculating charges led to the same result, there can be little doubt about the conclusion. The absence of any sort of "saturation effect" on the ability of successive fluorine atoms to withdraw electron density from the carbon atom is in contradiction with conventional wisdom and constitutes a noteworthy result in itself.

The Coulombic attraction between the carbon and a fluorine will then increase with increasing fluorine substitution, leading to a decrease in C–F bond length.[8] Another factor that operates in the same direction is hybridization. Bent's rule[5] predicts that the fluorine in methyl fluoride will prefer a p-rich orbital from carbon, leading to a lengthened C–F bond and a small H–C–F bond angle. With increasing fluorine substitution, the fluorines compete for the carbon p character, and each receives less. With carbon tetrafluoride, symmetry requires 25% s character for each C–F bond. As a result, the C–F bond length is reduced. Bond path angles can be used as an indicator for hybridization changes[20]

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and are listed in Table V. The bond path is defined as the path of maximum charge density connecting a pair of bonded nuclei, and the angle between two such bond paths when they meet at a nuclear center is the bond path angle. As the number of fluorines increases, the FCF bond path angles increases from 104.5° in difluoromethane to 109.5° in tetrafluoromethane. This is consistent with the competition for and consequent loss of p character discussed above.

It can be seen that negative hyperconjugation is not needed in order to explain the changes in bond lengths. Is it necessary in order to explain the changes in energy? The energy changes for isodesmic reactions in which fluorines are replaced by hydrogens are summarized in Table III. The calculated energy changes are somewhat basis set dependent. However, with the larger basis set, which gives satisfactory results for the 1,2-difluoroethanes and the 1,2-difluoroethenes,[25] there is little change in calculated energy on going from MP2 to MP3. Further, the calculated energies are in satisfactory agreement with the observed values and in all cases indicate that multiple fluorine substitution is energetically favored. Our results are in agreement with previous calculations carried out at a lower theoretical level.[8,12]

One problem associated with the experimental data is that the heat of formation of a key compound (methyl fluoride) has not been experimentally determined. It has been estimated to be −55.9 ± 4.0 kcal/mol at 298 K or −54.0 at 0 K.[26] Since this compound is involved in all of the isodesmic reactions, we have tried to make a theoretical estimate of its energy using the G2 procedure developed by Pople et al.[27] The data needed to calculate the atomization energy of methyl fluoride are available[27] and yield the value 399.8 kcal/mol. The experimental energy of a carbon atom, three hydrogen atoms, and a fluorine atom is 343.4 kcal/mol at 0 K.[28] This leads to a G2 heat of formation of −56.4 kcal/mol at 0 K, as compared with the previous estimated value of −54.0 kcal/mol. Thus, it appears that the estimated heat of formation is reasonable but may be ~2 kcal/mol too high. This will not significantly affect the conclusions derived from the isodesmic reactions.

In a study of substituent effects on carbonyl groups, we observed that the effect of increasing electronegativity on bond strengths was significantly greater for acetyl derivatives than for methyl derivatives.[29] With the series of substituents having similar hybridization, increasing electronegativity, and no π-stabilization (i.e., 90° rotated acetic acid, acetamide, and thioacetic acid) PH_2, SH, Cl, NH_2, OH, and F, the slope of a plot of acetyl–X BDEs against methyl–X BDEs was 1.6, with $r^2 = 0.99$. The BDE for methyl fluoride is 21 kcal/mol greater than that for ethane.[30] The increased BDE for methyl fluoride results from the greater polarization of the C–F bond and the resultant Coulombic attraction between carbon and fluoride. Pauling noted many years ago the general trend of increased bond dissociation energy with increased polarity of bonds.[31] In the case of the acetyl compounds, the effect is the same in the C–X bond, but increased polarization not only strengthens the C–X bond but by increasing the positive charge at the carbonyl carbon it also *increases the strength of the strongly polarized* $C^+–O^-$ *bond.* As a result, the effect of electronegative substituents is larger in the acetyl series than in the methyl series.

The same factor should apply to the fluoromethanes. On going from methyl fluoride to methylene fluoride, the charge at carbon increases (Table IV). This strengthens the new C–F bond, but it also *strengthens the original C–F* bond. This will result in the observed increased stability with increasing fluorine substitution. Thus, considerations of electrostatics may account for both the changes in C–F bond length and the changes in energy with increasing fluorine substitution. In order to see if the Coulombic stabilization would be large enough to explain the experimental observations, we have made a rough estimate of its magnitude. Here we need effective nuclear-centered "point charges", and so we have used the CHELPG charges.[32] All of the interactions among C, H, and F were summed. The electrostatic energies thus estimated were CF_4, −202; CHF_3, −129; CH_2F_2, −71; and CH_3F, −16 kcal/mol. For the isodesmic reaction $CF_4 + 3CH_4 \rightarrow CH_3F$, the change in estimated electrostatic energy is 138 kcal/mol. One would expect the estimate to be too large because the electrons are not symmetrically distributed about each atom but rather are polarized toward the regions between nuclei. It can be seen that this rough estimate is of the correct magnitude to account for the observed energy changes.

Table VI. Estimated Bond Dissociation Energies and Their Differences (kcal/mol)[a]

R	R–X BDE	R–H BDE	diff
	a. Fluoromethanes		
CH_3	95.2	97.8	+2.6
CH_2F	105.6	96.0	−9.6
CHF_2	113.9	97.1	−16.8
CF_3	117.3	102.2	−15.1
	b. Silylmethanes		
CH_3	80.8	97.8	+17.0
CH_2SiH_3	80.7	95.8	+15.1
$CH(SiH_3)_2$	80.7	93.2	+12.5
$C(SiH_3)_3$	81.2	91.3	+10.1
	c. Chloromethanes		
CH_3	73.3	97.8	+24.5
CH_2Cl	70.3	94.2	+23.9
$CHCl_2$	66.2	91.5	+25.3
CCl_3	59.6	89.2	+29.6
	d. Cyanomethanes		
CH_3	119.5	97.8	−21.7
CH_2CN	102.4	89.1	−13.3
$CH(CN)_2$	87.0	80.2	−6.8
$C(CN)_3$	71.9	71.2	−0.7

[a] Includes correction for zero-point energy changes. The calculated BDEs are smaller than the experimental values because of neglect of higher order terms. However, they are linearly related to the observed values for the cases in which they are known.

Silicon and fluorine, which are known to form very strong bonds, have an even larger electronegativity difference (2.34 on the Allred–Rochow scale) than do carbon and fluorine (1.60). By this line of reasoning, the series of compounds from silane to tetrafluorosilane ought to show the same energetic trend—increasing stability with increasing fluorine substitution—as is observed with carbon tetrafluoride. Calculations by Ignacio and Schlegel have shown that this is, indeed, the case; the isodesmic reaction of tetrafluorosilane with three silanes to give four fluorosilane molecules is calculated to be endothermic by 25.1 kcal/mol.[33] The smaller energy change than for CF_4 is expected because of the longer Si–F bonds and the resultant decrease in Coulombic attraction.

