Table II. Relative Energies[a] (kcal/mol) of the QUEST and ab Initio Intramolecular Transition Structures of 1,3,9-Decatriene and 1,3,8-Nonatriene

	1,3,9-decatriene		1,3,8-nonatriene	
basis set	endo (cis)	exo (trans)	endo (cis)	exo (trans)
QUEST	0.0	0.18	0.0	1.07
STO-3G	0.24	0.0	0.0	0.17
3-21G	0.0	0.04	0.0	0.70
6-31G*//3-21G[b]	0.18	0.0	0.0	0.99
AM1//3-21G[c]	1.39	0.0	0.0	0.40
PM3//3-21G[d]	1.26	0.0	0.0	0.17
experimental	0.0	0.10	0.0	1.03

[a] The error limits associated with these relative energies for the QUEST, semiempirical, and ab initio calculations are ±0.5, ±0.1, and ±0.1 kcal/mol, respectively. [b] This calculation represents a single-point calculation at the 6-31G* level for the geometry found for the 3-21G TS. [c] This calculation represents an optimized stationary point calculation using AM1 fixing the forming bonds to that found for the 3-21G TS. [d] This calculation represents an optimized stationary point calculation using PM3 fixing the forming bonds to that found for the 3-21G TS.

isomer in the nonatriene system. These preferences can be alter dramatically based on the substitutions as indicated in Table I.

Semiempirical TS. The structures were optimized employing both AM1[12] and PM3[13] holding the forming bond lengths fixed to those found for the authentic ab initio structures for all cases. The resulting structures were nearly identical to those determined by the ab initio methods. However, these stationary points had two negative eigenvalues. A local transition structure search was carried out both by automated procedures found in MOPAC and by a systematic variation of the forming bonds. No transition structures resembling the ab initio structures were found. The systematic procedure indicated that a very unsymmetrical structure was favored. The ΔE for the IDA systems, constrained to the ab initio forming bond lengths, was quite inaccurate. This is reminiscent of semiempirical calculations on the intermolecular systems, where constrained symmetric geometries are reasonable but the energies are not.[4b]

Conclusion

These studies provide evidence that the QM/MM method correctly predicts structural features found in the ab initio TS. The good agreement between the full ab initio and QUEST structures demonstrates that a highly coupled and highly strained system can be qualitatively studied using the combined gradient method in QUEST.

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Supplementary Material Available: Internal and cartesian coordinates of the QUEST and ab inito 3-21G fulminic acid-ethylene intramolecular transition structures and internal and cartesian coordinates of the QUEST and ab initio STO-3G and 3-21G determined Diels–Alder intramolecular transition structures (34 pages). This material is contained in many libraries on microfiche, immediately following this article in the microfilm version the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

Effect of Multiple Halide Substituents on the Acidity of Methanes and Methyl Radicals. Electron Affinities of Chloro- and Fluoromethyl Radicals

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Ab initio molecular orbital calculations are reported for methanes, methyl radicals, and methyl anions CH_mF_n and CH_mCl_n where n takes values from 0 to 3, and for mixed halides $CH_mF_nCl_p$ where $(p + n)$ takes values from 1 to 3. Structures were optimized at HF/6-31++G(d,p), and single-point calculations are reported at MP4SDTQ/6-31++G(d,p) and, for the smaller molecules, at MP4SDTQ/6-311++G(2df,p). For methyl anions containing chlorine atoms optimization at the Hartree–Fock level gave unrealistically long bond lengths, and more satisfactory structures were obtained by including correlation energy in the optimization calculations (MP2/6-31++G(d,p)). Stabilization energies for isodesmic reactions of the type $X_nCH_m + (n - 1)\ CH_{m+n} \rightarrow nXCH_{(m+n-1)}$ show geminal interactions to be largest between F atoms in methyl anions (in CF_3^-, 43.1 kcal/mol), somewhat smaller between F atoms in methanes and methyl radicals (in CHF_3, 26.7 kcal/mol; in CF_3, 16.6 kcal/mol), very small between Cl atoms in anions (in CCl_3^-, 5.3 kcal/mol) and negligible in chloromethanes (in $CHCl_3$, −0.7 kcal/mol). The acidity of methane increases by approximately 19 kcal/mol for every additional Cl substituent; i.e., the effect of multiple substitution is roughly additive. One F atom increases the acidity of methane by only 10.4 kcal/mol, two by an *additional* 14.9 kcal/mol, and three by a further 21.7 kcal/mol; i.e., in the fluoromethanes, F–F interactions have a synergistic effect. Electron affinities evaluated from isodesmic reactions using energies from MP4SDTQ/6-311++G(2df,p) molecular orbital calculations are within 0.03 eV of the experimental values for CH_3 and CH_2Cl. This same level of theory gives calculated electron affinities for CHF_2 of 0.79 eV and for CH_2F of 0.27 eV.

In organic molecules, halogens function as powerful σ-acceptors and somewhat weaker π-donors.[1,2] In carbanions, σ-withdrawal to the halogen assists in delocalizing the negative charge onto the more electronegative sub-

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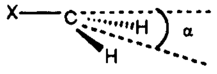
stituent and away from the electron-rich carbanion center. This interaction is strongly stabilizing. The four-electron-two-orbital π-interaction between the lone pair on the carbanion center and a lone pair on the halogen is, however, destabilizing. Overall the σ-effect is dominant and halogens are stabilizing substituents in carbanions.[2-4] The geometric consequences of these interactions for organohalide anions are a long carbon–halogen bond (C–F in CH_2F^- is ~1.577 Å[5] compared to 1.383 Å in CH_3F[6]) and an increase in the out-of-plane angle, α, in the anion relative to that in CH_3^-.



