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Fluorine as a π Donor. Carbon 1s Photoelectron Spectroscopy and Proton Affinities of Fluorobenzenes

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

Keuka College, Keuka Park, New York 14478, Oregon State University, Corvallis, Oregon 97331, University of Uppsala, 751 05 Uppsala, Sweden, University of Bergen, N-5020 Bergen, Norway

t.darrah.thomas@oregonstate.edu

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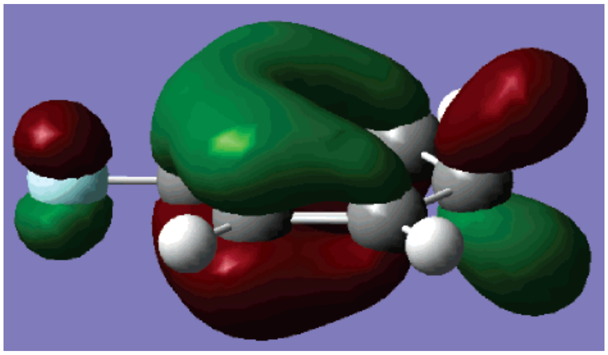

The carbon 1s ionization energies for all of the carbon atoms in 10 fluorine-substituted benzene molecules have been measured by high-resolution photoelectron spectroscopy. A total of 30 ionization energies can be accurately described by an additivity model with four parameters that describe the effect of a fluorine that is ipso, ortho, meta, or para to the site of ionization. A similar additivity relationship describes the enthalpies of protonation. The additivity parameters reflect the role of fluorine as an electron-withdrawing group and as a π-electron donating group. The ionization energies and proton affinities correlate linearly, but there are four different correlations depending on whether there are 0, 1, 2, or 3 fluorines ortho or para to the site of ionization or protonation. That there are four correlation lines can be understood in terms of the ability of the hydrogens at the site of protonation to act as a π-electron acceptor. A comparison of the ionization energies and proton affinities, together with the results of electronic structure calculations, gives insight into the effects of fluorine as an electron-withdrawing group and as a π donor, both in the neutral molecule and in response to an added positive charge.

Introduction

Fluorine as a substituent on benzene is considered to be both σ-electron withdrawing and π-electron donating. On one hand, the Hammett parameter for fluorine in the meta position is +0.34, reflecting the electron-withdrawing power.[1] On the other, that for the para position is only +0.15.[2] The difference, $\sigma_p - \sigma_m = -0.20$, can be attributed to the π-donating power of fluorine. Although fluorine is generally considered to be a deactivating substituent, the reactivity of the para position in fluorobenzene is anomalously high,[3] in some cases greater than that of benzene, reflecting the π-donating ability of fluorine. As another example, the proton affinity of fluorobenzene, 755.9 kJ/mol, is greater than that of benzene, 750.4 kJ/mol.[4] Theoretical calculations show that fluorobenzene protonates at the para position,[5,6] and, thus, the higher proton affinity for fluorobenzene

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[†] Keuka College.

[‡] Oregon State University.

[§] University of Uppsala.

[||] University of Bergen.

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can be taken to indicate a strong ability of the fluorine to stabilize positive charge at the para position.[7] By contrast, the proton affinity at the meta position of fluorobenzene is calculated to be less than that of benzene, reflecting the electron-withdrawing effect of fluorine.

The π-donating ability of fluorine has been called into question by Wiberg and Rablen[8] who concluded that π donation by fluorine is small except in situations of high-electron demand, such as protonation. They further concluded that the strong preference for para substitution in electrophilic reactions with fluorobenzene could be accounted for by the inductive effect of fluorine.

Inner-shell electron spectroscopy can provide useful insights into such substituent effects, because core-ionization energies reflect the ability of a molecule to accept positive charge at a particular site. These ionization energies are, therefore, closely related to chemical properties that depend on this ability, such as proton affinities and rates for electrophilic attack, and it has been shown that carbon 1s ionization energies in substituted benzenes correlate well with Hammett σ parameters.[9] Some of the earliest studies of carbon 1s ionization energies involved the fluorobenzenes,[10-13] but in these studies it was impossible to do more than resolve the spectra into peaks due to carbons with attached fluorine atoms (CF) and those due to carbons with attached hydrogen atoms (CH). Thus, it was not possible to resolve contributions of inequivalent CH carbons from each other or those of inequivalent CF carbons. In addition, the energy calibration of these early experiments was not satisfactory. Thus, these investigations were able to map out only the gross features of the effects of fluorine substituents on a benzene ring. Now, however, with third-generation synchrotrons and high-resolution electron-energy analyzers, aided by advanced theoretical techniques, it is possible unambiguously to assign carbon 1s ionization energies to every carbon atom in the molecule.

Proton affinities provide another probe of the ability of a molecule to accept positive charge. Protonation and core ionization are similar in that they both involve adding a positive charge to a specific site in a molecule. Linear correlations between proton affinities and core-ionization energies are well-known,[14,15] and deviations from these correlations have been used to determine the site of protonation[15a,b] and to investigate geometric changes during protonation.[15c,d] Correlations using experimental proton affinities are, however, limited, because there is only one measured proton affinity per molecule, whereas core-ionization energies can be measured for each atom in the molecule. However, it has been found that proton affinities can be calculated with reasonable accuracy,[16] and using theoretically calculated proton affinities, we can consider a wider range of correlations between proton affinities and core-ionization energies.