The C–F bond strengths may be further examined by calculating the bond dissociation energies. The energies of the radicals are included in Table I, and the dissociation energies are given in Table VI. The calculated BDEs will not be quite correct because of neglect of higher order terms,[18] but we have shown

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that the MP3/6-311++G** BDEs for methyl derivatives are linearly related to the observed values.[29] Therefore, the calculated energies should be satisfactory in a comparative sense.[34] It can be seen that there is a marked increase in the C–F dissociation energy with increasing fluorine substitution but only a relatively small change in the C–H dissociation energies. Thus, the changes in bond strength are in accord with the idea that the energy changes are due to Coulombic stabilization that increases with increasing fluorine substitution.

A proper comparison of bond dissociation energies would require that one partner be constant, and so it would be more appropriate to compare C–F and C–H BDEs which relate to the same substituted methyl radical. The values are given in Table VI. It can be seen that the differences increase with increasing fluorine substitution.

It was possible that the energy changes were in some way related to the replacement of hydrogens by first-row atoms because increasingly methyl substitution also stabilizes methane.[19] Therefore the replacement of methyl groups in neopentane by fluorines also was examined. The data are shown in Table III. It can be seen that the isodesmic reactions with ethane are all endothermic, as was found in the methane series. Thus, the effect is due to the fluorine substitution. Similarly, the C–F bond length decreases substantially with increasing fluorine substitution, just as was found with the fluoromethane case.

If the stabilization of carbon tetrafluoride is mainly due to Coulombic interactions, how can this be reconciled with the calculations of Salzner and Schleyer? In applying the natural bond orbital analysis (NBO) to the 6-31G* wave functions for carbon tetrafluoride, it is found that the σ^* CF orbitals have significant electron populations (0.09 e each). Annihilation of the Fock matrix element between the F lone pairs and the CF σ^* orbitals and recalculation of the energy led to a considerable increase in energy that was attributed to the loss of a hyperconjugative interaction.

There are two disturbing features of this analysis. First, the occupancies of the CH σ^* orbitals are comparable to those for the C–F σ^* orbitals (CH_3F, 0.013 for CH and 0.003 for CF; CH_2F_2, 0.026 for CH and 0.038 for CF; HCF_3, 0.039 for CH and 0.066 for CF; and CF4, 0.092 for CF). Thus, one concludes that it is difficult to perfectly localize the bonds in any molecule. If one wishes to attribute this difficulty in localization to hyperconjugation, then the latter will be found everywhere. Then, there is little point in distinguishing it from ordinary bonding. Further, it can be seen that the inclusion of electron correlation has only a small effect on the isodesmic reaction of carbon tetrafluoride with methane. However, at the same time, the population calculated for the CF σ^* orbitals increases by roughly a factor of 2![35] Thus, the populations do not correlate with the energetics of the isodesmic reactions.

We shall return to this question after we examine the effect of other substituents on methane.

Silylmethanes

Two hypotheses have been advanced to explain the increasing stability of the fluoromethanes with increasing fluorine substitution: negative hyperconjugation and internal Coulombic attraction. A test case is then needed that will distinguish between these two hypotheses.

We have previously noted the unusually high C–Si bond dissociation energy of methylsilane (i.e., greater than that for methyl chloride and considerably larger than for methanethiol) and explained it as being due to the polarization of the C–Si bond which results from the large difference in electronegativity.[29] The polarity is, of course, opposite to that found with C–F bonds, but it will still result in Coulombic stabilization. If our explanation for the energy changes in the fluoromethane series is correct, then one would predict that increasing silyl substitution should lead to stabilization, just as was found with fluorine substitution. Each successive SiH_3 group will donate charge to the central carbon (Table IV), strengthening both the new C–Si bond and also the previous C–Si bonds. So, the prediction is for a preference for multiple SiH_3 substitution without a possibility for hyperconjugation and with reversed polarization as compared to the fluoromethane case.

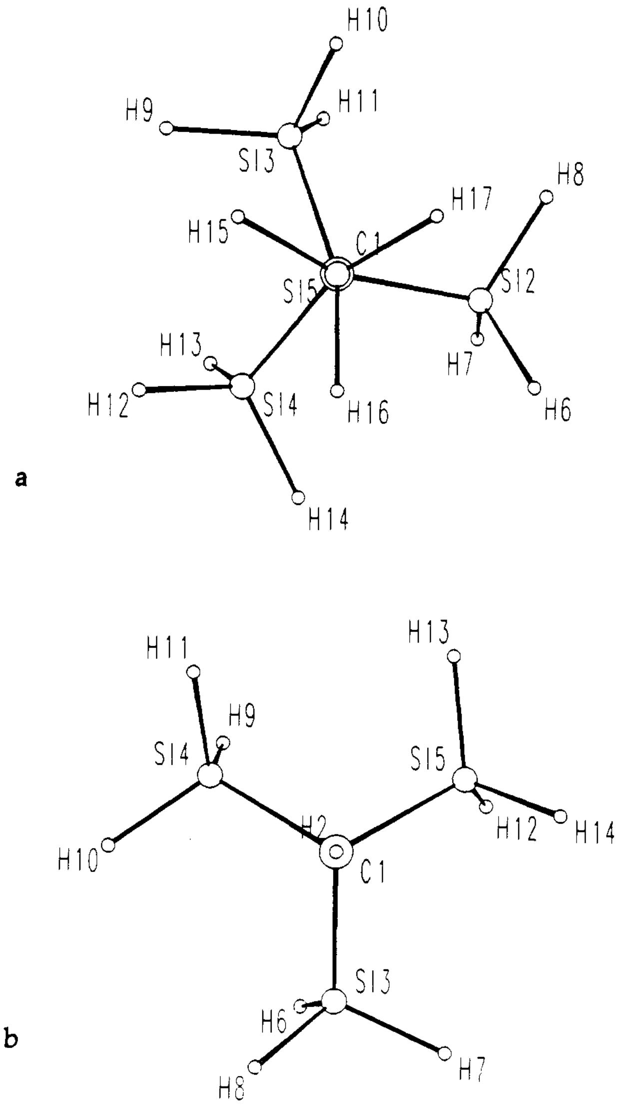

Figure 2. Structures of tetrasilylmethane (a) and trisilylmethane (b) as viewed along the C_3 axis.

The data for the isodesmic reactions are shown in Table III. In accord with the prediction, all of the isodesmic reactions with ethane are endothermic. The effect is not as large as found with fluorine, but that is to be expected since the difference in electronegativity between carbon and silicon is less (−0.74 on the Allred–Rochow scale) than that between carbon and fluorine (1.60) and the bond lengths are considerably greater. Furthermore, the hybridization changes would be in the opposite direction to those found with the fluoromethanes. Carbon prefers to form a bond to the electropositive SiH_3 substituent using an orbital with relatively high s character, leading to bond strengthening and shortening. As more SiH_3 groups are introduced, there will be a decrease in s character to the sp^3 value for four groups, which will progressively weaken the bond. The decrease of the SiCSi bond path angle from disilylmethane (112.2°) to tetrasilylmethane (109.5°) (Table V) illustrates this loss of excess s character along the series. Additionally, one might suspect the presence of a steric

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(34) Table I also lists the s^2 expectation value for the UHF/6-311++G**(6d) wave functions before annihilation of any spin contaminants. Spin contamination is negligible except in the species containing one or more cyano groups. In all cases, the value of $\langle s^2 \rangle$ became 0.750 upon annihilation of the first four spin contaminants.

