Additivity of Substituent Effects. Core-Ionization Energies and Substituent Effects in Fluoromethylbenzenes

Thomas X. Carroll,[†] T. Darrah Thomas,*[,‡] Leif J. Sæthre,[§] and Knut J. Børve[§]

Division of Natural Sciences, Mathematics, and Physical Education, Keuka College, Keuka Park, New York 14478; Department of Chemistry, Oregon State University, Corvallis, Oregon 97331; and Department of Chemistry, University of Bergen, NO-5007 Bergen, Norway

Received: December 2, 2008; Revised Manuscript Received: February 12, 2009

Carbon 1s ionization energies have been measured for all of the carbon atoms in eight fluoromethylbenzenes. Enthalpies of protonation have been calculated for protonation at all of the ring carbons in the same molecules. These data together with previously reported data on fluorobenzenes and methylbenzenes provide the basis for studying the additivity of substituent effects and the correlation between enthalpies of protonation with core-ionization energies. Although a linear additivity model accounts reasonably well for both the ionization energies and the enthalpies of protonation, a better description, especially for the enthalpies, is obtained by inclusion of nonlinear terms that account for interactions between two substituents on the same molecule. There are families of nearly parallel correlation lines between enthalpies of protonation and core-ionization energies. The existence of several families can be primarily understood in terms of the linear additivity picture and more completely understood when the nonlinear terms are taken into account. The role of the methyl group as a polarizible π-electron donor is contrasted with the role of fluorine, which is a substituent of low polarizibility that acts to withdraw electrons from the adjacent carbon and to donate electrons through resonance to the ring. The role of the hydrogen atoms as π-electron acceptors in the protonated species is illustrated.

Introduction

Substituents have a major effect on the properties of benzene and its derivatives. As a result, substituent effects and their systematics have been the subject of many investigations. Carbon 1s photoelectron spectroscopy is potentially an important tool for studying such effects, since it is, in principle, possible to measure the carbon 1s ionization energy for every chemically unique carbon in the benzene ring. Until recently, however, the resolution of the technique has not been adequate to resolve reliably the contributions of the inequivalent carbon atoms to the photoelectron spectra. With the availability of third-generation synchrotrons, high-resolution electron spectrometers, and high-level theoretical calculations, this situation has now changed, and it is now possible to analyze such spectra so as to provide credible information on the various carbon atoms in substituted benzenes. We have recently reported on the carbon 1s photoelectron spectra of fluorobenzenes[1] and methylbenzenes.[2] In these studies, we were able to assign carbon 1s ionization energies to all of the chemically unique carbon atoms and to show that the experimental results are in good agreement with theoretical predictions. Here, we extend the previous work by considering substituted benzenes having both methyl and fluoro substituents, and, for this purpose, we have measured the carbon 1s photoelectron spectra for eight fluoromethylbenzenes, giving 47 new ionization energies.

Core-ionization energies are closely related to other chemical properties that depend on the ability of a molecule to accept charge at a specific site. Among these are acidity, basicity, enthalpies of protonation,[3] rates of electrophilic reactions, and Hammett parameters. Of particular interest have been correlations between core-ionization energies and enthalpies of protonation, since both of these processes involve addition of a positive charge at a specific site in the molecule. Linear correlations between enthalpies of protonation and core-ionization energies are well established for nitrogen, oxygen, and a few other elements, and these correlations have provided insight into the site of protonation and geometric changes that occur upon protonation.[4,5] However, until recently there have not been sufficiently good data available for carbon 1s ionization energies to make investigation of these relationships for carbon possible. We have recently demonstrated that such correlations exist for 1,3-butadiene and 1,3-pentadiene,[6] the fluorobenzenes,[1] and the methylbenzenes.[2] For the fluorobenzenes these correlations provide insight into the π-donating effect of fluorine. The data for the methylbenzenes have extended these correlations and have provided insight into the differences between the π-donating action of the two substituents.

For core ionization, we can measure a carbon 1s ionization energy for each carbon atom in the molecule. For protonation this is not the case. In general, experimental enthalpies of protonation are known only for the most favorable site of protonation in each molecule. However, there exist theoretical techniques that allow us to predict these enthalpies for all sites in the molecule,[7,8] and, where experimental data are available, there is good agreement between theory and experiment.[1] We have used the procedure suggested by Maksić et al.[8] for calculating the relevant enthalpies (38 energies) and use these theoretically predicted enthalpies for comparison with the core-ionization energies.

The idea that the effect of two or more substituents on the properties of a benzene ring is simply the sum of their individual effects is referred to as the "additivity principle". Investigations of this principle in a variety of situations have a long history.[8−10]

---

* Corresponding author. E-mail: t.darrah.thomas@oregonstate.edu.

[†] Keuka College.

[‡] Oregon State University.

[§] University of Bergen.

10.1021/jp810612x CCC: $40.75

We have shown that an additivity model that includes only linear terms gives a reasonably good description of the core-ionization energies and enthalpies of protonation of the methyl-[2] and fluorobenzenes.[1] However, an improved description can be obtained by including nonlinear terms. Here, we extend the previous investigations of the additivity model and establish the relationship between the additivity model and the correlations between enthalpies of protonation and core-ionization energies.

The nonlinear terms are of special interest in that they provide information on nonadditive substituent effects. Although these have been much less studied than additive effects, there are numerous examples of chemical properties that differ from those expected from an additivity model.[11,12] An example is the dipole moment of nitroaniline, which is significantly larger than the sum of the dipole moments of aniline and nitrobenzene. Recently, a study of substituent interaction energies, combined with a Hammett dual-parameter approach, has shown that field/inductive effects interact with resonance effects in 1,3- and 1,4-disubstituted benzenes.[13] A theoretical analysis of intersubstituent interactions in disubstituted benzenes having one donor substituent and one acceptor substituent predicts that the ability of the donor to donate electrons to the ring and the ability of the acceptor to withdraw electrons from the ring are both enhanced if the two substituents are ortho or para to each other and suppressed if they are meta to each other.[11]

In this study, we have investigated electron-donating and electron-accepting properties of methyl and fluoro substituents, with the object of determining both linear and nonlinear substituent effects. This series of molecules offers a unique possibility to study both of these effects since all sites of the ring carbons can be probed.

Procedures and Results

Experimental Procedures. Measurements of the carbon 1s photoelectron spectra for eight fluoromethyl-substituted benzene molecules in the gas phase were carried out at beamline I411 of the MAX II synchrotron facility.[14] The samples were obtained from commercial sources, and the purity ranged from 97 to 99%. The photon energy was 330 eV. The monochromator slits and the settings of the Scienta SES-200 electron-energy analyzer were chosen to give an overall resolution of about 75 meV. Calibration of the ionization-energy scale and measurement of the actual resolution was made with each compound mixed with carbon dioxide, for which the ionization energies and natural line width are well-known.[15,16] The actual resolutions determined in this way ranged from 67 to 96 meV.

The spectra were fit by least-squares with peak shapes that include the effects of resolution, core-hole lifetime, vibrational excitation, and the interaction of the photoelectron with the Auger electron that accompanies core ionization (postcollision interaction, or PCI).[17] For the effects of PCI and lifetime broadening, we have used the shape given by eq 12 from van der Straten et al.[18] This is convoluted with a Gaussian function that represents the instrumental broadening.