1

Additional halogen substituents are expected to have similar interactions with the carbanionic carbon and should lead to further stabilization. These interactions with halogen atoms would be expected to be somewhat smaller in magnitude as the number of halogens increases, i.e., there should be a saturation effect and the stabilization afforded by three halogen atoms should be considerably less than three times the effect of a single halogen atom. If halogen atoms behave in this way, then one halogen atom would be expected to increase the acidity of methane and further substitution by halogens would lead to further, smaller increases in acidity.

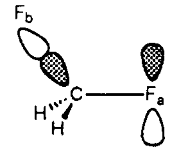
The above analysis of the additivity of interactions between halogens and a carbanion center ignores interactions between halogens attached to the same carbon atom. Such geminal interactions between fluorine atoms have been shown to be strongly stabilizing in fluoromethanes.[2,7-9] Reed and Schleyer[7] used natural bond orbital analysis to calculate energies for *localized* structures for fluoromethanes, and by using isodesmic reactions of the type in eq 1 they found that geminal interactions between fluorine

$$CH_2F_2 + CH_4 \rightarrow 2CH_3F \qquad (1)$$

atoms in *localized* structures are in fact *destabilizing* (ΔE is −15.6 kcal/mol for eq 1). However, when *delocalization* is allowed as in SCF calculations the fluorine–fluorine interaction is stabilizing (ΔE = +14.0 kcal/mol).

The stabilizing interaction between two fluorine atoms involves π-donation from the lone pair on one fluorine, F_a, to the σ^* antibonding orbital of the C–F_b bond, which is located mainly on the carbon (structure **2**).[7,10] There is, of course, an identical interaction between the lone pair on F_b and σ^* for the C–F_a bond. In valence bond terms, these interactions are described by structures **3a**, **3b** and **3c**.

The magnitude of the stabilization resulting from negative hyperconjugation in carbanions compared with that in methanes will be an additional factor in determining whether increasing the number of halogen atoms will increase the acidity of methane. In carbanions the C–F bonds are considerably longer and weaker than in methanes.[3-5,11] Consequently, the σ^* orbital for C–F is lower in energy. Also the fluorine atoms carry more negative charge and are therefore better π-donors; i.e., the energy of the donor p-orbital is higher in energy. The two orbitals involved in negative hyperconjugation then are closer together in energy in the anions and increased interaction should occur. This energetically favorable situation could conceivably be outweighed by geometric factors. The C–F distance is considerably longer in the carbanions, and positive overlap between the lone pair and σ^*_{C-F} could be smaller.



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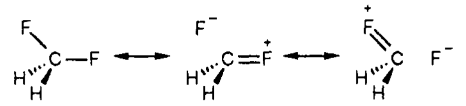

3a 3b 3c

Second-row elements are less effective both as σ-acceptors and as π-donors. The overall interaction between two chlorine atoms in CH_2Cl_2 is slightly destabilizing,[2] i.e., any stabilization from negative hyperconjugation in this molecule is more than offset by repulsion between two negatively charged chlorine atoms.

Fluorinated and chlorinated methanes[12] and methyl[12-17] radicals have been the subject of previous ab initio studies aimed mainly at structure determination and, in the radicals, calculation of negative hyperconjugation, barriers to inversion, and heats of formation. Polyhalogenated carbanions have been less well studied,[11,18] possibly because it is necessary to use larger basis sets incorporating diffuse functions for a satisfactory description of negative ions.

In this work we have used high-level ab initio molecular orbital calculations coupled with isodesmic reactions of the type given in eq 1 to calculate the interaction energies between various combinations of fluorine and chlorine atoms in methanes, in methyl anions, and in methyl rad-

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Table I. HF/6-31++G(d,p) Optimized Geometries for Chloro- and Fluoro-Substituted Methanes, Methyl Radicals, and Methyl Anions