(35) The sum of the occupancies of the C–H and C–F σ^* orbitals increases by a factor of 2.7 in CH_3F, by a factor of 1.9 in CH_2F_2, by a factor of 1.6 in CHF_3, and by a factor of 1.5 in CF_4 upon changing the level of theory from HF/6-31G* to MP2(fu)/6-31G*.

factor. While fluorine atoms are highly compact and should not cause any steric interference, the much bulkier silyl groups might be expected to crowd each other as more of them are placed on a central carbon atom. This would further moderate the energetic favorability of multiple silyl substitution. The fact that trisilylmethane and tetrasilylmethane both prefer C_3 structures (see Figure 2) rather than the C_{3v} and T_d structures preferred by isobutane and neopentane supports this possibility. At the MP2/6-31G* level, the T_d transition state for tetrasilylmethane lies 1.6 kcal/mol above the ground state.

There is essentially no change in C–Si bond length with increasing Si substitution. This is consistent with the smaller difference in electronegativity between silicon and carbon compared to that between fluorine and carbon. It also reflects the participation of hybridization changes, which would be in the direction to increase the C–Si bond length. The fact that the bond lengths do not grow *longer* with the silyl substitution shows that the Coulombic attraction between carbon and silicon must be increasing.

It is interesting to note that the trends in the bond dissociation energy differences (Table VI) are quite similar to those for the fluoromethanes, i.e., decreasing with increasing substitution. This again supports the contention that the changes in isodesmic energies have a common origin. It may also be noted that the energy of reaction of tetrasilylmethane with methane is about the same as that of the corresponding reaction of neopentane. The stabilization of neopentane appears to involve an attractive force between the methyl carbon nuclei and the electrons on adjacent methyl groups.[19] This interaction depends on the distance between groups and would be expected to be considerably smaller for silyl groups having the longer C–Si bonds. Therefore, another factor must be involved in the preference for multiple silyl substitution, and it appears to be the Coulombic interaction.

The charges for the silylmethanes given in Table IV are also worthy of note. The charge of the carbon atom changes in a linear fashion as the degree of silyl substitution increases, becoming more negative by 0.78 ± 0.03 with each additional silyl group. Furthermore, the charge of the silyl group remains constant at 0.746 ± 0.006 along the entire series. Thus the silylmethanes behave in the same manner as the fluoromethanes, except that the sense of polarity is reversed.

A corollary of our hypothesis is that the attachment of both electron-releasing and electron-attracting groups to a carbon would lead to its having a relatively small charge, and consequently there would be little Coulombic stabilization. Thus, the reaction

$$FCH_2SiH_3 + CH_4 \rightarrow CH_3F + CH_3SiH_3$$

should be exothermic because of the Coulombic stabilization of the two products and the lack of stabilization of the reactants. This type of stabilization has been examined by Apeloig, leading to the above conclusion.[36] In the above case, at the MP3/6-311++G**//MP2/6-31G* theoretical level (corresponding to the last column in Table III) with correction for zero-point energies, $\Delta H = -7.1$ kcal/mol. The charge at carbon is calculated to be −0.084, considerably smaller than the calculated charges for either methyl fluoride or methylsilane.[37] In accord with the lower charge at carbon and the smaller Coulombic interaction, both the C–F and C–Si bond lengths (1.411 and 1.898 Å, respectively) are longer than those in methyl fluoride (1.390 Å) and methylsilane (1.888 Å).

Cyanomethanes

Cyano substitution has the opposite effect of fluorine substitution (Table III), with multiple cyano substitution being disfavored.[12] Whereas the fluorine in the fluoromethanes has a negative charge, the cyano carbon of the cyanomethanes has a large positive charge that results from the electronegative nitrogen.[38] Calculations of charges (Table IV) show that the central carbon acquires a positive charge as a result of cyano substitution and that the charge increases steadily with the number of cyano groups. Here, there will be Coulombic repulsion between the central carbon and the cyano carbons, resulting in destabilization. It may also be noted that the C–C bonds become longer with increasing cyano substitution, again suggesting a repulsive interaction. The bond path angles (Table V) for the cyanomethanes barely change as the number of substituents is increased and always remain very close to the ideal sp^3 value of 109.5°, suggesting that hybridization changes are relatively unimportant for this series of compounds.

The bond dissociation energies listed in Table VI illustrate the same trends that are observed in the isodesmic reaction energies. The strength of the C–CN bond undergoes a dramatic decrease from 119.5 kcal/mol in acetonitrile to 71.9 kcal/mol in tetracyanomethane. However, the C–H bond dissociation energies also drop substantially along this series. Thus it seem likely that a large part of the observed decrease in bond strengths results from the ability of the cyano substituent to stabilize the radicals formed in the bond dissociation reactions. The bond dissociation energy differences listed in the last column can be used to eliminate this complication, since the comparison is between reactions which yield the same radical. In contrast to the fluoromethane series, the bond dissociation energy difference increases steadily as cyano substitution increases. Each cyano group leads to a destabilization of the C–CN bond relative to the C–H bond of about 7 kcal/mol.

The same destabilizing effect was observed in a comparison of the bond dissociation energies of acetyl derivatives and methyl derivatives.[29] The electronegative substituents CN and CF_3 were found to give lower than expected bond dissociation energies in the acetyl series. In the acetyl group, the carbonyl carbon has a significant positive charge as a result of the electronegativity of the attached oxygen. Both the CN and CF_3 groups have a partial positive charge at carbon resulting from the electronegativity of the attached atoms. As a result, they gave a repulsive Coulombic interaction with the carbonyl carbon, leading to reduced bond strength.

On this basis, one would expect that any strongly electron-withdrawing group with a positively charged terminus when substituted at the carbon of methane would have the same effect. Thus, the destabilizing effect of the cyano group should also be found with CF_3, NO_2, and similar groups. The key factor is that these groups are electron withdrawing and so induce a positive charge on the carbon atom of a substituted methane yet bear a positive charge rather than a negative charge at the point of attachment (e.g., the C of CN or CF_3 or the N of NO_2). In the case of nitro substitution, the experimental data show that an isodesmic reaction of tetranitromethane with three methanes to give four nitromethanes would have $\Delta H = -37.3$ kcal/mol at 298 K,[39] confirming the prediction.