The carbon dioxide calibration spectrum has three closely spaced peaks, arising from excitation of the symmetric stretching mode in the core-ionized molecule. These spectra are fit constraining the lifetime width, relative positions, and relative heights of the three peaks to previously determined values.[15] Thus, the only fitting variables are the instrumental resolution and the peak position for the transition that leaves the molecule with no vibrational excitation—the adiabatic transition. For carbon dioxide this energy is known from previous measurements to be 297.664 eV with an absolute uncertainty of 0.03 eV.[16]

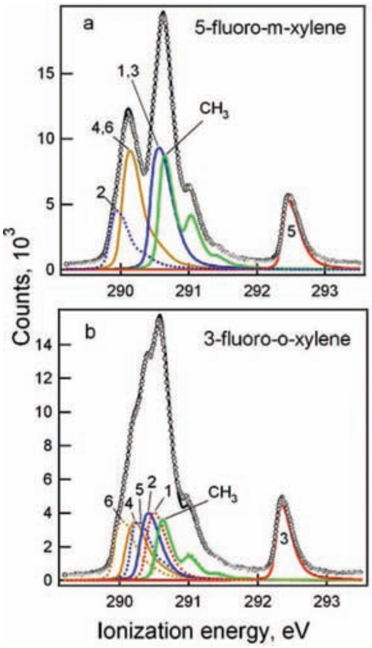

Figure 1. Carbon 1s photoelectron spectra of 5-fluoro-*m*-xylene and 3-fluoro-*o*-xylene measured at a photon energy of 330 eV. Open circles represent the experimental data. Solid black lines show the overall fit to the data. Colored lines show the contributions from the different carbon atoms.

The fluoromethylbenzene molecules have five to eight chemically inequivalent carbon atoms. This is in contrast to our previous studies, where the maximum number of inequivalent carbon atoms was four for the fluorobenzenes and five for the methylbenzenes. To aid in resolving these spectra, we note that each type of carbon atom produces a unique pattern of vibrational excitation. For each carbon atom we calculate theoretically the vibrational structure associated with core ionization; see below for details. This structure is convoluted with functions that represent the instrumental broadening and the effects of lifetime and postcollision interaction. For the lifetime width we have used 100 meV, which is typical of the lifetime width found for a number of hydrocarbons.[19] For the resolution width, we have taken the value given from fitting the carbon dioxide spectrum. The set of profiles are fit to the experimental data by least squares. The fitting parameters are a constant background and the overall intensities and adiabatic (threshold) energies for each carbon. In some cases, it has been necessary to constrain relative intensities to the values expected from the stoichiometry of the molecule.

In Figure 1 we present two examples of the experimental carbon 1s photoelectron spectra. These are 5-fluoro-*m*-xylene (Figure 1a) and 3-fluoro-*o*-xylene (Figure 1b). For 5-fluoro-*m*-xylene, where there are five chemically different carbon atoms, the fitting is completely straightforward and unambiguous. For 3-fluoro-*o*-xylene, there are eight chemically distinct carbon atoms, and, in consequence, the fitting presents significant problems.

In these figures, the open circles represent the experimental data, the black lines the overall fits, and the colored lines the contributions from the individual peaks. As noted above, the shapes of these individual peaks, which reflect the vibrational profiles, are established by the theoretical calculations. The only free fitting parameters are the positions and intensities of the peaks. Where several peaks are overlapping, their relative intensities have been constrained by the stoichiometry of the molecule.

For 5-fluoro-*m*-xylene, the C5 peak is shifted to higher ionization energy by the fluorine that is attached at this position. In Figure 1a we see this peak at an ionization energy of 292.4 eV, and we see that the shape calculated for this peak agrees well with the observed shape. The shoulder at an ionization energy of 291 eV arises from excitation of the CH stretching mode in the peak resulting from ionization of the methyl carbons. This mode has strong excitation because there are three hydrogens on each methyl group. The presence of this shoulder in the spectrum allows for an unambiguous placement of the methyl peak. The weak shoulder at low ionization energy is assigned to the C2 peak on the grounds that this peak, which is due to a single carbon, will have only half the intensity of the peaks due to the C4/C6 and C1/C3 carbons. The two remaining peaks (C4/C6 and C1/C3) can be placed as shown in Figure 1a or can be interchanged. The order shown in Figure 1a provides a much better fit than the reverse choice and is in agreement with the order predicted by theory.

For the fit shown in Figure 1a, we have required that the four peaks contributing to the left-hand structure have relative areas dictated by the stoichiometry of the molecule. If we relax this requirement, we obtain a slightly better fit, but without a significant change in the peak positions, which are within an average of 2 meV of those found from the fits shown in Figure 1a. The relative areas agree with those expected, with a root-mean-square deviation of less than 6%. If we interchange the C4/C6 and C1/C3 peaks, then the resulting fit gives relative intensities that are far from the stoichiometric values.

For 3-fluoro-*o*-xylene, with eight inequivalent carbon atoms, the situation is more complicated. C3 can be uniquely assigned to the small peak at an ionization energy of 292.3 eV, and we see, just as for 5-fluoro-*m*-xylene, the shape of this peak is predicted well by the theory. The shoulders on the high-energy side of the main peak can, as with 5-fluoro-*m*-xylene, be associated with the strong vibrational structure from the methyl peak, allowing unambiguous placement of the contribution from ionization of the methyl groups. The two methyl groups are, however, inequivalent, and, consequently we include two peaks. For the remaining five peaks, there are 120 different orders possible for the initial guesses of their positions. Previous experience with *m*-xylene and fluorobenzene suggests that the ionization energies should be in the order C6 < C4 < C5 < C2 < C1 < CH_3. This is also the order indicated by theory and by both an additivity model and correlations with enthalpies of protonation, discussed below. We have tried all 120 possible different initial orderings in the least-squares fits and find that, although there is some variation in the values of χ^2, there is no convincing statistical evidence that one is significantly better than another. For lack of a better choice, we have chosen the fit that gives an order that is the same as the order predicted by theory. The corresponding spectrum is shown in Figure 1b.

The spectra for the other molecules fall between these extremes. Where the fits do not give unambiguous information on the order of the peaks, we have used the order that agrees with theory. This is the case for three compounds, 3-fluoro-*o*-xylene, 2,5-difluorotoluene, and 2,4-difluorotoluene.

Theoretical Procedures. Theoretical calculations include prediction of the vibrational profiles, relative carbon 1s ionization energies, and enthalpies of protonation. For all of these, the Gaussian set of programs was used.[20]

Core Ionization. For the calculations related to core ionization, the B3LYP method was used with a triple-ζ basis set plus polarization functions. The core hole was simulated with an effective core potential. Details of the basis set and the effective core potential are given elsewhere[21] and in the Supporting Information. For each molecule and for each core-ionized species, we calculate the optimized geometry, vibrational frequencies, and normal modes. Using the harmonic oscillator approximation, we calculate Franck−Condon factors for the excitation of each normal mode in the core-ionized molecule. These sets of Franck−Condon factors are convoluted to produce intensities for the combination modes, and, hence, the full vibrational profile. Typically, each profile includes about 1000 lines, and 50 to 100 lines account for 90% of the intensity. The profile is used in the fitting procedure as described above. Calculations using this method have been found to overestimate the shrinkage of a CH bond that accompanies core ionization of the carbon to which the hydrogen is attached. The overestimate is about 0.3 pm for an sp^3 CH bond and about 0.2 pm for an sp^2 CH bond.[22] The calculated CH bond lengths have, therefore, been adjusted accordingly. For the CH stretching mode of the methyl group, we have found that it is necessary to include the effects of anharmonicity. For this purpose we use Franck−Condon factors calculated using a Morse potential. The vibrational frequencies calculated by this procedure are typically higher than those observed experimentally. On the basis of our experience with other molecules,[23] we have scaled all of the calculated frequencies by 0.99 except for those of the CH stretching modes for the hydrogens attached to the core-ionized carbon. In these cases, the scaling factor is 0.95.

The electronic structure calculations give energies for the various core-ionized species. Since these involve the approximation of the effective-core potential, they cannot be viewed as absolute energies. However, from the calculated energies of the ionized species, corrected for zero-point energies, we can obtain the predicted ionization energies relative to that of benzene. These are listed in Table 1.