	bond distances[n] (Å)			
	C–H	C–F	C–Cl	angles[n] (deg)
methanes				
CH_4[a]	1.084 (1.091)			HCH = 109.5
CH_3F[b]	1.082 (1.100)	1.372 (1.383)		HCH = 110.4 (110.6); HCF = 108.5 (108.3)
CH_2F_2[c]	1.079 (1.093)	1.342 (1.357)		HCH = 113.4 (113.7); HCF = 108.8 (108.7); FCF = 108.2 (108.3)
CHF_3[d]	1.076 (1.098)	1.319 (1.333)		HCF = 110.5 (110.3); FCF = 108.4 (108.8)
CH_3Cl[e]	1.078 (1.096)		1.786 (1.781)	HCH = 110.6 (108.0); HCCl = 108.4 (110.92)
CH_2Cl_2[f]	1.075 (1.068)		1.769 (1.772)	HCH = 108.2 (112.0); ClCCl = 112.8 (111.8)
$CHCl_3$[g]	1.073 (1.100)		1.763 (1.758)	HCCl = 107.6 (107.6); ClCCl = 111.3 (111.3)
CH_2FCl[h]	1.076 (1.078)	1.347 (1.378)	1.768 (1.759)	HCH = 112.6 (111.9); HCCl = 108.3 (109.1); HCF = 108.9; FCCl = 109.8 (110.0)
CHF_2Cl[i]	1.075 (1.090)	1.324 (1.350)	1.755 (1.740)	HCCl = 109.8 (107.0); HCF = 109.9; FCF = 108.0 (107.0); FCCl = 109.6 (110.5)
$CHFCl_2$[j]	1.074 (1.090)	1.333 (1.367)	1.757 (1.750)	HCCl = 108.7; HCF = 109.2; FCCl = 109.0 (109.0); ClCCl = 112.2
methyl radicals				
CH_3[k]	1.073 (1.079)			HCH = 120.0; α = 0.0
CH_2F	1.073	1.334		HCH = 122.6; HCF = 113.8; α = 33.0
CHF_2	1.076	1.316		HCF = 113.9; FCF = 110.8; α = 44.4
CF_3[l]		1.301		FCF = 111.13 (110.7); α = 50.0
CH_2Cl	1.070		1.717	HCH = 123.1; HCCl = 116.7; α = 19.3
$CHCl_2$	1.071		1.713	HCCl = 116.5; ClHCl = 118.6; α = 29.2
CCl_3[m]			1.715	ClCCl = 117.0 (116.0); α = 29.4
CHFCl	1.073	1.320	1.717	HCCl = 116.5; CHF = 113.9; FCCl = 113.9
$CFCl_2$		1.312	1.717	ClCCl = 117.9; FCCl = 112.9; α = 40.9
methyl anions				
CH_3^-	1.096			HCH = 109.7, α = 54.1
CH_2F^-	1.104	1.492		HCH = 104.4; HCF = 101.2; α = 71.5
CH_2F^- (MP2)	1:106	1.515		HCH = 105.4; HCF = 101.2; α = 71.3
CHF_2^-	1.103	1.447		HCF = 99.5; FCF = 100.4; α = 75.0
CF_3^-		1.405		FCF = 100.0; α = 74.4
CH_2Cl^-	1.096		2.076	HCH = 104.4; HCCl = 95.8; α = 80.6
CH_2Cl^- (MP2)	1.101		1.894	HCH = 105.4; HCCl = 101.6; α = 70.6
$CHCl_2^-$	1.086		1.930	HCCl = 97.3; ClCCl = 104.8; α = 78.0
$CHCl_2^-$ (MP2)	1.099		1.883	HCCl = 98.8; ClCCl = 105.6; α = 75.3
CCl_3^-			1.874	ClCCl = 103.8; α = 67.3
CCl_3^- (MP2)			1.873	ClCCl = 103.9; α = 66.9
$CHFCl^-$	1.092	1.333	2.631	FCH = 102.8; ClCH = 78.0; FCCl = 99.6
$CHFCl^-$ (MP2)	1.105	1.469	1.927	FCH = 99.1; ClCH = 96.8; FCCl = 102.8
CF_2Cl^-		1.291	3.093	dissociates into CF_2 and Cl^-
CF_2Cl^- (MP2)		1.418	2.003	ClCF = 100.1; FCF = 100.0; α = 74.1
$CFCl_2^-$		1.344	1.964	ClCF = 100.9; ClCCl = 102.4; α = 72.4

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icals. Ab initio molecular orbital calculations are capable of yielding proton affinities and acidities in excellent agreement with experimental values,[19] and we have used our calculations to obtain acidities for halogenated methanes and methyl radicals. Finally it is possible, in principle, to obtain electron affinities for the methyl radicals from eq 2. However, accurate evaluation of electron affinities

$$CH_mF_nCl_p^- \rightarrow CH_mF_nCl_p + e \tag{2}$$

from this equation using energies from molecular orbital calculations is notoriously difficult due to problems in treating the correlation energies of the radicals and anions in a balanced manner.[20-22] We have used our highest level calculations including correlation energy (MP4SDTQ) to estimate electron affinities for halogenated methyl radicals both from isogyric reactions involving the dissociation of hydrogen molecule (eq 3)[22] and also from combining the experimental electron affinity of methyl radical with the isodesmic reaction in eq 4.

$$CH_mF_nCl_p^- + 2H \rightarrow CH_mF_nCl_p + e + H_2 \tag{3}$$

$$CH_3^- + CH_mF_nCl_p \rightarrow CH_3 + CH_mF_nCl_p^- \tag{4}$$

Computational Method

Standard ab initio molecular orbital calculations were carried out with the GAUSSIAN 82[23] and GAUSSIAN 86[24] programs. Singlet states were calculated using closed-shell Hartree–Fock theory (RHF)[25] and doublet states using Pople–Nesbet spin unrestricted

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Table II. Total Energies (Hartrees) Using Structures Optimized at HF/6-31++G(d,p) (Except Where Noted)