An examination of Table IV shows that the charge of the central carbon atom does not increase in a strictly linear fashion with the degree of cyano substitution. Furthermore, the charge of neither the cyano carbon nor the cyano nitrogen nor of the cyano group as a whole remains particularly constant along this series. In fact, the charge of the cyano group becomes progressively less negative. Thus there appears to be a saturation effect which diminishes the electron-withdrawing power of the cyano group, much as one might intuitively expect. This behavior stands in striking contrast to the remarkable constancy observed in the fluoromethane and silylmethane series.

The energy differences in the cyanomethanes, measured by either the isodesmic reaction energies or by the bond dissociation energies, are among the strongest of any of the compounds we have studied. The charge separations, however, are smaller than

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[36] Apeloig, Y.; Abu-Freih, A.; Biton, R.; Stanger, A. *Abstracts of the 11th IUPAC Conference on Physical Organic Chemistry*; 1992; p IA-4.

[37] The charges at fluorine and silicon are −0.704 and +2.978, respectively, extremely close to the values in the other substituted methanes.

[38] It should be noted that Salzner and Schleyer (ref 12) found via the NBO analysis that increasing the number of cyano groups led to a negative charge at the central carbon. This seems odd considering the common view that a cyano group is a strong electron-withdrawing group. The atoms in molecules calculation gives the central carbon a positive charge.

[39] Pedley, J. B.; Naylor, R. D.; Kirby, S. P. *Thermochemical Data of Organic Compounds*, 2nd ed.; Chapman and Hall: London, 1986.

in the fluoromethane or silylmethane series. The cyano carbon atom is highly positively charged (close to +1.00), but the central carbon atom is only +0.47, even in tetracyanomethane. Thus some other factor may also contribute to the energy changes found for the cyano compounds.

Chloromethanes

The difference in electronegativity between carbon and chlorine (0.33 on the Allred–Rochow scale) is considerably less than that between carbon and silicon (–0.74), and so one might expect that the energy changes for isodesmic reactions with ethane should be quite small. This is, indeed, found (Table III). The introduction of the second chlorine onto methyl chloride is slightly stabilizing, the third is slightly destabilizing, and the fourth is significantly destabilizing. The bond dissociation energy differences in Table VI follow the same pattern. The addition of successive chlorine atoms leads only to very small changes in the bond dissociation energy difference, except that the final chlorine atom causes a destabilization of about 4 kcal/mol. One reason for this variation may be found in a comparison of the structures of the fluorocarbons and chlorocarbons. Methylene fluoride has a F–C–F bond angle of 108.8°, whereas the Cl–C–Cl angle in methylene chloride is 113°. This suggests a significant steric interaction between the chlorines, which will result in destabilization with increasing chlorine substitution and the concomitant reduction of the angle toward the tetrahedral value. The difference between the bond path angle and the geometric bond angle has previously been used as a measure of steric repulsion.[40] Geminal atoms or groups which repel each other will have bond paths which bend away from each other. Bond bending in the chloromethane series was found to be much greater than in any of the others. In dichloromethane, for instance, the Cl–C–Cl bond path angle (Table V) is smaller than the conventional angle by 7.6°, while the H–C–H bond paths are bent in the other direction by 7.0°. This strongly suggests that the chlorine atoms have a substantial steric repulsion. Consistent with these findings, steric repulsions between two chlorine atoms, but not between two fluorine atoms or between a fluorine atom and a chlorine atom, have been observed in the torsional energetics of chlorofluoroethanes.[41]

We previously observed that the charge on carbon varied in a linear fashion and that the substituent charge remained highly constant in the fluoro and silyl compounds, in which multiple substitution was favorable. This behavior was not observed with the cyanomethanes, in which multiple substitution was disfavored. Table IV shows that in the chloro compounds the charge changes are also not linear. The successive increases in the carbon atom charge have small absolute values, owing to the small electronegativity difference between carbon and chlorine. Thus the deviations from linearity are also small in an absolute sense, but they are substantial in a relative sense. The increase in the positive charge of the carbon on going from trichloromethane to tetrachloromethane is only 73% as large as the increase on going from methane to chloromethane. Furthermore, the charge on chlorine changes steadily from –0.32 in chloromethane to –0.12 in tetrachloromethane. This stands in striking contrast to the remarkable constancy of the charge on fluorine.

Discussion

Relationship between Energy Changes and Atomic Populations. The charges in Table IV present an interesting pattern when all the compounds are considered together. In two cases, the fluoromethanes and silylmethanes, the charge on the substituent is observed to remain constant to within ±0.01 of an electron. These are the same cases in which a large electronegativity difference is present and in which stabilization increases with multiple substitution. The absence of any saturation effect acting to moderate the ability of a substituent to donate or withdraw charge density as the charge on the carbon atom changes seems to contradict traditional intuition. The carbon charge in these compounds changes in a linear fashion which parallels the constancy of the substituent charge. In the case of the fluoromethanes, which exhibit the strongest stabilization, the charge of the carbon even grows *more rapidly* as the number of fluorines increases.

In the chloro and cyano compounds, on the other hand, a saturation effect is clearly evident. The absolute value of the charge on the substituent decreases with increasing substitution, from –0.398 to –0.118 in the cyano series and from –0.322 to –0.125 in the chloro series. Furthermore, the changes in the charge on carbon also decrease along the series. The first cyano substitution increases the methyl carbon charge by 0.133, while the final substitution increases it by only 0.053. The first chlorine atom causes a change of 0.104, while the last causes a change of only 0.076. These compounds, which behave so differently from the fluoromethanes and silylmethanes, are also the ones in which multiple substitution is thermoneutral or unfavorable. The cyano series seems to experience the strongest saturation effect, and it also represents the case in which multiple substitution is the least favorable.

Thus there appears to be a correlation between the behavior of the charges and whether or not multiple substitution is beneficial in a given series. The reason for this relationship is open for debate. One might speculate, however, that in those cases where strong Coulombic stabilization results from a progressive buildup of positive or negative charge on the central carbon, the saturation effect which one would ordinarily expect to observe is overcome. In other words, the expected decrease in the electron-withdrawing or electron-donating power of the substituent is counteracted by the progressively greater Coulombic attraction between the positively and negatively charged centers. The fluoromethanes and silylmethanes conform to this pattern. On the other hand, in the cases where there is little Coulombic stabilization to be gained, or even a Coulombic repulsion, the saturation effect operates in the manner one would expect.

Lone Pair Delocalization. The negative hyperconjugation hypothesis states that the lone pairs of fluorine donate electron density into the adjacent C–F σ^* orbitals. Due to the electronegativity difference between carbon and fluorine, the C–F σ^* orbitals should have a much larger lobe on the carbon atom than on the fluorine. Thus the hyperconjugative interaction should result in some back donation of charge from fluorine to carbon. One would predict on this basis that the negative charge on fluorine ought to decrease with increasing fluorine substitution of the central carbon, in parallel with the increasing degree of negative hyperconjugation. Contrary to this prediction, however, the charge on fluorine remains almost perfectly constant at –0.70 ± 0.01 from fluoromethane to tetrafluoromethane, and the charge on carbon increases with striking linearity (Figure 1). This behavior closely resembles that of the silylmethane series, in which no lone pairs are present and negative hyperconjugation cannot operate.