Enthalpies of Protonation. We are interested in correlations between enthalpies of protonation and carbon 1s ionization energies. For the latter we have measurements for every position in the molecule, whereas for the former even if measured values are available they are only for the most favorable site of protonation. For a more complete view of protonation, we need to rely on theoretical calculations. For this, we have used the method suggested by Maksic et al.,[8] which has been found to give reasonably accurate predictions of enthalpies of protonation. This method involves finding the optimum geometries and zero-point corrections using the Hartree−Fock method with the 6-31G(d) basis set. With these geometries, the energies are then calculated with the MP2 method and the 6-31G(d,p) basis set. The energies of the molecules are taken to be the MP2 energies plus the zero-point energies corrected by the empirical factor of 0.89.[24] Enthalpies of protonation ($\Delta E^\circ_0 = \Delta H^\circ_0$) calculated in this way are listed in Table 1.

Results. The results of our experimental measurements and theoretical calculations are given in Table 1 for the eight fluoromethylbenzene molecules that we have investigated. Also included for comparison are the results for benzene.[25] The first column of numbers gives the adiabatic ionization energy, which is the energy needed to produce the core-ionized ion in its vibrational ground state. It is obtained directly from the fitting of the experimental data. The second column gives the vertical ionization energy, which is the energy needed to produce the ion in the same geometry as that of the neutral molecule. It is

TABLE 1: Carbon 1s Ionization Energies and Theoretically Calculated Enthalpies of Protonation for the Fluoromethylbenzenes (eV)

compound		adiabatic	vertical	rel adiabatic	rel theory	enthalpy of protonation
benzene		290.241	290.377	0.000	0.000	−7.798
p-fluorotoluene	C1	290.425	290.577	0.184	0.211	−7.855
	C2	290.305	290.463	0.064	0.072	−7.768
	C3	290.363	290.548	0.122	0.107	−7.910
	C4	292.485	292.570	2.244	2.216	−7.313
	CH_3	290.644	290.851	0.403	0.478	
2,4-difluorotoluene	C1	290.684	290.874	0.443	0.475	−7.841
	C2	292.802	292.892	2.561	2.550	−7.010
	C3	290.583	290.757	0.342	0.389	−7.858
	C4	292.806	292.906	2.565	2.573	−7.020
	C5	290.452	290.668	0.211	0.246	−7.997
	C6	290.632	290.805	0.391	0.405	−7.501
	CH_3	290.821	291.030	0.580	0.653	
2,5-difluorotoluene	C1	290.850	291.025	0.609	0.675	−7.462
	C2	292.572	292.682	2.331	2.329	−7.443
	C3	290.651	290.849	0.410	0.453	−7.634
	C4	290.620	290.825	0.379	0.347	−7.834
	C5	292.679	292.797	2.438	2.449	−7.245
	C6	290.509	290.700	0.268	0.325	−7.747
	CH_3	290.863	291.065	0.622	0.697	
2,6-difluorotoluene	C1	290.769	290.922	0.528	0.593	−7.737
	C2,6	292.764	292.852	2.523	2.522	−7.021
	C3,5	290.444	290.657	0.203	0.234	−8.007
	C4	290.662	290.837	0.421	0.420	−7.555
	CH_3	290.836	290.993	0.595	0.676	
3,5-difluorotoluene	C1	290.927	291.085	0.686	0.768	−7.165
	C2,6	290.365	290.571	0.124	0.142	−8.115
	C3,5	292.914	293.014	2.673	2.689	−6.794
	C4	290.546	290.735	0.305	0.296	−8.049
	CH_3	290.880	291.092	0.639	0.734	
3-fluoro-*o*-xylene	C1	290.415	290.536	0.174	0.141	−7.761
	C2	290.301	290.444	0.060	0.090	−8.024
	C3	292.297	292.370	2.056	2.035	−7.439
	C4	290.101	290.288	−0.140	−0.157	−8.214
	C5	290.202	290.363	−0.039	−0.081	−7.949
	C6	289.953	290.125	−0.288	−0.290	−8.269
	CH_3 (1)	290.575	290.800	0.334	0.397	
	CH_3 (2)	290.535	290.762	0.294	0.352	
2-fluoro-*m*-xylene	C1,3	290.372	290.529	0.131	0.152	−7.892
	C2	292.183	292.248	1.942	1.891	−7.644
	C4,6	290.077	290.236	−0.164	−0.211	−8.094
	C5	290.007	290.187	−0.234	−0.207	−8.161
	CH_3	290.571	290.775	0.330	0.381	
5-fluoro-*m*-xylene	C1,3	290.462	290.597	0.221	0.246	−7.606
	C2	289.858	290.032	−0.383	−0.405	−8.410
	C4,6	290.020	290.203	−0.221	−0.262	−8.347
	C5	292.415	292.497	2.174	2.145	−7.247
	CH_3	290.597	290.808	0.356	0.422	

obtained from the adiabatic ionization energy by adding the average vibrational excitation energy, which is obtained from the theoretical calculations of the vibrational profile. The third and fourth columns of numbers give the shifts in adiabatic ionization energy relative to benzene as given by experiment and theory. The final column gives the calculated enthalpies of protonation. The uncertainty in the absolute values for the experimental ionization energies is approximately the uncertainty in the ionization energy of the carbon dioxide reference standard, 0.03 eV. Comparisons of the experimental values with the predictions of theory and of an additivity model, discussed below, suggest that the relative uncertainties are less than 0.02 eV and possibly as small as 0.01 eV.

The average difference between the experimental and theoretical values (experiment minus theory) of the ionization energies given in Table 1 is −20 meV and the standard deviation is 41 meV. If we consider not only these energies but also the previously reported values for fluorobenzenes and methylbenzenes (85 energies in all), then the corresponding values are −14 and 42 meV.

Closer examination of the results indicates that this comparison is misleading as to the extent of disagreement between experiment and theory. In earlier papers[1,2,6,26] we noted that the theoretical method that we have used overestimates the substituent-induced shifts. This overestimation appears to arise from the use of the B3LYP method. Calculations based on the cc-pVTZ basis set and the CCSD(T) method for 66 different carbon atoms in 25 different compounds lead to underestimates of the shifts by about 3%.[27] For the same set of compounds, the B3LYP method with the cc-pVTZ basis set overestimates the shifts by 6%. Although the CCSD(T) procedure gives a better prediction, it is not easily used for the highly substituted benzene molecules considered here.

If we consider all of the data for the substituted benzenes, we find that the shifts predicted by the B3LYP procedure are overestimated by about 6% for a CF carbon (a carbon atom bonded to fluorine) and by about 9% for other carbon atoms. Allowing for this effect, we find that this theory accounts for the observed shifts with a standard deviation of 16 meV for the first class of carbon atoms and 21 meV for the second class. This generally good agreement between the experimentally determined shifts and the theoretically calculated shifts indicates that the methods that we have used to extract the experimental values from the spectra are approximately correct. Also, as noted above, this agreement provides us with an estimate that the uncertainties in the experimental values are no more than about 20 meV.

Additivity of Substituent Effects

The effects of multiple substituents on benzene have often been described in terms of an additivity model. That is, the total effect of the substituents is considered to be the sum of independent effects of the individual substituents. A more complete model allows for the possibility of quadratic or cross terms. Thus, we can write

$$\Delta E_{\mathrm{r}} = \sum_{k} n_k \alpha_{k\mathrm{r}} + \sum_{k} (n_k(n_k - 1)\beta_{k\mathrm{r}}/2 + \sum_{l>k} n_k n_l \gamma_{kl\mathrm{r}})$$

where ΔE_{r} is the energy change for the reaction of interest relative to that of some reference compound (benzene, in this case). The indices k and l identify the type of substituent and its location. Thus, for the case at hand, we have methyl substituents that can be ipso (i), ortho (o), meta (m), or para (p) to the site of interest and fluoro substituents that can be similarly located, identified as i′, o′, m′, and p′. The coefficients α, β, and γ are characteristic of the substituent, its location, and the reaction. The term that involves the coefficient α represents the linear additive effect of the substituents. The remaining terms reflect, to first approximation, departures from simple additivity. The term involving β is nonzero only for ortho and meta substituents; for the fluoromethylbenzenes there are potentially four such terms, oo, mm, o′o′, and m′m′.[28] For the summation over γ, there are potentially 26 terms, six involving pairs of methyl groups (io, im, ip, om, op, mp), 6 similar terms for the fluoro groups, and 14 involving one methyl group and one fluoro group. In all, there are 38 terms.