	HF	MP2 (full)[a]	MP4SDTQ	ZPE[b]	thermal correction[c]
(a) 6-31++G(d,p) Basis Set					
methanes					
CH_4	−40.202 17	−40.371 41	−40.390 24	26.3	1.8
CH_3F	−139.049 17	−139.384 52	−139.403 73	23.5	1.8
CH_2F_2	−237.913 71	−238.415 54	−238.434 27	19.8	1.9
CHF_3	−336.787 80	−337.455 62	−337.473 23	15.5	2.1
CH_3Cl	−499.098 95	−499.396 97	−499.417 08	22.5	1.9
CH_2Cl_2	−957.990 02	−958.423 45	−958.444 54	17.7	2.2
$CHCl_3$	−1416.873 44	−1417.447 83	−1417.469 74	12.2	2.7
CH_2FCl	−597.948 81	−598.416 99	−598.437 16	18.8	2.0
CHF_2Cl	−696.810 91	−697.448 97	−697.468 56	14.3	2.3
$CHFCl_2$	−1056.839 33	−1057.446 23	−1057.467 21	13.3	2.5
methyl radicals					
CH_3	−39.566 79	−39.701 45	−39.718 65	17.2	2.0
CH_2F	−138.415 25	−138.718 68	−138.736 08	14.9	1.8
CHF_2	−237.278 06	−237.749 53	−237.766 11	11.7	1.9
CF_3	−336.144 68	−336.782 20	−336.797 43	7.5	2.1
CH_2Cl	−498.466 59	−498.733 53	−498.752 36	13.6	2.0
$CHCl_2$	−957.361 75	−957.765 48	−957.785 56	9.5	2.2
CCl_3	−1416.250 25	−1416.794 45	−1416.815 60	4.4	2.7
$CHFCl$	−597.316 44	−597.754 42	−597.773 11	10.6	2.0
$CFCl_2$	−1056.209 50	−1056.766 93		5.4	2.5
methyl anions					
CH_3^-	−39.510 56	−39.686 88	−39.703 66	16.7	1.8
CH_2F^-	−138.370 35	−138.713 73	−138.733 38	13.6	1.9
CH_2F^-	MP2 optimized	−138.713 96			
CHF_2^-	−237.255 21	−237.767 63	−237.788 00	10.1	2.0
CF_3^-	−336.160 10	−336.841 89	−336.861 45	5.8	2.2
CH_2Cl^-	−498.446 40	−498.736 15	−498.758 16	12.9	2.1
CH_2Cl^-	MP2 optimized	−498.740 29		13.0	1.9
$CHCl_2^-$	−957.371 65	−957.796 99	−957.820 34	8.6	2.4
$CHCl_2^-$	MP2 optimized	−957.797 94	−957.820 00		
CCl_3^-	−1416.281 51	−1416.851 18	−1416.875 62	3.2	3.0
CCl_3^-	MP2 optimized	−1416.851 19	−1416.875 60		
$CHFCl^-$	−597.319 20	−597.765 55	−597.790 47	8.8	2.6
$CHFCl^-$	MP2 optimized	−597.783 08	−597.805 23	9.0	2.2
CF_2Cl^-	−696.219 85				
CF_2Cl^-	MP2 optimized	−696.847 19	−696.870 33	4.3	2.7
$CFCl_2^-$	−1056.242 99	−1056.845 69		3.7	2.9
(b) 6-311++G(2df,p) Basis Set					
methanes					
CH_4	−40.210 68	−40.398 08	−40.425 01		
CH_3F	−139.089 87	−139.513 17	−139.544 89		
CH_2F_2	−237.987 10	−238.648 71	−238.684 65		
CH_3Cl	−499.138 38	−499.497 57	−499.543 75		
methyl radicals					
CH_3	−39.575 36	−39.725 44	−39.750 06		
CH_2F	−138.456 75	−138.846 36	−138.875 70		
CHF_2	−237.352 81	−237.982 27	−238.015 61		
CH_2Cl	−498.506 39	−498.831 82	−498.876 22		
methyl anions					
CH_3^-	−39.520 01	−39.720 77	−39.744 90		
CH_2F^-	−138.409 56	−138.845 68	−138.877 14		
CHF_2^-	−237.324 17	−237.999 19	−238.035 84		
CH_2Cl^-	−498.485 41	−498.846 93	−498.893 94		
CH_2Cl^- MP2 optimized		−498.851 37	−498.896 20		
(c) 6-311++G(3df,3pd) Basis Set					
CH_4	−40.212 61	−40.411 98	−40.437 65		
CH_3	−39.576 91	−39.736 22	−39.759 99		
CH_3^-	−39.521 77	−39.735 65	−39.759 24		

[a] The MP2 level calculations with the 6-311++G(2df,p) and 6-311++G(3df,3pd) basis sets used a frozen core. [b] Zero-point energies were scaled by a factor of 0.89 and are reported in kcal/mol. [c] Thermal energies are in kcal/mol.

theory (UHF).[26] Geometry optimization was achieved by gradient techniques at the Hartree–Fock level, and all optimized structures were shown to be minima by harmonic frequency calculations (Table I).

The 6-31G basis set used in the structure optimization was augmented by addition of both polarization functions (d-functions on C, F, and Cl, and p-functions on H)[27] and diffuse functions (s and p on C, F and Cl, and s on H).[28] Here we use the conventional notation 6-31++G(d,p) to denote this basis set.

At the Hartree–Fock level some of the chloro-substituted anions were found to dissociate into a chloride anion solvated by carbenes. For these anions inclusion of correlation energy in the wavefunction was found to shorten and strengthen the C–Cl bond, and we optimized structures for these anions at the MP2/6-31++G(d,p) level.[29]

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Single-point MP4SDTQ[30] calculations were performed on all the optimized structures using either the 6-31++G(d,p) basis set or, for some of the smaller molecules, the larger basis sets 6-311++G(2df,p) and 6-311++G(3df,3pd) in which the valence s and p orbitals are triply split[31] and more polarization functions are added (Table II).[32]

Results and Discussion

(a) Molecular Structures. The structures of the fluoro- and chloromethanes as optimized at the HF/6-31++G(d,p) level are listed in Table I. There is excellent agreement between the experimental and calculated structural parameters. As noted previously,[7,8] increasing the number of halogen substituents has the effect of decreasing the length of all the C-halogen and C–H bonds. This structural change is attributed to the increased positive charge on carbon which results in a decrease in the covalent radius.[7,8,33]

Similar structural trends occur in methanes containing both fluorine and chlorine, but here the agreement between theory and experiment is slightly less satisfactory, particularly for the C-F bonds which are consistently underestimated by about 0.03 Å by the calculations. In general, all the structural parameters in Table I, calculated at the HF/6-31++G(d,p) level, are consistently slightly closer to the experimental values than literature[7,12] values optimized at the HF/6-31G(d) level.