However, the charges do not provide a definitive test of the hyperconjugation hypothesis, since it is possible that any resulting charge transfer would be counteracted by an equal and opposite polarization of the C–F σ orbitals. This sort of cancellation has been observed in the polarization of σ and π systems.[42] In a previous investigation, we found it useful to localize the orbitals of a molecule in order to estimate the extent of electron delocalization.[43] The inability of an orbital to be localized on a particular atom is a direct consequence of its bonding character. To the extent that delocalization is absent, the localized orbitals end up on a single atom (core and lone pair orbitals) or on a specific pair of atoms (bond orbitals). In reality, the localization never succeeds perfectly, and some charge density from the localized orbitals remains associated with the other atoms. The amount of charge density in an orbital which cannot be localized serves as a measure of the delocalization. This approach has philosophical similarities to both the natural bond orbital formalism of Reed and Weinhold[13] and the definition of bond order

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(40) Wiberg, K. B.; Murcko, M. A. *J. Mol. Struct.* **1988**, *169*, 355.
(41) Paige, H. L.; Schwartz, M. *J. Phys. Chem.* **1992**, *96*, 1702.
(42) Wiberg, K. B.; Rosenberg, R. E.; Rablen, P. R. *J. Am. Chem. Soc.* **1991**, *113*, 2890.
(43) Wiberg, K. B.; Rablen, P. R.; Marquez, M. *J. Am. Chem. Soc.* **1992**, *114*, 8654.

Table VII. Delocalization Indices, HF/6-311++G**(6d)//MP2(fu)/6-31G*

compd	orbitals[a]		
	C–H		
CH_4	0.0297		
	F–lp	C–H	C–F
CH_3F	0.0143	0.0369	0.0092
CH_2F_2	0.0171	0.0486	0.0155
CHF_3	0.0184	0.0633	0.0235
CF_4	0.0194		0.0316
	Cl–lp	C–H	C–Cl
CH_3Cl	0.0169	0.0319	0.0189
CH_2Cl_2	0.0210	0.0359	0.0211
$CHCl_3$	0.0247	0.0407	0.0242
CCl_4	0.0277		0.0275
	N–lp	C–H	C–N
FCH_2NH_2	0.0589	0.0490	0.0320
FCH_2NH_2 rot[b]	0.0450	0.0445	0.0347
CH_3NH_2	0.0458	0.0390	0.0303

[a] The delocalization indices indicate the fraction of charge density in a localized orbital (e.g., a fluorine lone pair orbital, a C–H bond orbital, or a C–F bond orbital) not found in the basins of the atoms constituting its primary locus. For a lone pair orbital, for instance, the delocalization index is the fraction of charge density found on all the atoms *other* than the one on which the lone pair is actually located. [b] The "lone pair" axis is rotated 80° from the anti position, which is the highest energy conformer. This is at the maximum in the torsional potential for the C–N bond.

Table VIII. C–F Bond Orders,[44] HF/6-311++G**(6d)//MP2(fu)/6-31G*

compd	π	σ	total	% π	ρ_{crit}[a]
CH_3F	0.093	0.654	0.747	12.4%	0.2316
CH_2F_2	0.094	0.594	0.688	13.7%	0.2417
CHF_3	0.054	0.562	0.616	8.8%	0.2537
CF_4	0.047	0.496	0.543	8.7%	0.2667

[a] ρ_{crit} is the electron density at the bond critical point, as defined in Bader's theory of atoms in molecules.[21] These values were obtained using the RHF/6-311++G**(6d)//MP2(fu)/6-31G* wave functions, except that the C–F bond lengths were kept constant at the value for fluoromethane so as to eliminate artifacts which might result from changes in these bond lengths.

proposed by Cioslowski and Mixon.[44] It does not physically alter the wave function since only unitary transformations among occupied orbitals are involved.

The same methodology can be applied to the question of hyperconjugation in the fluoromethanes. As in our previous study, the procedure begins with a Boys localization of the orbitals from an HF/6-311++G**(6d)//MP2(fu)/6-31G* calculation. This capability is built into the GAUSSIAN 91 package of programs. In order to quantify the degree of localization, we then calculate the fraction of charge transfer from the primary locus of the orbital to the other associated atoms. We designate this quantity as the delocalization index, defined as the fraction of charge in a localized MO which residues in the "wrong" parts of the molecule. The atomic populations are calculated by integrating the electron density in each of the atomic basins as defined by Bader's topological theory of atoms in molecules.[21] This integration can be performed separately for each orbital of a localized wave function, such that the atomic populations are broken down into the contributions from each of the orbitals. Thus one can define the population on each atom *for a single localized orbital.* The delocalization index of an orbital, then, is computed as the sum of the populations of the orbital on the atoms other than the one or two which comprise its primary locus divided by the sum of the populations over all the atoms. The sum over all atoms should be exactly 2 for a properly integrated orbital from a Hartree–Fock wave function. For instance, the delocalization index of a fluorine lone pair in fluoromethane is calculated as the total integrated density of the lone pair orbital over the methyl group divided by the integrated density over all space (=2.0000). Analogously, the delocalization index of the C–F bond in difluoromethane is the density of the C–F bond orbital on the other fluorine and two hydrogen atoms divided by 2.0000.

The results of this analysis are given in Table VII. It is readily apparent that the fluorine lone pairs are highly localized in every compound. If the negative hyperconjugation hypothesis were correct, we would expect to see a large increase in the value of the lone pair delocalization index on going from fluoromethane (no negative hyperconjugation possible) to difluoromethane (negative hyperconjugation is possible), followed by further increases as the number of fluorine atoms increased (more and more hyperconjugative interactions possible). Instead, what we observe is that the lone pair delocalization indices remain very small and almost constant. In fact, the C–H bond orbitals have considerably larger delocalization indices than do the fluorine lone pairs. This is consistent with the expectation that the lone pairs on fluorine would be tightly bound and therefore unavailable for any sort of bond formation.