Using either measured adiabatic or theoretical ionization-energy shifts or calculated enthalpies of protonation, we have used least-squares methods to determine the coefficients for the effects of methyl and fluoro substituents on the core-ionization energies and enthalpies of protonation of substituted benzenes. We have used two different approaches. In the first, we consider only the linear terms; in the second, we include also the quadratic terms.

Additivity Model for Ionization Energies. With only linear parameters, the additivity model accounts well for the experimental ionization energies with an rms deviation of 0.026 eV. The value of R^2 for the correlation is 0.9996, indicating that linear additivity alone provides a quite satisfactory description of the shifts. The linear model works equally well for the theoretically calculated shifts (rms = 0.025 eV, $R^2 = 0.9997$).

Although the linear additivity model gives a good description of the ionization-energy shifts, inspection of the results shows a few striking discrepancies between the actual values of the shifts and those predicted by the additivity model. For instance, the ionization-energy shifts predicted for 1,2,4,5-tetramethylbenzene are too high by 0.076 eV (C1,2,4,5) and 0.063 eV (C3,6). This effect is seen in both the experimentally measured and the theoretically predicted shifts. Similarly, for 1,3-difluorobenzene and 1,3,5-trifluorobenzene, the shifts predicted for the CF carbons are too high by 0.047 and 0.071 eV. It is useful, therefore, to consider the possible contributions from the nonlinear terms.

TABLE 2: Additivity Coefficients for Methyl and Fluoro Substituents (eV)

		carbon 1s ionization energies		
	number	theory	expt	protonation
CH_3 i	15	0.055(5)	0.044(6)	0.039(4)
CH_3 o	24	−0.280(4)	−0.262(5)	−0.268(3)
CH_3 m	24	−0.170(3)	−0.159(4)	−0.136(3)
CH_3 p	15	−0.264(6)	−0.227(8)	−0.329(6)
F i′	24	2.499(4)	2.496(5)	0.853(5)
F o′	36	0.281(3)	0.256(3)	0.018(3)
F m′	36	0.365(3)	0.339(4)	0.312(3)
F p′	24	0.139(4)	0.121(5)	−0.080(3)
io	4	0.044(9)	0.051(12)	
om[a]	6	0.025(4)	0.024(6)	0.019(3)
op	5	0.019(7)	0.027(10)	0.025(6)
mp	4			0.038(7)
i′o′	10			−0.115(4)
i′p′	8			−0.061(6)
o′(o′ − 1)	12			0.032(6)
o′m′[a]	18	−0.020(3)	−0.011(4)	
m′p′	10			−0.025(4)
i′o	5	−0.027(7)	−0.019(9)	−0.085(6)
i′m	4			−0.016(6)
i′p	2			−0.035(10)
io′	5			−0.021(5)
im′	4			−0.015(5)
oo′	4			0.010(6)
om′[a]	7	−0.024(6)	−0.0015(8)	−0.025(4)
mm′	4			−0.014(6)
pm′	5	−0.022(7)	−0.017(9)	−0.024(5)

[a] A pair of substituents at the ortho and meta positions can be either ortho to each other or para to each other. We see some evidence that these two possibilities should be treated separately, but since the ortho−meta coefficients are small we do not pursue this question here.

A fit to the data using all 38 possible terms gives excellent agreement between observation and prediction, but for 6 of the nonlinear parameters the uncertainty in the parameter is larger than its value and for a number of the nonlinear parameters the statistical significance is small. We find that we can get a good description of the results by including only 7 of the nonlinear parameters. These are io (two methyl groups, one at the ipso position relative to the site of ionization and one at the ortho position), om, op, o′m′ (two fluoro groups, one ipso, and one meta), oi′, om′, and pm′. The values of the parameters determined in this way are listed in Table 2. Also shown as the first column of numbers in Table 2 is the number of data points that contribute to the determination of each coefficient. The experimentally determined shifts differ from those predicted by this model by an rms deviation of 0.019 eV, with $R^2 = 0.9998$. The corresponding values for the theoretically calculated shifts are 0.014 eV and 0.99990. Adding additional nonlinear parameters to the correlation makes only small improvements in these numbers. (The difference between the rms values for theory and experiment presumably arises from experimental errors in the measurements. The square root of the difference between the squares of these two values provides an estimate of 0.013 eV for the experimental uncertainty for the relative ionization energies.)

Of the seven nonlinear parameters, six involve at least one methyl group, and for five of these the methyl group is ortho to the site of ionization. Only one of the nonlinear terms involves two fluoro substituents. These results can be understood, at least qualitatively, in terms of the polarizibility of the methyl group. When a polarizible group is added to a molecule, it tends to be polarized in such a direction as to counteract whatever effects were produced by the already existing substituents.[29,30] In support of this view we note that the nonlinear terms om, op, oi′, om′, and pm′ all have signs that are opposite to that of the corresponding linear terms: m, p, i′, and m′. This effect is less apparent for fluoro substituents owing to the lower polarizibility of fluorine relative to methyl.

Additivity and Enthalpies of Protonation. With only linear terms the additivity model describes 85 enthalpies of protonation with an rms deviation of 0.046 eV (4.5 kJ/mol) and $R^2 = 0.993$. This restricted model does not describe the enthalpies of protonation as well as it describes the core-ionization energies (0.026 eV and 0.9996, as noted above). If we use the full set of 38 parameters we have an rms deviation of 0.0097 eV with $R^2 = 0.9998$, but 12 of the parameters are not statistically significant and two others are small enough to be neglected (<0.01 eV). A fit with 24 parameters gives a satisfactory description (rms deviation = 0.010 eV, $R^2 = 0.9997$) and appears to include most of the important quadratic terms. Smaller numbers of parameters give less satisfactory fits. The results of the fit with 24 parameters are listed in Table 2.

A discussion of the relationship between the linear parameters for methyl substituents and those for fluoro substituents has been presented previously.[1,2] Summarizing, we note first that the substituent parameters for ortho, meta, and para substituents are negative for methyl and positive for fluorine. These results reflect the electron-donating character of the methyl group and the electron-withdrawing character of the fluoro group. Next, we see that the additivity parameters for a substituent in the meta position, where resonance effects do not play a significant role, are nearly the same for core ionization as they are for protonation, for both methyl and fluoro substituents. However, for substituents in the ortho and para positions, where resonance does play a role, the additivity parameters are all less than the meta parameters, reflecting the ability of both of ortho and para substituents to donate electrons to the ring via resonance. There is, in addition, a striking contrast between the effect of a fluorine substituent in the ortho or para position on the ionization energy and the effect of such a substituent on the enthalpy of protonation. In the first case the additivity coefficients are distinctly positive (0.256 and 0.121 eV), whereas in the second case they are close to zero or negative (0.018 and −0.080 eV). In the protonated species two hydrogen atoms on the same carbon atom lie above and below the plane of the molecule. The hydrogen 1s orbitals on these protons can combine to form an orbital that has the same symmetry as the π orbitals of the ring. There is thus an opportunity for electron donation from the lone pairs of the fluorine atom into the π system to influence the proton affinity in a way that is not possible for core ionization. In terms of Hammett parameters, the core ionization energies correlate with σ, whereas the enthalpies of protonation correlate with σ^+.