The methyl radical is planar,[34,35] and the C–H bonds (1.073 Å) have more s-character and are shorter than the C–H distances in methane (1.084 Å). Similarly, the C–F and C–Cl distances in the halogenated methyl radicals are ~0.03 and ~0.06 Å, respectively, shorter than in the identically substituted methanes. Substitution of hydrogen atoms by halogens in the methyl radical introduces a destabilizing π-interaction between the unpaired electron on carbon and lone pairs on the halogens.[13,36] The interaction is decreased by the radical becoming pyramidal and the out-of-plane angle α (structure 1) increases with the number of halogen substituents.[12a,37] Fluorine is a better π-donor than chlorine, and the fluorinated methyl radicals have larger α-values than the chlorinated radicals (for CH_2F and CH_2Cl α is 33.0° and 19.3°, respectively, while for the perhalogenated radicals CF_3 and CCl_3 α is 50.0° and 29.4°). A more extensive study of the chloromethyl radical, including correlation energy, concluded that this radical is probably nonplanar but that the barrier to inversion is less than 0.1 kcal/mol.[12a]

In methyl radicals increasing the number of fluorine substituents results in shorter C–F bonds, but the changes are smaller than in the methanes. Increasing the number of halogen atoms results in little or no change in the C–H and C–Cl distances in radicals. This is the result of two conflicting effects. The increase in electronegativity of the central carbon atom, which led to bond shortening in the methanes, is also present in the radicals, but the increase in the out-of-plane angle α with increasing substitution by halogens leads to an increase in the p-character of the bonding at carbon, and this weakens and lengthens the bonds.

The C–H bonds in the methyl anion, CH_3^-, are 0.012 Å longer than in methane. Previous lower level ab initio molecular orbital studies[3,4] have shown the C–X bond lengths in CH_2X^- (where X is a saturated substituent, F, OH, NH_2, or CH_3) to be considerably longer than in the methanes CH_3X. Comparison of the anion structures in Table I with those of the methanes shows the same trend for the polyhalogenated anions. In general, the C–halogen bonds are ~0.1 Å longer in the anions.

As in the methanes, the C–F bond lengths decrease with the number of fluorine substituents and the decreases (from 1.492 Å in CH_2F^- to 1.405 Å in CF_3^-) are more pronounced in the anions, i.e., interaction between fluorine atoms in carbanions leads to the same geometric effects in both carbanions and methanes (and to an even smaller extent in fluoromethyl radicals).

The four-electron-two-orbital repulsion between the lone pairs on the carbanion center, C^-, and on a halogen result in halogenated methyl anions being pyramidal with larger out-of-plane angles, α, than the identically substituted radicals. Attempts to optimize planar structures for CF_3^- and CHF_2^- led to dissociation into a carbene and F^-; i.e., these ions dissociate rather than invert through the planar structure. We note that NF_3 (isoelectronic with CF_3^-) has also been found to have a higher inversion barrier (78.5 kcal/mol) than the N–F dissociation energy (57 kcal/mol).[38]

Optimization of the structures of the carbanions at the HF/6-31++G(d,p) level proved to be less reliable than for the neutral species. For ions containing the C–Cl bond optimization at the Hartree–Fock level invariably resulted in C–Cl bond which were unreasonably long. In these structures most of the negative charge was on the chlorine atom, and the ion resembled a chloride ion solvated by a carbene, i.e., one of the resonance structures, $Cl^- \cdots CH_nY_m$, used to describe negative hyperconjugation. This problem was most extreme in chlorofluoromethyl anions, where removal of Cl^- leaves a carbene stabilized by fluorine atoms.

Optimization of carbanions at the MP2/6-31++G(d,p) level resulted in dramatic shortening of all C–Cl bonds (from 3.09 to 2.003 Å in CF_2Cl^-), and structures optimized at this level will be used in subsequent discussions. By contrast, for carbanions containing only fluorine, optimization at the Hartree–Fock level appears to be satisfactory; indeed, for CH_2F^- optimization at the MP2/6-31++G(d,p) level had a small but opposite effect, resulting in a slightly longer C–F bond length than in the structure optimized at the HF/6-31++G(d,p) level (1.515 Å compared with 1.492 Å).

(b) Geminal Interactions. The energies resulting from geminal interactions between halogen atoms in methanes, in methyl anions, and in methyl radicals can be estimated from eq 5. A positive energy for this reaction indicates

$$X_nCH_m + (n-1)CH_{m+n} \rightarrow nXCH_{(m+n-1)} \qquad (5)$$

that the interaction between the n atoms of X is stabilizing.

Stabilization energies as calculated at three levels of theory are reported in Table III. For molecules containing only fluorine substituents, the calculated stabilization energies are essentially the same at all levels of theory; i.e., as expected for an isodesmic reaction, inclusion of correlation energy is not important. However, this is not the

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Table III. Stabilization Energies (kcal/mol) from eq 5

species	HF/6-31++G(d,p)	MP2(full)/ 6-31++G(d,p)	MP4SDTQ/ 6-31++G(d,p)
CH_2F_2	11.0 (11.3)[a]	11.2	10.7 (12.5)[a]
CHF_3	28.0	28.2	26.7
CHF_2	9.0 (9.2)[a]	8.5	7.9 (9.0)[a]
CF_3	20.4	18.2	16.6
CHF_2^-	15.7 (15.7)[a]	17.0	15.6 (16.6)[a]
CF_3^-	44.6	46.7	43.1
CH_2Cl_2	-3.6	0.6	0.4
$CHCl_3$	-12.0	-0.2	-0.7
$CHCl_2$	-2.9	-0.1	-0.3
CCl_3	-10.0	-2.0	-2.6
$CHCl_2^-$	-6.6	7.3 (2.6)[b]	4.8
CCl_3^-	-22.9	10.3 (2.5)[b]	5.3
CH_2FCl	1.8	4.3	4.1
CHF_2Cl	11.3	16.2	15.4
$CHFCl_2$	-2.2	6.6	6.1
$CHFCl$	0.9	2.3	2.1
$CFCl_2$	-3.4	-10.0	
$CHFCl^-$	8.2	1.6 (9.9)[b]	1.6
CF_2Cl^-	33.8	(33.1)[b]	33.1
$CFCl_2^-$	0.5	20.9 (15.6)[b]	

[a] 6-311++G(2df,p)//HF/6-31++G(d,p) level calculations. [b] Using structures optimized at MP2/6-31++G(d,p) level.

situation for chlorine-substituted molecules; here, inclusion of correlation energy results in increased stabilization. The most pronounced effect is for CCl_3^- where at the Hartree–Fock level geminal interactions are predicted to be *destabilizing* by 22.9 kcal/mol but to be *stabilizing* by 5.3 kcal/mol at the MP4 level.