A comparison with the chloromethane series serves to further illustrate the point. Multiple chlorine substitution is not thermodynamically favored, as has already been pointed out, and negative hyperconjugation is not thought to contribute to the stability of these compounds. The p orbitals of chlorine are too diffuse to overlap well with carbon p orbitals, and also the C–Cl bond length is too long to permit effective π overlap. However, an examination of Table VII shows that the delocalization indices of the chlorine atoms, though small in absolute magnitude, are nonetheless *larger* than those of the fluorine atoms. Their gradual increases with the degree of chlorine substitution also mirrors the trend observed in the fluoromethane series. This would seem to suggest that negative hyperconjugation is no more important with the fluoromethanes than it is with the chloromethanes. The most natural conclusion to draw is that negative hyperconjugation plays little or no role in either case. It is also worth noting that the percentage changes in delocalization indices observed here are considerably smaller than those we have observed previously for π bond orbitals in connection with torsion about the central single bond in heteroatom-substituted butadienes.[43]

Consideration of the covalent bond orders of the fluoromethanes calculated by the method of Cioslowski and Mixon[44] leads to a similar conclusion. As can be seen in Table VIII, the C–F bond order decreases monotonically from 0.75 to 0.54 along the series from fluoromethane to tetrafluoromethane. This is contrary to the hypothesis that covalent bonding increases as a result of negative hyperconjugation but is consistent with the increasingly ionic character of the C–F bonds. Furthermore, the fraction of the bond order attributable to π orbitals also decreases along this series, again as shown in Table VIII. The point groups of CH_3F, CHF_3, and CF_4 do not yield a σ/π separation, so this analysis cannot be performed directly. However, the symmetries of these molecules can be lowered to C_s by slightly perturbing the true geometries,[45] and then one obtains well-defined π systems. Only one of the two p-like lone pairs on each fluorine atom constitutes a part of the π system defined in this manner. As a result, the computed proportion of the bond order due to the lone pairs on fluorine is probably an underestimate by a factor of 2. However, this measure should serve adequately to describe the trend in π participation as the degree of fluorine substitution changes. The negative hyperconjugation hypothesis predicts an increase in the proportion of π character as the number of fluorine atoms increases, due to the increasing extent of fluorine lone pair donation. The most dramatic change ought to occur between fluoromethane, in which there is no negative hyperconjugation, and difluoromethane, in which it is present. While the fraction of π bond order does indeed increase from fluoromethane to difluoromethane, the increase is very slight, and the overall trend along the series is clearly down rather than up. This remains true despite the decrease in the C–F bond lengths which accompany the increasing fluorine substitution.

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(44) Cioslowski, J.; Mixon, S. T. *J. Am. Chem. Soc.* **1991**, *113*, 4142.

(45) Changing a bond length by 0.001 Å is sufficient for this purpose.

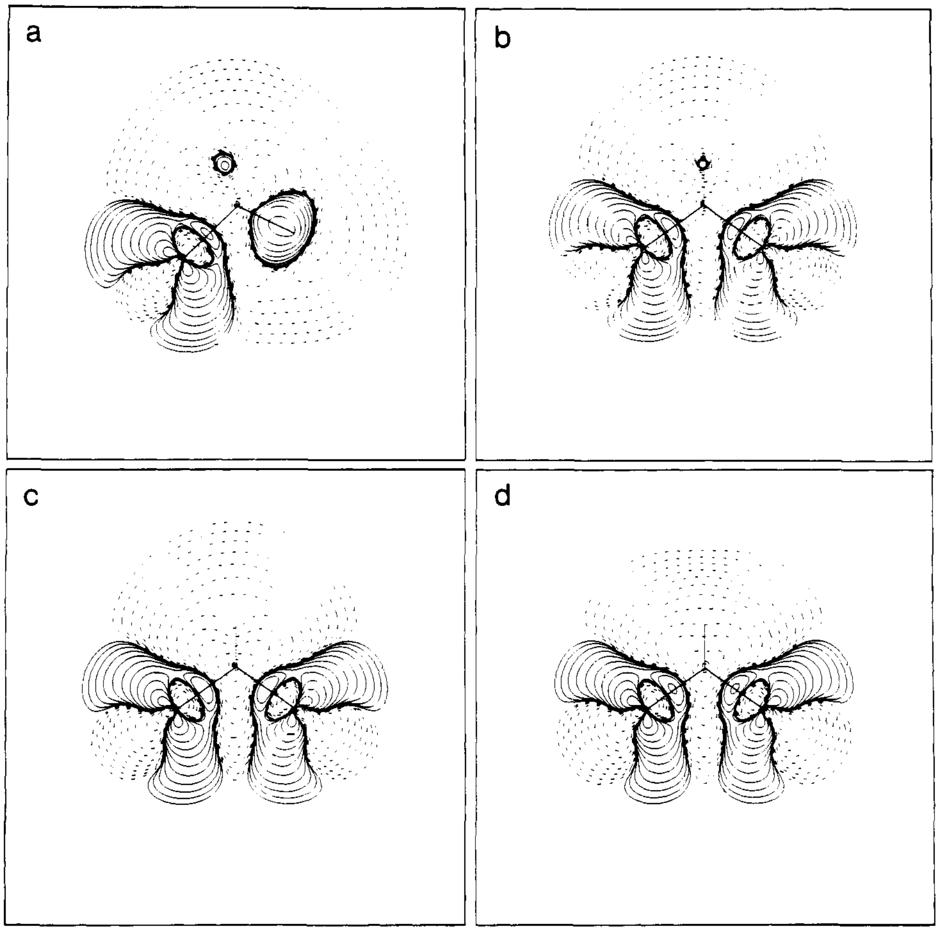

Figure 3. Deformation density plots for fluoromethane (a), difluoromethane (b), trifluoromethane (c), and tetrafluoromethane (d).

One way to analyze the charge distribution in a molecule is to examine the deformation density. In a direct analogy to the deformation density plots derived in X-ray crystallography,[46] the charge distributions of idealized, spherically symmetric atoms ("proatoms" in the nomenclature of Hirshfeld[47]) can be subtracted from the overall charge distribution of a molecule.[48] The resulting deformation density plot shows how charge is redistributed in the process of bringing isolated atoms together to form a molecule. For instance, bonds appear as positive regions, since electron density accumulates between bonded atoms. There are also regions of charge accumulation that approximately correspond to lone pairs.

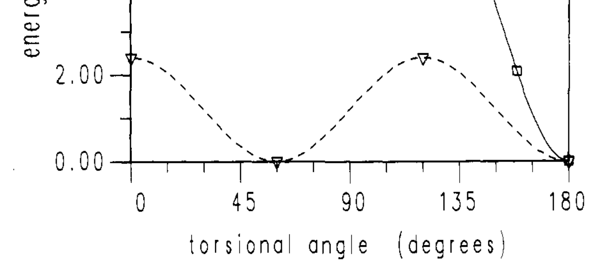

Figure 4. Torsional potential energy profiles for methylamine (dashed line) and (fluoromethyl)amine (solid line) calculated at MP2/6-31+G*.

Deformation density plots of the fluoromethanes are shown in Figure 3. The positive regions corresponding largely to the lone pairs on the fluorine atoms are clearly visible in each case. At first glance it might appear that each fluorine atom has two such regions, but if the deformation density were calculated in three dimensions, then the two branches would meet to form a single cone-shaped structure. A careful comparison of the shapes of the charge density accumulations on the fluorine atoms reveals that the "leading edge" (the side facing the carbon atom) remains almost identical for all four compounds. This area, which extends away from the C–F bond axis and into the cylindrical "π" space around the bond, is precisely where one might expect to observe a shift in the charge density if the lone pairs on the fluorine atoms were donating increasing amounts of charge density to the carbon atom. The absence of any such change suggests that negative hyperconjugation is of little importance here. On the other hand, the "trailing edges" (the sides facing away from the carbon atom) do contract noticeably as the degree of fluorine substitution increases. The loss of charge density occurs quite close to the axis of the C–F bond, in an area which corresponds more closely to the backside of the C–F bond orbital than to the lone pairs of "π"

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(46) Dunitz, J. D. *X-Ray Analysis and the Structure of Organic Molecules*; Cornell Univ. Press: Ithaca, NY, 1979.