There is a large difference in the linear additivity coefficients for fluorine at the ipso position. Addition of fluorine at this position causes a shift of +2.5 eV in the carbon 1s ionization energy but a shift of only +0.8 eV in the enthalpy of protonation. This difference can be accounted for by considering the electrostatics of the situation. The principal effect of the fluorine is to transfer about 0.2e of charge from the ipso carbon to the fluorine, leaving a charge of +0.2e on this carbon atom. This charge is closer to the carbon 1s orbital than it is to the position of the proton in the protonated species, and, as a consequence, its effect on the ionization energy is greater than its effect on the enthalpy of protonation. A calculation of the relevant electrostatic potentials is approximately in accord with this view. The potential at the nucleus of C1 in fluorobenzene is calculated to be 2.4 V more positive than the corresponding potential in benzene. This result agrees well with the observed difference of 2.49 eV in ionization energies. By contrast, the potential at a proton added to C1 in fluorobenzene is only 0.4 V more positive than the potential at the site of the added proton in protonated benzene. Because of geometric changes that occur with protonation, the two types of calculations are not perfectly comparable, but they do indicate that the electrostatic effect is smaller for protonation than it is for core ionization, and that the difference is of the right magnitude. An alternate approach is to compare the potentials in the neutral molecule at 1.15 Å from the ipso carbon in a direction perpendicular to the plane of the molecule. For fluorobenzene the potential is 0.9 V more positive than that for benzene, and again we see that the difference in potentials is in approximate accord with the difference in enthalpies of protonation.

Turning to the nonlinear terms for protonation, we note that these are more important than the corresponding terms for core ionization. For core ionization, we are able to obtain a satisfactory description with only seven nonlinear terms. The largest coefficient of these is 0.05 eV and the other terms are typically less than half of this. By contrast, for the proton affinities, we need 16 nonlinear terms. The coefficient with the greatest magnitude, −0.115 eV, is larger in magnitude than three of the coefficients for the linear terms. Four of the five largest nonlinear coefficients involve addition of a proton to a fluorinated carbon. These are i′o′ = −0.115 eV (one fluorine at the site of protonation and one fluorine ortho to this site), i′o = −0.085 eV (one fluorine at the site of protonation and one methyl ortho to this site), i′p′ = −0.061 eV (one fluorine at the site of protonation and one fluorine para to this site), and i′p = −0.036 eV (one fluorine at the site of protonation and one methyl group para to this site). We note that the sign of each of these coefficients is negative. Thus, the effect of the additional substituent is to partially counteract the effect of the fluorine at the site of protonation, which is positive. These results can be understood as the effect of a π-electron donor that can contribute electrons to the site of protonation (via resonance) to diminish the effects of the ipso fluorine on the enthalpy of protonation. It is noteworthy that the terms involving a substituent at the meta position, i′m and i′m′, are negligible, indicating that resonance plays a role in this process. It is also to be noted that a corresponding effect is not seen for the core-ionization energies, indicating that the electron acceptor character of the hydrogen−fluorine pair at the site of protonation also plays a role.

Of the remaining nonlinear terms, the largest is mp = 0.038 eV (methyl groups meta and para to the site of protonation). It is not obvious why this term should be important. Conspicuously absent from the nonlinear terms is the one for two methyl groups with each ortho to the site of protonation. One might have expected steric effects to influence the enthalpy of protonation in this case, but the contribution from such a term is less than 0.01 eV. There is, however, a nonlinear term for two fluoro groups with each ortho to the site of protonation, and this is comparable in magnitude to the effect of a single fluoro group ortho to the site of protonation. However, both terms are small.

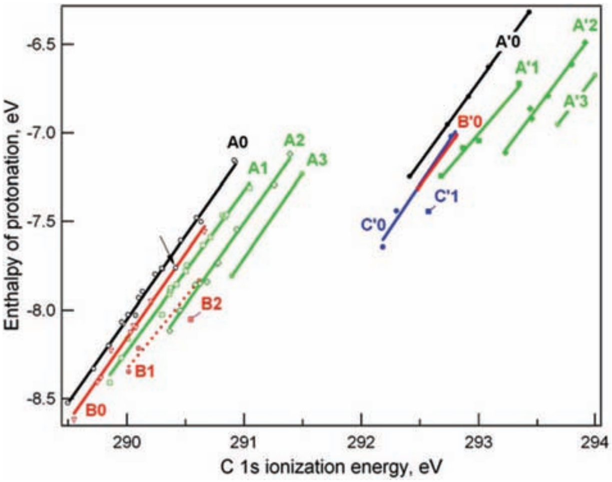

Figure 2. Enthalpy of protonation plotted versus carbon 1s ionization energy. Open points refer to ionization/protonation at carbon atoms that do not have an adjacent fluorine. Closed points refer to CF carbons. Black: (A0, A′0) no resonance contribution expected from the substituents except that A0 includes data for a methyl group at the ortho position. Green: (A1, A′1) one fluorine either ortho or para; (A2, A′2) two fluorines ortho or para; (A3, A′3) three fluorines ortho or para. Red: (B0, B′0, B1, B2) methyl at the para position and zero, one, and two fluorines at the ortho position. Blue: (C′0, C′1) methyl group at the ortho position with zero or one fluorine ortho or para. The black arrow identifies the point for carbon 1 in 3-fluoro-*o*-xylene, which falls significantly off of the expected correlation line, A0.

Correlations between Enthalpies of Protonation and Ionization Energies

Many chemical processes involve adding a positive charge at a particular site in a molecule and among these is protonation. Although the absolute energies for ionization and protonation are quite different, the changes in these energies brought about by substituents that are remote to the site of ionization/protonation may be expected to correlate linearly with one another. Linear correlations between enthalpies of protonation and core-ionization energies are well established for nitrogen, oxygen, and a few other atoms.[4,5] We have recently demonstrated that such correlations exist for 1,3-butadiene and 1,3-pentadiene,[6] the fluorobenzenes,[1] and the methylbenzenes.[2] Here we are able to extend the correlations and to investigate possible interactions between different substituents.

In Figure 2, we have plotted the enthalpies of protonation versus the carbon 1s ionization energies. We see, as has been noted before, that there are linear correlations between these two quantities. However, there is not a single correlation line, but a family of correlation lines. Points for molecules that share certain common characteristics fall on a single line. For instance, if there are expected to be no resonance effects of the substituent, as is the case when the substituent is at a position meta to the site of ionization/protonation, then the points fall on the black lines, A0 and A′0. Addition of one, two, or three fluorine substituents either ortho or para to the site of ionization gives the green lines, A1 and A′1, A2 and A′2, and A3 and A′3. Addition of a methyl substituent para to the site of ionization/protonation gives the red lines B0, B′0, and addition of both a para methyl group and one or two ortho fluorines gives B1 and B2. The line and point labeled C′0 and C′1 arise when ionization/protonation involves a CF carbon that has an ortho methyl substituent. If, however, there is an ortho methyl group but no ipso fluorine the corresponding points fall on line A0 rather than on a separate line. The slopes of the correlation lines are close to 1, indicating that the enthalpies of protonation and the core-ionization energies are approximately equally affected by the substituents The data on the fluoromethylbenzenes allow us to see additional correlation lines that were not apparent from the previous results, which did not include compounds with more than one type of substituent.

In the experimental section, we noted the problems of assigning the peaks in the spectrum for 3-fluoro-*o*-xylene to the appropriate carbon atoms. With the assignments we have made all of the data (except the point for carbon 1) for this molecule fall on the appropriate correlation line. Any of the other possible assignments of the peaks would lead to points that were well away from their correlation lines. The exception (carbon 1), indicated by the arrow in Figure 2, is displaced from the appropriate line (A0). This displacement arises, as is discussed subsequently, from nonlinear terms in the additivity model.