Geminal interactions between halogen atoms are strongly stabilizing only when two or more fluorine atoms are involved. The interaction between a chlorine and a fluorine atom is weakly stabilizing, while the chlorine–chlorine interaction is negligible except in the methyl anions. The relative magnitudes of the interhalogen interactions are best illustrated by the disubstituted methanes where the stabilization energies of CH_2F_2, CH_2FCl, and CH_2Cl_2 are 10.7, 4.1, and 0.4 kcal/mol respectively.

For identically substituted species the stabilization energies generally are largest in the anions and smallest in the radicals; e.g., for CF_3^-, CF_3H, and CF_3 the stabilization energies are 43.1, 26.7, and 16.6 kcal/mol, respectively.[39] For these same species the FCF angles are 100.0°, 108.4°, and 111.3°. From these data one might be tempted to conclude that the stabilizing negative hyperconjugative interaction increases with a decrease in the bond angle. However, Reed and Schleyer[7] used natural bond orbital calculations to obtain geometries for *localized* structures for fluorinated methanes and, somewhat surprisingly, found that the *absence* of delocalization leads to a decrease in the FCF angles; i.e., negative hyperconjugation is responsible for the larger FCF angles. They rationalize this phenomenon in terms of overlap. At all F_aCF_b angles (structure 2) there is positive overlap between the occupied p-orbital on F_b and the orbital contribution from C to σ^* for the $C-F_a$ bond. This interaction is the source of the stabilizing negative hyperconjugative interaction. As the F_aCF_b angle decreases, the overlap between the p-orbital on F_b and the out-of phase lobe of the σ^* orbital located on F_a also increases, and this interaction is destabilizing. The latter interaction is most significant when the contribution to σ^* from F_a is relatively large. In anions this is not the situation, as the $C-F_a$ bond is much weaker than in neutral fluoromethanes and the σ^* orbital is predominantly located on the carbon atom. In the anions then the σ^* orbital is in close proximity to F_b, the negative charge makes F_b a better donor, and the destabilizing F_a-F_b negative overlap is diminished. As a result the perfluoromethyl anions have the largest stabilization from hyperconjugation and the smallest FCF bond angles.

(c) Acidities of Methanes and Methyl Radicals. The enthalpies for deprotonation of methanes and methyl radicals as defined by eq 6 are given in Table IV. A small

$$CH_nX_m \rightarrow CH_{(n-1)}X_m^- + H^+ \tag{6}$$

enthalpy for this reaction indicates a high acidity. Thus, chloroform, $CHCl_3$, is the most acidic molecule and methane CH_4 is the least acidic. The enthalpies were calculated by using eq 7. Here ΔE^{elec} is the difference in

$$\Delta H_r(298) = \Delta E^{elec} + \Delta ZPE + \Delta E_{0-298}{}^{thermal} + \Delta(PV) \tag{7}$$

electronic energies of the neutral molecule CH_nX_m and the anion $CH_{(n-1)}X_m^-$. ΔZPE is the difference in the zero-point energies obtained from the harmonic frequency calculations and was scaled by a factor of 0.89.[40] $\Delta E_{0-298}{}^{thermal}$ is the correction required to take the molecules from 0 to 298 K and consists of classical terms for translational ($^3/_2$ RT per molecule) and rotational ($^3/_2RT$ for nonlinear molecules) energies and the change in vibrational energy calculated from statistical mechanics.[2] The pressure–volume term, Δ(PV), for eq 7 is RT.

The $\Delta H_r(298)$ values from MP4SDTQ calculations in Table IV are generally higher than the experimental values[41] by between 4 and 9 kcal/mol. The one exception to this generalization is $\Delta H_r(298)$ for CHF_3 which has a calculated value 2.8 kcal/mol lower than the experimental value. The reactants and products in eq 6 have the same number of electron pairs, and inclusion of correlation energy should have little effect on the calculated acidity. However, with the 6-31++G(d,p) basis set for the fluoro-substituted methanes and methyl radicals inclusion of correlation energy consistently results in slightly smaller $\Delta H_r(298)$ values. By contrast, inclusion of correlation energy *increases* $\Delta H_r(298)$ for the chloro-substituted molecules, but the effect is smaller than in the fluoro-substituted molecules, and extension of the basis set to 6-311++G(2df,p) results in the same trend as in the fluoro-substituted molecules.

From the calculated acidities in Table IV it is clear that methyl radicals are more acidic than the identically substituted methanes. The methyl radical, CH_3, is more acidic than methane by ~8 kcal/mol, and for the unsubstituted hydrocarbons the order of acidity is $CH_4 < CH_3 < CH_2(t) < CH$.[42] For methyl radicals the difference in acidities increases with the number of halogen substituents and at the MP4SDTQ/6-31++G(2df,p) level CHF_2 is more acidic than CH_2F_2 by 25.8 kcal/mol. Substitution by chlorine systematically increases the acidities more than substitution by the same number of fluorine atoms. This trend is attributed to the greater ability of the larger, more polarizable, chlorine atom to assist in accommodating the excess negative charge.[43]

The acidity of methane increases by approximately 19 kcal/mol for each additional chlorine substituent and that