(47) Hirshfeld, F. L. *Theor. Chim. Acta* **1977**, *44*, 129.

(48) The procedure used to obtain the charge density distributions of the spherically symmetric isolated atoms (proatoms) is not discussed here. This topic will be addressed in a future publication. In brief, the following ab initio calculations are used. For atoms such as hydrogen, nitrogen, and phosphorous, which have half-filled outer shells, an ROHF calculation on the isolated atom at the appropriate basis set yields a suitable wave function. For other atoms, a GVB (generalized valence bond) calculation at the appropriate basis set is required in order to ensure spherical symmetry. For the special cases of carbon and silicon, a calculation is performed on CH_4 or SiH_4 at the appropriate basis set and level of theory. The hydrogen-centered basis functions are then stripped out of the resulting wave functions. The wave functions are renormalized to yield the correct total integrated electron density and are then used as proatom charge distributions.

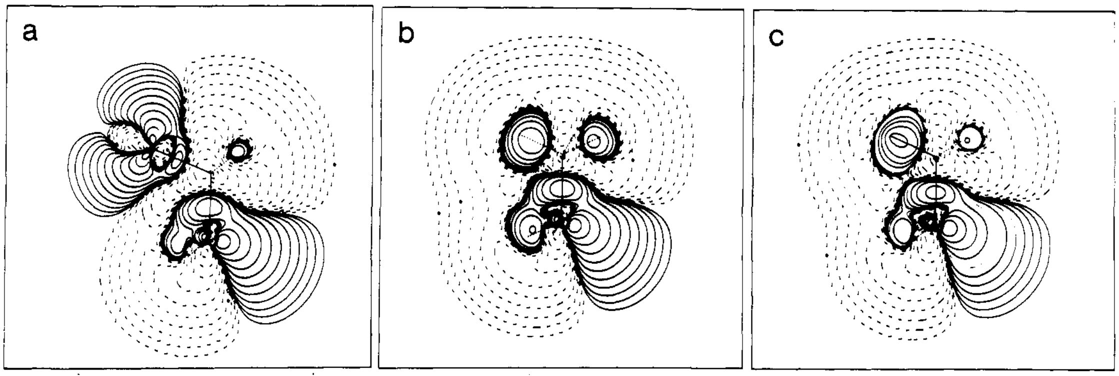


Figure 5. Deformation density plots for (fluoromethyl)amine in the anti conformation (a), (fluoromethyl)amine in the conformation corresponding to the peak in the torsional potential (b), and methylamine (c).

symmetry which could participate in negative hyperconjugation. It therefore seems reasonable to interpret the depletion of charge in this region as a result of the increasing positive charge at carbon which will polarize the charge density at fluorine toward the carbon. We have integrated the deformation density in the positive regions near the fluorine atoms, and as might be expect in light of the above discussion the integrated electron density decreases along the series fluoromethane (0.370 electrons), difluoromethane (0.344 electrons), trifluoromethane (0.328 electrons), and tetrafluoromethane (0.319 electrons).[49] Interpretation of these numbers is complicated by the fact that the "lone pair" region is contiguous with the accumulation of charge corresponding to the C–F bond.

When is Negative Hyperconjugation Likely To Be Important? The energy changes for multiple substitution onto methane, as well as the bond length changes, appear to be easily accounted for on the basis of Coulombic interactions and hybridization changes, and there does not appear to be any evidence for negative hyperconjugation. The case of the silylmethanes is of particular significance, for here the energetic effect found with fluorine substitution was reproduced in the absence of an opportunity for hyperconjugation and despite the opposite polarization of the bond to the substituent. Furthermore, direct examination of the localized ab initio wave function strongly suggested that the degree of delocalization of the fluorine lone pairs was very small and did not increase significantly as more fluorine atoms were introduced.

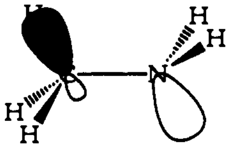
Negative hyperconjugation may well be operative in other cases in which there is an opporunity for charge transfer.[50] However, it might be noted that the observation of structural or energetic consequences of rotation about a bond to an atom having a lone pair does not, by itself, provide evidence for negative hyperconjugation. Methylamine and (fluoromethyl)amine provide an interesting comparison. The rotational profiles are shown in Figure 4. Methylamine has a 3-fold barrier with a magnitude $\sim^2/_3$ that for ethane. There is good reason to believe that the barrier for methylamine has the same origin as that for ethane.[51]

The one unique aspect of methylamine is that the CH bond anti to the lone pair is longer and weaker than the other CH bonds.[52] This has been attributed to negative hyperconjugation.[53] We have examined the changes in electron population during rotation about the C–N bond and found essentially no change in the N population but rather a shift of charge from C to the H anti to the lone pair. This behavior can easily be explained as due to a repulsive interaction between the nitrogen lone pair and the backside of the CH bond orbital.[20]

Table IX. Bond Orders[44] in Amines, HF/6-311++G**(6d)//MP2(fu)/6-31+G*

compd	C–N	C–F	C–H(av)	N–H(av)	
FCH_2NH_2 anti	0.950	0.680	0.926	0.859	
FCH_2NH_2 rot[a]		0.939	0.692	0.938	0.862
CH_3NH_2	0.962		0.967	0.894	

[a] The "lone pair" axis is rotated 80° from the anti position, which is the highest energy conformer. This is at the maximum in the torsional potential for the C–N bond.



It can be seen in Figure 4 that (fluoromethyl)amine, which has been extensively discussed,[7,8,54] is quite different from methylamine. The syn form (0°) is higher in energy than the trans (180°) by 4.8 kcal/mol, and it is converted to trans via inversion with no activation barrier. Its higher energy is due to its larger dipole moment, resulting from the aligned and repulsive C–F and N-lone pair dipoles. The high-energy point for rotation about the C–N bond is found to be close to 90°. If the repulsive interactions found with the syn rotamer were a linear function of the torsional angle, they would amount to ~2 kcal/mol at 90°. The net destabilization at this angle would then be 9 – 2, or about 7 kcal/mol.

There is no reason to believe that (fluoromethyl)amine should be destabilized at 90°, and so there is general agreement that it is stabilized at 180° and to a lesser extent at 0°. We have examined (fluoromethyl)amine in the same fashion as the fluoromethanes. The deformation density plots for (fluoromethyl)amine in the anti conformation and in the conformation corresponding to the peak in the torsional profile are shown in Figure 5. The delocalization indices and covalent bond orders for these two conformations of (fluoromethyl)amine as well as for methylamine are listed in Table VII and Table IX, respectively.