Correlation and the Linear Additivity Model. That there are not one but several correlation lines can be understood in terms of the additivity model and the differences between the additivity coefficients for protonation and those for ionization. The linear additivity model can be written as $\vec{I} = \bar{S}\cdot\vec{A}$ and $\vec{P} = \bar{S}\cdot\vec{B}$, where $\vec{I}$ and $\vec{P}$ are arrays of the shifts in ionization energies and protonation enthalpies (relative to that of benzene), that is, the values listed in Table 1. $\bar{S}$ is the matrix that describes the number of each type of substituent at each position in the ring. A row in $\bar{S}$ defines the substitution pattern around a given site in a given molecule in terms of the number of each kind of substituent in ipso, ortho, meta, and para positions.[31] $\vec{A}$ and $\vec{B}$ are arrays of the additivity coefficients for ionization and protonation and are common to all molecules. If the additivity coefficients are the same for ionization and protonation ($\vec{B} = \vec{A}$), then the shifts in the enthalpy of protonation are identical to the shifts in ionization energy ($\vec{P} = \vec{I}$). Or, if $\vec{B} = f\cdot\vec{A}$, where f is a scaling factor, then $\vec{P} = f\cdot\vec{I}$; that is, the shifts of the enthalpy of protonation are proportional to the shifts in the ionization energy. In either case there will be a single correlation line between the enthalpies of protonation and the ionization energies.

In general, $\vec{B} \neq f\cdot\vec{A}$, but we can write $\vec{B} = f\cdot\vec{A} + \vec{\Delta}$. In this case, $\vec{P} = f\cdot\vec{I} + \bar{S}\cdot\vec{\Delta}$. This relationship implies that for series of similar compounds there will be linear correlations between enthalpies of protonation and core ionization, but that one series may be offset from another. As an example, we consider the case where all of the elements of $\vec{\Delta}$ are zero except for that for a fluorine attached at the site of ionization/protonation, Δ_{ipso}. Then we will have two correlation lines, one for compounds without such a fluorine and one for compounds that have an ipso fluorine. The two lines will have the same slope but have intercepts that differ by Δ_{ipso}.

We now consider the case at hand, fluoro and methyl substituents. The slopes of the various correlation lines in Figure 2 are typically between 0.9 and 1.0. From the slopes determined with the best accuracy, we choose a value for f of 0.925. Then from the values of the additivity coefficients given in Table 2 we obtain the components of $\vec{\Delta}$ listed in Table 3. Inasmuch as the value chosen for f is only approximate, the values given in Table 3 are also only approximate and should be used only to illustrate the expected effects, as in the discussion that follows.

In this table we note that four of the components are small: i, o, m, m′. For molecules that have only these substituents $\vec{P} \approx f\cdot\vec{I}$, and all of the data for such compounds fall on a single correlation line, indicated as A0 in Figure 2. With the exception

TABLE 3: Differences between the Linear Additivity Coefficients for Core-Ionization and the Scaled Linear Additivity Coefficients for the Enthalpy of Protonation (eV)

substituent	position	component, Δ_k
CH_3	i	−0.00
	o	−0.03
	m	0.01
	p	−0.12
F	i′	−1.46
	o′	−0.22
	m′	−0.00
	p′	−0.19

of a methyl group in the ortho position, substituents at these positions do not influence the site of ionization/protonation via resonance.

The largest component shown in Table 3, approximately −1.5 eV, is for a fluorine atom ipso to the site of ionization/protonation. The data for molecules that have an ipso fluorine and the substituents indicated by i, o, m, and m′ will fall on a line defined by $\vec{P} \approx f \cdot \vec{I} - 1.5$ eV. This line, indicated by A′0 in Figure 2, is nearly parallel to line A0, and displaced from it vertically by about −1.5 eV. As has been discussed above, this displacement appears to arise primarily from electrostatic effects that are quite different for the two processes.

The remaining three components, p, o′, and p′, relate to the ability of the substituents to donate electrons via resonance to the site of ionization or the site of protonation. We note that the two components for fluoro substituents, o′ and p′, are both approximately −0.2 eV. Thus, the effect of a fluoro substituent in either of these positions is approximately the same. When we include these substituents in the correlations we have additional correlation lines defined by $\vec{P} \approx f \cdot \vec{I} - 0.2n$ eV and $\vec{P} \approx f \cdot \vec{I} - 0.2n$ eV − 1.5 eV, where n is the number of fluoro substituents in ortho and para positions. Since n can take on values of 0, 1, 2, and 3, there are six additional correlation lines. These lines are labeled A1, A2, A3, A′1, A′2, and A′3 in Figure 2. Next we notice that the effect of a methyl substituent in the para position is about half that of a fluoro substituent in either the ortho or the para position. Thus, there will be two additional correlation lines, B0, lying about halfway between A0 and A1, and B′0, lying between A′0 and A′1. In addition, there are points for compounds with both a para methyl group and one or more ortho fluoro groups. Three such points, B1, fall approximately halfway between lines A1 and A2, and one point, B2, corresponding to one para methyl and two ortho fluorines, is about halfway between A2 and the extension of A3.

Line C′0 and point C′1 in Figure 2 appear to be anomalous. These points represent molecules in which there is a methyl group ortho to the site of ionization/protonation, which is the CF carbon. For C′1 (carbon 2 in 2,5-difluorotoluene) there is also a fluoro substituent para to this site of ionization/protonation. If, however, there is no fluorine at the site of ionization/protonation, then the points for the corresponding compounds do not fall on separate lines but on lines A0 and A1. We note also that several lines have slopes that are distinctly different from the slopes of the other lines. We believe that these slope differences as well as the anomalous behavior seen in C′0 and C′1 arise from nonlinear effects that are not included in the linear additivity model. This point is discussed below.

From the foregoing discussion we see that the major features of the correlations between enthalpies of protonation and core-ionization energies can be understood in terms of the linear additivity model. There are several different correlation lines because substituents in the ortho and para positions affect the core-ionization energies and enthalpies of protonation differently. The two hydrogen atoms at the site of protonation are better electron acceptors than is a core-ionized atom at the same site. Thus, the π-electron-donating power of the fluoro and methyl groups is more effective for protonation than for core ionization.

Effect of Nonlinearity of Additivity on the Correlation. The linear additivity model that has just been discussed implies that we should have a set of correlation lines all of which have the same slope. The slopes of the lines in Figure 2, however, range from 0.77 to 0.99. In addition, the set of lines associated with molecules that have an ipso fluorine (lines A′) should be spaced apart with the same spacing as the lines for the molecules without such a substituent (lines A). This is not the case; the spacing of the lines A′ is greater than the spacing for the lines A. Moreover, the slopes of A′1 and B1 are distinctly different from those of the other lines. The anomalous position of C′ has been noted. Finally, there are a few points that are significantly off from their correlation lines. For example, the point for carbon 1 in 3-fluoro-*o*-xylene, marked with an arrow in Figure 2, which would have been expected to fall on the A0 correlation line, falls on the B0 line. Although one might be tempted to attribute these discrepancies to experimental errors in the ionization energies, correlations done with the theoretically calculated ionization energies show the same discrepancies. To a large extent these additional effects can be accounted for by considering the nonlinear terms in the additivity model.

From Table 2 we see that there are significant nonlinear terms for one fluorine ipso to the site of protonation and another one either ortho (i′o′ = −0.115 eV) or para (i′p′ = −0.061 eV) to this site. This leads to an additional spacing of between −0.06 and −0.12 eV between lines A′0 and A′1 that is not present for the spacing between lines A0 and A1, and to corresponding increases in the spacings between lines A′1 and A′2 and between lines A′2 and A′3. For the two points at the right-hand end of A′1, the contributing nonlinear term is the i′p′ term of −0.06 eV, whereas for the two points at the left-hand end, the contributing term is i′o′ (−0.12 eV). Thus, these nonlinear terms account for not only the change in spacing but also the difference in slope.[32] This effect is particularly striking for the two points on line A′3 (hexafluorobenzene and carbons 2 and 4 of pentafluorobenzene). For both of these the i′o′ term contributes twice and the i′p′ term once for a total displacement of nearly 0.3 eV from where these points would be expected if there were no nonlinear terms.