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Table IV. Acidities (kcal/mol) of Methanes and Methyl Radicals[a]

	basis set	SCF	MP2(full)	MP4SDTQ	expl[b]
methanes					
CH_4	6-31++G(d,p)	425.9	421.4	422.7	417 ± 2
	6-311++G(2df,p)	425.3	416.9	418.7	
	6-311++G(3df,3pd)	425.4	416.3	417.6	
CH_3F	6-31++G(d,p)	417.7	412.6	412.3	
	6-311++G(2df,p)	418.6	410.5	410.7	
CH_2F_2	6-31++G(d,p)	405.1	398.5	397.4	387 ± 7
	6-311++G(2df,p)	407.9	399.5	399.0	
CHF_3	6-31++G(d,p)	385.8	377.0	375.8	377 ± 2
CH_3Cl	6-31++G(d,p)	401.6[d]	406.8	405.6	396 ± 1
	6-311++G(2df,p)	402.7	400.4 (397.7)[c]	399.8 (398.5)[c]	
CH_2Cl_2	6-31++G(d,p)	380.6	385.7 (385.1)[c]	384.3 (384.5)[c]	375 ± 3
$CHCl_3$	6-31++G(d,p)	364.2	367.2	365.6	357 ± 6
CH_2FCl	6-31++G(d,p)		389.7[c]	388.4[c]	
CHF_2Cl	6-31++G(d,p)	anion dissociates	369.5[c]	367.3[c]	378 ± 8
$CHFCl_2$	6-31++G(d,p)	366.5[d]	369.1[d]		
methyl radicals					
CH_3	6-31++G(d,p)	419.0	415.7	415.9	409.3 ± 0.5
	6-311++G(2df,p)	417.8	410.5	410.9	
	6-311++G(3df,3pd)	417.8	410.2	410.2	
CH_2F	6-31++G(d,p)	402.1	397.7	396.8	
	6-311++G(2df,p)	403.5	396.8	396.1	
CHF_2	6-31++G(d,p)	378.7	372.4	371.2	
	6-311++G(2df,p)	381.8	370.7	373.2	
CH_2Cl	6-31++G(d,p)	388.7	396.0	394.5	
	6-311++G(2df,p)	389.6	389.1	389.6	
$CHCl_2$	6-31++G(d,p)	363.0	369.6	367.9	
$CHFCl$	6-31++G(d,p)	anion dissociates	368.6[c]	367.4[c]	

[a] Defined as $\Delta H_r(298)$ for $CH_nX_m \rightarrow CH_{n-1}X_m^- + H^+$. [b] Reference 41. [c] Uses structure of anion optimized at MP2/6-311++G(d,p). [d] Only an upper estimate due to inadequate structure for anion from HF/6-31++G(d,p).

of methyl radical increases by ~24 kcal/mol per chlorine atom; i.e., substituent effects are slightly larger in the radical but in both molecules the effect of chlorine substitution is roughly additive. By contrast, fluorine substitution in methane results in sequential *increases* in acidity of 10.4, 14.9, and 21.6 kcal/mol, and in the methyl radical the increases are 19.1 and 25.6 kcal/mol (all results at the MP4SDTQ/6-31++G(d,p) level). Thus, each additional fluorine is more effective than the previous ones at increasing the acidity. The explanation for this unusual behavior lies in the large stabilization energies generated by the negative hyperconjugative interaction between fluorine atoms. In any acid–base pair both species have the same number of fluorine atoms but the anions always have the larger stabilization energies (Table III).

(d) Electron Affinities. The electron affinity of a radical $CH_mF_nCl_p$ is defined as the enthalpy of 0 K of the reaction in eq 2. The difference in the electronic energies of $CH_mF_nCl_p^-$ and $CH_mF_nCl_p$, when corrected for contributions from zero-point energies, then provides a theoretical estimate of the electron affinity of $CH_mF_nCl_p$.

Electron affinities are usually small, and accurate determination by theory (and quite frequently by experiment) has proven to be very difficult.[20-22,44-46] From a theoretical perspective the main source of the problem is that the anion has one more pair of electrons than the products (a radical and an electron), and this results in the reactant having a larger correlation energy. Hartree–Fock level calculations then are expected to underestimate the endothermicity of the reaction in eq 2. In fact, at the Hartree–Fock level many of the methyl anions have smaller electronic energies than the methyl radicals and the calculated electron affinities are negative. Even at the MP4SDTQ/6-31++G(d,p) level the electron affinity of CH_3 calculated from eq 2 is −0.41 eV compared with an experimental value of 0.08 eV.[45]

High levels of theory are clearly necessary to obtain satisfactory estimates of electron affinities. A review of the literature[20-22,44-46] indicated that extensive basis sets coupled with Møller–Plesset perturbation theory calculations taken to the fourth order are necessary to obtain electron affinities within 0.1 eV of the experimental value. For the methyl radical at the MP4/6-311++G(2d,2p) level the calculated electron affinity was −0.18 eV.[21a] Such large basis set calculations are not feasible for polyhalogenated radicals and, rather than using equation 2, we have estimated electron affinities by using the isogyric reactions given in equations 3 and 4. For eq 3 the electronic dissociation energy of H_2 was taken to be 0.17447 hartrees[48] and for eq 4 the electron affinity of CH_3 was taken to be 0.08 eV.[47] Zero-point energy corrections, taken as 0.89 of the calculated harmonic frequencies, were applied to eq 3. The results from MP4SDTQ calculations with two different basis sets are given in Table V.