The lone pair region on nitrogen in the deformation density for methylamine integrates to 0.634 electrons.[49] In the anti structure for (fluoromethyl)amine, in which the lone pair is expected to donate into the C–F σ^* orbital, the nitrogen lone pair integrates only to 0.622 electrons. At the highest point in the torsional profile, on the other hand, it integrates to 0.638 electrons. The fluorine lone pairs show the opposite trend, integrating to 0.391 electrons in the anti structure and to 0.367 in the rotated structure. This appears to support the hypothesis that donation by the nitrogen lone pair into the C–F σ^* orbital stabilizes the anti conformation.

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(49) Integrations were performed by summing all points which could be reached from a given starting point without crossing any contours representing a charge density of less than 4.0×10^{-4} e/a_0^3. The value derived in this manner differed from that obtained by using a cutoff contour of exactly 0 by at most 2% in a series of test cases. The integrations were performed on a three-dimensional grid of deformation density values in all cases.

(50) Eyermann, C. J.; Jolly, W. L.; Xiang, S. F. *J. Fluorine Chem.* **1983**, *23*, 389.

(51) Bader, R. F. W.; Cheeseman, J. R.; Laidig, K. E.; Wiberg, K. B.; Breneman, C. *J. Am. Chem. Soc.* **1990**, *112*, 6530.

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(53) Pross, A.; Radom, L.; Riggs, N. V. *J. Am. Chem. Soc.* **1980**, *102*, 2253.

(54) (a) Reed, A. E.; Schleyer, P. v. R. *Inorg. Chem.* **1988**, *27*, 3969. (b) Kost, D.; Raban, M. *J. Am. Chem. Soc.* **1982**, *104*, 2960. (c) Raban, M.; Kost, D. *Tetrahedron* **1984**, *40*, 3345. (d) Dorie, J.; Gouesnard, J.-P. *J. Chim. Phys. Phys.-Chim. Biol.* **1984**, *81*, 15. (e) Rahman, M. M.; Lemal, D. M.; Dailey, W. P. *J. Am. Chem. Soc.* **1988**, *110*, 1964.

However, the interpretation of these numbers is ambiguous due to the fact that the "lone pairs" defined in this manner include the σ bond, as in the case of the fluoromethanes discussed earlier.

A careful comparison of the three deformation density plots reveals that, in contrast to the fluoromethanes, the "leading edge" of the nitrogen lone pair changes at least as much as the "trailing edge". The "lone pair" regions for (fluoromethyl)amine and its rotated conformer are essentially superimposible except for being rotated by 6° toward the fluorine in the former.

The delocalization index of the nitrogen lone pair of (fluoromethyl)amine decreases from 0.0589 to 0.0450 upon rotation, which also suggests that the lone pair donates charge density in the anti conformation. The value of 0.0450 in the rotated structure is very close to that of the lone pair in methylamine (0.0458), as might be expected. The percentage change in the delocalization index is about the same as that between the fluorine lone pairs in fluoromethane and tetrafluoromethane, but the absolute change is almost three times as great. Table IX shows that the C–N covalent bond order in (fluoromethyl)amine undergoes a slight decrease upon rotation about the bond, concurrent with a slight increase in the C–F bond order, which is again consistent with the negative hyperconjugation hypothesis. The C–N covalent bond order in both conformers is less than that in methylamine, however, presumably because the presence of the fluorine atom increases the charge on carbon and hence the ionic character of the C–N bond in (fluoromethyl)amine. Thus there is at least some evidence that interaction of the lone pair of nitrogen with the C–F σ^* orbital stabilizes the C_s symmetric conformers of (fluoromethyl)amine, but even in this highly favorable case the effect appears to be of only a modest magnitude.

Conclusions

Internal Coulombic stabilization appears to be an important factor in stabilizing some types of organic compounds. With both strongly electron-withdrawing (F) or electron-releasing (SiH_3) groups, the charge at carbon changes linearly with the number of substituents, leading to increased Coulombic stabilization with increasing substitution. Other types of electron-withdrawing substituents such as NO_2 or CN, which have positively charged atoms as the first atom, lead to the opposite result, causing increasing Coulombic destabilization as the degree of substitution increases.

Although negative hyperconjugation does not appear to play an important role in stabilizing the perfluoroalkanes, it probably is a significant factor in other cases such as (fluoromethyl)amine, in which the substituted carbon is electron deficient and the substituent (NH_2) has a relatively high energy lone pair.

We have also observed an interesting relationship between the variation in the charges of substituents as the degree of substitution increases and the energetic consequences of this substitution. In cases where multiple substitution is thermoneutral or disfavored, a saturation effect is found which diminishes the electron-withdrawing or electron-donating ability of a substituent as a greater number of these substituents are placed around a single carbon atom. These are also the compounds (the cyanomethanes and chloromethanes) which have little Coulombic stabilization from adjacent positively and negatively charged atoms or even have strong repulsions. This sort of saturation principle agrees well with common notions regarding charge distributions in organic molecules. However, in those cases where multiple substitution is favorable (the fluoromethanes and silylmethanes), the ability of the substituent to withdraw or donate charge does *not* diminish with increasing substitution. Instead, the substituent charge remains highly constant as the number of substituents increases, and the charge on carbon changes in a linear fashion.

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Supplementary Material Available: Tables of GAPT and CHELPG atomic charges, interatomic distance matrices for fluoromethanes, and MP2/6-31G* optimized geometries in the form of Z-matrices (13 pages). Ordering information is given on any current masthead page.

Simple Electrostatic Model for Enthalpies of Formation of Singly Substituted Alkanes

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Abstract: In earlier work, Benson and Luria (*J. Am. Chem. Soc.* **1975** *97*, 704–709) showed that the greater stability of branched alkanes, compared to normal alkanes, could be explained on the basis of the electrostatic interactions between the atoms involved. This approach is extended herein to molecules containing single heteroatoms, N, O, S, Cl, Br, and I. Charges are assigned to atoms according to differences between their electronegativities and the electronegativities of atoms to which they are covalently bonded. Carbon atoms partially share the charges so established. Electrostatic energies are calculated for all pairs of atoms in the molecules. Covalent bonds are assigned energies in a simple scheme of bond additivity. Enthalpies of formation of 23 alkyl derivatives, estimated in this way, agree with experimental values within 1.4 kJ mol^{-1} on average, a difference which is close to the average quoted experimental uncertainty.

I. Introduction

Why is the C–O bond in ethanol 5 kJ mol^{-1} stronger than that in methanol, when the C–H bond in ethane is 19 kJ mol^{-1} weaker than that in methane?[1] This reversal cannot be attributed to differing stabilities of the radicals formed but must involve the molecules themselves. The question could be rephrased: what is the source of the extra stability of methane and ethanol or of the relative instability of ethane and methanol?

The principle of bond additivity,[2] while conceptually attractive, would predict that both the differences above would be zero. Empirical group additivity methods[2] could reproduce the differences, but at the expense of adding more parameters without providing an explanation. Quantum mechanical methods[3] do not add parameters and do provide an explanation at a sophisticated level, but the explanation can be difficult to express in simple terms.

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