For line C′0 the points represent molecules in which the ionization/protonation takes place at a CF carbon with an ortho methyl group. We see from Table 2 that the corresponding nonlinear term, i′o, is significant, −0.085 eV. For the left-hand point, which represents carbon 2 in 2-fluoro-*m*-xylene, this nonlinear term contributes twice, or −0.17 eV, and this is very close to the displacement of this point below the extension of line A′0. For the other points on C′0, the i′o interaction occurs only once, leading to the observed displacement of about −0.085 eV from A′0. A similar displacement for C′1 brings it approximately in line with the A′1.

The noticeable displacement of the point for carbon 1 in 3-fluoro-*o*-xylene has been pointed out. This displacement arises primarily from the io nonlinear term affecting the core-ionization energy.

Discussion and Conclusions

We have seen that the data for carbon 1s ionization energies and enthalpies of protonation can be accounted for, to first approximation, by a linear additivity model. The effects of multiple substituents are to a large extent additive. As noted above, the linear model can account for the ionization energies with an rms deviation of 0.026 eV and the enthalpies of protonation with an rms deviation of 0.046 eV. These correspond to 2.5 and 4.4 kJ/mol, values that are not large as far as chemical effects are concerned.

The signs of the substituent coefficients are as expected: negative (electron donating) for the methyl group and positive (electron withdrawing) for the fluoro group. For substituents that are meta to the site of ionization/protonation resonance effects play only a small role. In this case the substituent coefficients for ionization and protonation are found to be nearly the same, −0.143 and −0.136 eV, respectively, for a methyl substituent, and +0.339 and +0.312 for a fluoro substituent. For compounds that differ only in the number of such substituents, the enthalpies of protonation vary linearly with the core-ionization energies with a slope of close to 1.

When the substituents are ortho or para to the site of ionization/protonation, resonance effects play a role. In particular, both methyl and fluoro substituents in these positions act as π-electron donors. This effect is apparent in that all of the coefficients for ortho and para substituents are less than the corresponding meta coefficients. The effect of this electron donation is greater for enthalpies of protonation than it is for core-ionization energies. As illustration, we examine pairs of coefficients—ionization/protonation—for para fluorine, 0.121/−0.080, ortho fluorine, 0.256/0.018, and para methyl, −0.226/−0.329. This difference arises because the pair of hydrogen atoms at the site of protonation is an even better electron acceptor than is the core-ionized carbon atom. As noted, the two hydrogen atoms at the site of protonation lie one above the plane of the molecule and one below. Their 1s orbitals can form a π orbital that mixes with the π orbitals of the ring and the substituent, thus allowing for enhanced electron transfer to the site of protonation. The effect is about twice as large for fluoro substituents as it is for para methyl substituents, indicating that the fluoro group is a better π donor than the methyl group. These differential resonance effects give rise to the sets of nearly parallel correlation lines that are seen in Figure 2. (The effect is, however, not seen for an ortho methyl group, where the substituent constants for ionization and protonation are nearly the same, −0.264 and −0.269 eV. This result is not understood.)

If the site of ionization/protonation is a CF carbon, then the effect of the fluorine on the ionization energy is much greater than the effect on the enthalpy of protonation. Electrons are withdrawn by the fluorine from the carbon, leaving a partial positive charge. This positive charge is closer to the carbon 1s orbital than it is to the proton, with the result that its effect is greater in the former case than in the latter.

Although the linear additivity model accounts well for the overall picture of core-ionization energies and enthalpies of protonation and their correlations, it is apparent from the results shown in Figure 2 and in Table 2 that there are additional effects that are not included in this model. In particular, we have noted that the lines A′ are spaced farther apart than the lines A, that the line C′0 is displaced from the line A′0, and that the various correlation lines do not have the same slope, as would be predicted by the linear additivity model. However, inclusion of a small number of nonlinear terms in the additivity model can account for these observations. The most important of these terms are i′o′ (−0.115 eV), i′o (−0.085 eV), i′p′ (−0.061 eV), i′p (−0.036 eV), and mp (−0.038 eV) for enthalpies of protonation, and io (0.051 eV) for ionization. The first four of these represent the effect on the enthalpy of protonation of an ortho or para substituent when the protonation takes place at the CF carbon. In each case the effect of the second-order term (negative) is to reduce the effect of the fluoro substituent (positive). This arises because both the fluoro and methyl substituents at ortho or para positions can donate elections through the π system to reduce the effects of the strong electron withdrawal by the fluorine. For substituents in the same position, the coefficient is smaller in magnitude for methyl than it is for fluoro, indicating that the fluoro group is better than the methyl group at responding to the demand produced by the added proton. The significant io coefficient for core ionization is possibly best understood not as modification of the effect of an ipso methyl group (which is small) by an ortho methyl group but rather as a modification of the effect of an ortho methyl group (−0.262 eV) by an ipso methyl group; the polarizible ipso methyl group reduces the effect of the ortho methyl group. The mp term for protonation is not yet understood.

The overall picture that emerges from the results reported here and previously[1,2] is consistent with standard views of substituent effects. The primary effect is electron withdrawal by fluorine and electron donation by methyl. For fluorine, the electron withdrawal does not extend beyond the ipso carbon; the overall influence of the fluorine arises because the dipole of the polarized CF bond creates a positive potential throughout the entire ring.[1] The secondary effect of both substituents is π-electron donation to the ortho and para positions. This effect is greater for fluorine than for the methyl group; fluorine is a better π donor than methyl. The presence of a polarizable substituent, such as methyl, can reduce the effect of the other substituents by being polarized to partially cancel the changes to the charge distribution made by the other substituents. This effect is more important for methyl than for fluorine; the methyl group is more polarizable than the fluoro group. Finally, if electron demand is created by the addition of a positive charge and there is a modification of the π orbitals (as in the case of protonation), then there will be additional π-electron donation. Since fluorine is a better π donor than methyl, this effect is larger for fluorine than for methyl.

Acknowledgment. We thank Maxim Tchaplyguine for his assistance at MAX II and Henrik Bergersen, Jarle Harnes, Alf Holme, Andreas Lindblad, Velaug Myrseth, and Maria Gundersen Zahl for assistance during the taking of the experimental data. We also acknowledge support from the Divisions of Chemical and Material Sciences, Office of Energy Research, of the U.S. Department of Energy, the Nordic Research Board (NORDFORSK), the Swedish Scientific Council (VR), the Swedish Foundation for Strategic Research (SSF), the Research Council of Norway, the Norwegian High Performance Computing Consortium NOTUR, and the EC Transnational Access to Research Infrastructure Program (TARI).

Supporting Information Available: Details of the theoretical methods. Theoretically calculated positions of the atoms in the molecules considered. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Carroll, T. X.; Thomas, T. D.; Bergersen, H.; Børve, K. J.; Sæthre, L. J. *J. Org. Chem.* **2006**, *71*, 1961–1968.

(2) Myrseth, V.; Sæthre, L. J.; Børve, K. J.; Thomas, T. D. *J. Org. Chem.* **2007**, *72*, 5715–5723.

(3) Proton affinity is the negative of the enthalpy of protonation, generally at 298 K. To avoid some mathematical inconveniences that are

introduced by this sign convention, we will use enthalpies of protonation rather than proton affinities.