At the MP4/6-31++G(d,p) level the calculated electron affinities from eq 4 are systematically larger than those from eq 3 by 0.25–0.30 eV, approximately the amount by which eq 3 underestimates the electron affinity of CH_3. Comparison with experimental data for the chloromethyl radicals[49] show the results from eq 4 to be the better ones at this level of theory but even here the electron affinities are underestimated by ~0.1 eV. The experimental electron affinities of fluoromethyl radicals are less well established, making comparison with theory more difficult. For CF_3 there are many experimental estimates, falling in the range 1.8–3.3 eV; for CHF_2 the experimental value

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Table V. Electron Affinities (eV) As Obtained from MP4SDTQ Calculations

	from $CH_3 + CH_nX_m^- \rightarrow CH_3^- + CH_nX_m$		from $CH_nX_m^- + 2H \rightarrow CH_nX_m + e + H_2$			
radical	6-31++G(d,p)	6-311++G(2df,p)	6-31++G(d,p)	6-311++G(2df,p)	6-311++G(3df,3dp)	expl
CH_3	(0.08)	(0.08)	−0.22	0.06	0.06	0.08 ± 0.03[a]
CH_2F	0.41	0.26	0.15	0.27		
CHF_2	1.08	0.77	0.83	0.79		1.3 ± 0.3[a]
CF_3	2.23		1.98			1.84 ± 0.16[a]
CH_2Cl	0.65	0.76	0.36	0.75		0.73,[b] 0.84 ± 0.2[a]
$CHCl_2$	1.42		1.15			1.60,[b] 1.7 ± 0.2[a]
CCl_3	2.12		1.86			2.25,[b] 2.3 ± 0.3[a]
CHClF	1.36		1.11			

[a] Reference 41. [b] $\Delta H_f°(298)$ values were taken for the anions from ref 41 and for the radicals from ref 49. These were corrected to $\Delta H_f°(0)$ by using experimental $H°(298) - H°(0)$ for the elements (ref 51) and calculated (thermal energies + PV work term) for the anion and radical.

Table VI. Calculated and Experimental $\Delta H_f°$(298 K)[a]

	calcd value		
molecule	6-311++G(2df,p)	6-311++G(3df,3pd)	expl
CH_4	−19.0	−18.7	−17.9[b]
CH_3F	−58.9		−59.0[b]
CH_2F_2	−112.0		−108.2[b]
CH_3Cl	−21.3		−19.3,[b] −19.6[c]
CH_3	35.5	35.0	34.8[d]
CH_2F	−8.4		−7 ± 2[e]
CHF_2	−60.7		−58.6[e]
CH_2Cl	28.5		27.7 ± 2[f]

[a] kcal/mol. [b] Lias, S. G.; Karpas, Z.; Liebman, J. F. *J. Am. Chem. Soc.* **1985**, *107*, 6089. [c] Pedley, J. B.; Naylor, R. D.; Kirby, S. P. *Thermochemical Data of Organic Compounds*, 2nd ed.; Chapman and Hall: New York, 1986. [d] Reference 41. [e] From the compilation of literature values given in ref 12a. [f] Reference 49.

comes from potentially unreliable bracketing experiments, and for CH_2F we are unaware of any reliable experimental value. From the MP4/6-31++G(d,p) calculations then it is only possible to make qualitative conclusions. It is clear that both fluorine and chlorine atoms increase the electron affinity of the methyl radical, with the more polarizable chlorine atom being the more effective. From the results of eq 4, the addition of further chlorine atoms increases the electron affinity by approximately 0.7 eV per chlorine atom; i.e., the effect is roughly additive. By contrast the electron affinities of fluoro-substituted methyl radicals increase rapidly with increased substitution, showing a more synergistic effect.

From the limited data in Table V and from previous theoretical work[22] it seems that calculations at MP4/6-311++G(2df,p) are capable of reproducing electron affinities within 0.1 eV of the experimental value. For the parent methyl radical the electron affinity calculated from eq 3 is 0.06 eV, compared with an experimental value of 0.08 eV. As a consequence of this accurate prediction for CH_3, both eqs 3 and 4 yield essentially identical electron affinities for other radicals at this level of theory. The calculated values for CH_2Cl are in excellent agreement with experiment, but there is serious disagreement between theory and experiment for CHF_2, casting further doubt on the experimental value for this radical.

(e) Heats of Formation. Experimental heats of formation are firmly established for all the molecules and radicals for which we have performed calculations at the MP4/6-311++G(2df,p) level. We have used the method of Pople, Luke, Frisch, and Binkley[50] to obtain binding energies, D_0, from our ab initio molecular orbitals and then combined these with experimental heats of formation for atoms[51] to yield the $\Delta H_f°$(298 K) values in Table VI. Agreement between theory and experiment is excellent except for CH_2F_2 where the calculated heat of formation is 3.9 kcal/mol more exothermic than the experimental value.

Conclusions

Negative hyperconjugative interactions between halogens are strongly stabilizing when at least one of the halogens is a fluorine atom, while geminal interactions between chlorine atoms lead to little or no stabilization. Negative hyperconjugation between fluorine atoms is larger in methyl anions than in methanes, and this is the major factor in the rapid increase in acidity with increased substitution by fluorine. A single chlorine atom is more effective at enhancing the acidity of methane than one fluorine atom due to the higher polarizability of chlorine but, in the chloromethanes, additional chlorine substituents each further enhance the acidity by the same amount as the initial chlorine substituents; i.e., the enhancement of acidity by chlorine atoms is roughly additive.

Very high levels of theory are required to calculate electron affinities accurately. At MP4SDTQ/6-31++G-(d,p), using isodesmic reactions to help remove problems due to differences in correlation energies, all electron affinities are underestimated and only a qualitative picture emerges. From the highest level calculations we find that single chlorine and fluorine substituents increase the electron affinity of the methyl radical by 0.69 and 0.21 eV, respectively. The lower level calculations show that additional chlorine substituents increase the electron affinity by roughly equal increments. In the fluoromethyl radicals the situation is very different. Negative hyperconjugation between fluorine atoms is much larger in the methyl anions than in the radicals, and multiple substitution by fluorine results in large increases in electron affinities.

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