(4) (a) Martin, R. L.; Shirley, D. A. *J. Am. Chem. Soc.* **1974**, *96*, 5299–5304. (b) Davis, D. W.; Rabalais, J. W. *J. Am. Chem. Soc.* **1974**, *96*, 5305–5310. (c) Davis, D. W.; Shirley, D. A. *J. Am. Chem. Soc.* **1976**, *98*, 7898–7903. (d) Benoit, F. M.; Harrison, A. G. *J. Am. Chem. Soc.* **1977**, *99*, 3980–3984. (e) Cavell, R. G.; Allison, D. A. *J. Am. Chem. Soc.* **1977**, *99*, 4203–4204. (f) Smith, S. R.; Thomas, T. D. *J. Am. Chem. Soc.* **1978**, *100*, 5459–5466. (g) Nordfors, D.; Mårtensson, N.; Ågren, H. *J. Electron Spectrosc. Relat. Phenom.* **1990**, *53*, 129–139. (h) Nordfors, D.; Mårtensson, N.; Ågren, H. *J. Electron Spectrosc. Relat. Phenom.* **1991**, *56*, 167–187.

(5) (a) Carroll, T. X.; Smith, S. R.; Thomas, T. D. *J. Am. Chem. Soc.* **1975**, *97*, 659–660. (b) Mills, B. E.; Martin, R. L.; Shirley, D. A. *J. Am. Chem. Soc.* **1976**, *98*, 2380–2385. (c) Ashe, A. J.; Bahl, M. K.; Bomben, K. D.; Chan, W.-T.; Gimzewski, J. K.; Sitton, P. G.; Thomas, T. D. *J. Am. Chem. Soc.* **1979**, *101*, 1764–1767. (d) Brown, R. S.; Tse, A. *J. Am. Chem. Soc.* **1980**, *102*, 5222–5226.

(6) Thomas, T. D.; Sæthre, L. J.; Børve, K. J.; Gundersen, M.; Kukk, E. *J. Phys. Chem. A* **2005**, *109*, 5085–5092.

(7) Smith, B. J.; Radom, L. *J. Am. Chem. Soc.* **1993**, *115*, 4885–4888; *Chem. Phys. Lett*. **1994**, *231*, 345−351; *J. Phys. Chem.* **1995**, *99*, 6468−6471.

(8) (a) Eckert-Maksić, M.; Klessinger, M.; Maksić, Z. B. *J. Phys. Org. Chem.* **1995**, *8*, 435–441. (b) Maksić, Z. B.; Kovaèeviæ, B.; Kovaèek, D. *J. Phys. Chem. A* **1997**, *101*, 7446–7453.

(9) (a) Hollemman, A. F. *Chem. Rev.* **1924**, *1*, 187–230. (b) Condon, F. E. *J. Am. Chem. Soc.* **1948**, *70*, 1963–1964; **1952**, *74*, 2528−2529. (c) Eaborn, C.; Moore, R. C. *J. Chem. Soc.* **1959**, 3640. (d) Richards, K. E.; Wilkinson, A. L.; Wright, G. J. *Aust. J. Chem.* **1972**, *25*, 2369–2381.

(10) (a) Eckert-Maksić, M.; Klessinger, M.; Maksić, Z. B. *Chem. Eur. J.* **1996**, *2*, 1251–1257. (b) Eckert-Maksić, M.; Knežević, A.; Maksić, Z. B *J. Phys. Org. Chem.* **1998**, *11*, 663–669.

(11) Gineityte, V. *J. Mol. Struct. (Theochem)* **2001**, *546*, 107–117.

(12) Kuz'min, V. E.; Muratov, E. N.; Artemenko, A. G.; Gorb, L.; Qasim, M.; Leszczynski, J. *Chemosphere* **2008**, *72*, 1373–1380.

(13) Liu, L.; Fu, Y.; Liu, R.; Li, R.-Q.; Guo, Q.-X. *J. Chem. Inf. Comput. Sci.* **2004**, *44*, 652–657.

(14) http://www.maxlab.lu.se/. Bässler, M.; Forsell, J-.O.; Björneholm, O.; Feifel, R.; Jurvansuu, M.; Aksela, S.; Sundin, S.; Sorensen, S. L.; Nyholm, R.; Ausmees, A.; Svensson, S. *J. Electron Spectrosc. Relat. Phenom.* **1999**, *101−103*, 953–957.

(15) Carroll, T. X.; Hahne, J.; Thomas, T. D.; Sæthre, L. J.; Berrah, N.; Bozek, J.; Kukk, E. *Phys. Rev. A* **2000**, *61*, 042503-1-7.

(16) Myrseth, V.; Bozek, J. D.; Kukk, E.; Sæthre, L. J.; Thomas, T. D. *J. Electron Spectrosc. Relat. Phenom.* **2002**, *122*, 57–63.

(17) SPANCF, http://www.geocities.com/ekukk. Kukk, E. Department of Physics, Materials Science University of Turku, FIN-20014 Turku, Finland.

(18) Van der Straten, P.; Morgenstern, R.; Niehaus, A. *Z. Phys. D* **1988**, *8*, 35–45.

(19) Carroll, T. X.; Børve, K. J.; Sæthre, L. J.; Bozek, J. D.; Kukk, E.; Hahne, J. A.; Thomas, T. D. *J. Chem. Phys.* **2002**, *116*, 10221–10228.

(20) *Gaussian 03, Revision C.02*; Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A.; Jr., Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N. Petersson, G. A. Nakatsuji, H. Hada, M. Ehara, M. Toyota, K. Fukuda, R. Hasegawa, J. Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Adamo, J.; Jaramillo, R.; Gomperts, R. E.; Stratmann, O.; Yazyev, A. J.; Austin, R.; Cammi, C.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. Gaussian, Inc.: Pittsburgh, PA, 2003.

(21) Karlsen, T.; Børve, K. J.; Sæthre, L. J.; Wiesner, K.; Bässler, M.; Svensson, S. *J. Am. Chem. Soc.* **2002**, *124*, 7866–7873.

(22) Børve, K., unpublished result.

(23) Karlsen, T.; Sæthre, K. J.; Børve, K. J.; Berrah, N.; Kukk, E.; Bozek, J. D.; Carroll, T. X.; Thomas, T. D. *J. Phys. Chem. A* **2001**, *105*, 7700–7706.

(24) Hehre, W. J.; Radom, L.; Schleyer, P. v. R.; Pople, J. A. *Ab Initio Molecular Orbital Theory*; Wiley-Interscience: New York, 1986; pp 260−261.

(25) Myrseth, V.; Børve, K. J.; Wiesner, K.; Bässler, M.; Svensson, S.; Sæthre, L. J. *Phys. Chem. Chem. Phys.* **2002**, *4*, 5937–5943.

(26) Thomas, T. D.; Sæthre, L. J.; Børve, K. J.; Bozek, J. D.; Huttula, M.; Kukk, E. *J. Phys. Chem. A* **2004**, *108*, 4983–4990.

(27) Holme, A.; Børve, K. J.; Sæthre, L. J.; Thomas, T. D., unpublished results.

(28) The factor of 2 in the denominator of the term in β did not appear in our earlier treatments, refs 1 and 2, but should have been included to correctly count the number of interactions. As a result, the value of the one significant β coefficient, $o'(o'-1)$, is twice as large here as in the previous work, ref 1.

(29) Siggel, M. R. F.; Thomas, T. D. *J. Electron. Spectrosc. Relat.Phenom.* **1989**, *48*, 101.

(30) Siggel, M. R. F.; Thomas, T. D. *J. Am. Chem. Soc.* **1992**, *114*, 5795.

(31) For instance, for C3 in 3-fluoro-*o*-xylene the appropriate row in the matrix is 0,1,1,0,1,0,0,0, indicating first the number of methyl substituents at each location relative to C3 in the order i, o, m, p and then the number of fluoro substituents, i', o', m', p'.

(32) It is legitimate to ask whether or not there is circular reasoning here. The points for the line $A'1$ do not fall where expected. Possibly it is this discrepancy alone that gives rise to the nonlinear terms $i'o'$ and $i'p'$. If this were the case, then, indeed, the argument would be circular. In reality, however, the value for the $i'o'$ component is based on 10 measurements and that for the $i'p'$ is based on 8 measurements. Thus, these values can be established even without including the points on line $A'1$.

JP810612X