We report here the results of high-resolution measurements of the carbon 1s ionization energies in 10 fluorine-substituted benzene molecules. In each case, we have been able to determine the contributions to the spectra from all of the inequivalent carbon atoms. These measurements, together with the previously reported ionization energy for benzene,[17] give us a total of 30 different carbon 1s ionization energies. It is found that these ionization energies can be described by a simple additivity model involving four parameters, one each for fluorine atoms that are located ipso, ortho, meta, or para to the site of ionization. Using theoretically calculated proton affinities for all 12 fluorobenzenes as well as benzene, we find that a similar model can describe the 39 proton affinities. Examining the correlations between core-ionization energies and proton affinities, we obtain insight into the electron-withdrawing power and π-electron donating ability of fluorine.

Experimental Procedures and Results

Measurements of the carbon 1s photoelectron spectra of 10 fluorine-substituted benzene molecules in the gas phase were carried out at beamline I411 at the MAX II synchrotron facility.[18] The samples were obtained from commercial sources and were of greater than 99% purity, except for 1,2-difluorobenzene (>96%), 1,4-difluorobenzene (>98%), and 1,3,5-trifluorobenzene (>97%). The photon energy was approximately 330 eV. The monochromator slits and settings on the electron spectrometer were chosen to give an overall instrumental resolution in the carbon 1s region of about 75 meV. Calibration measurements were made with each compound mixed with carbon dioxide, which provides a means to determine the resolution and the ionization-energy calibration for each measurement. The actual resolution determined from the carbon dioxide measurements varied between 66 and 82 meV for 8 of the 10 measurements. For the measurements of 1,2,4,5-tetrafluorobenzene and hexafluorobenzene the beamline was not performing optimally, and the resolution for the carbon dioxide spectra accompanying these molecules was found to be 95 and 99 meV, respectively.

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 (post-collision interaction (PCI)).[19] For the effects of PCI and lifetime broadening, we have used the shape given by eq 12 from van der Straten et al.[20] This

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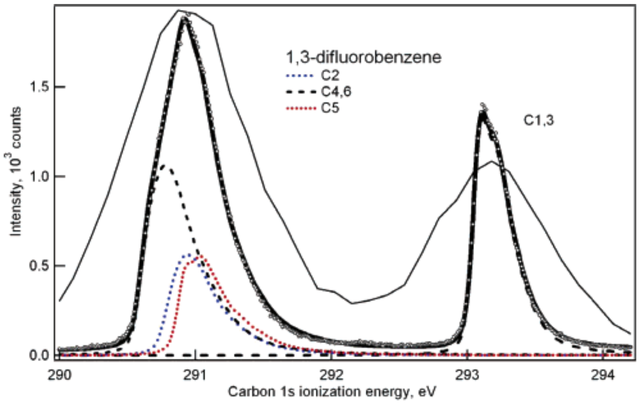

FIGURE 1. Carbon 1s photoelectron spectrum of 1,3-difluorobenzene. Open circles represent the data and the heavy solid line represents the least-squares fit to the data. The dashed and dotted lines represent the component spectra for the inequivalent carbons. The light solid line shows the data obtained by Banna and Shirley (ref 13).

is convoluted with a Gaussian function that represents the instrumental broadening. The carbon dioxide calibration spectrum has three closely spaced peaks, arising from the excitation of the symmetric stretching mode in the core-ionized molecule. These spectra are fit with the lifetime width and the relative positions and heights of the three peaks constrained to previously determined values.[21] 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.[22]

The fluorobenzene molecules have up to four chemically inequivalent carbon atoms. Where there are more than two, there are closely spaced peaks in the photoelectron spectra that must be resolved. 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 the predicted 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 PCI. For the lifetime width, we have used 100 meV, which is typical of the lifetime width found for a number of hydrocarbons.[23] 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.

A typical example of the data and the results of this fitting procedure are illustrated in Figure 1, where we show the carbon 1s photoelectron spectrum of 1,3-difluorobenzene. Spectra for the other molecules are shown in Supporting Information. 1,3-difluorobenzene has four inequivalent carbon atoms. Each of the carbons 1 and 3, which are equivalent, has an attached fluorine atom, and accordingly, these atoms have significantly higher ionization energies. They give rise to the peak at an ionization energy of 293.08 eV in Figure 1. It can be seen that the shape predicted for this peak agrees quite well with the observed spectrum. For the other carbon atoms, we expect three peaks with intensity ratios of 1/1/2; the peak at an average ionization energy of about 290.94 eV results from the ionization of these carbon atoms. For fitting this spectrum, we have constrained the two smaller peaks to have the same intensity. The order of the peaks in the spectrum is a priori unknown, and the fitting procedure gives different results, depending on what we assume as initial guesses for this order. The fit shown in Figure 1 gives the lowest value of χ^2. Visually, the fits obtained with the other choices show significant deviations between the data and the fit. In addition, the ordering of the peaks shown here is in agreement with that predicted by theory. (See below for additional comparisons between the experimental results and the theoretical predictions.) It is to be noted that this resolution of the spectrum into its components is possible only because theory gives a good representation of the vibrational profile.

TABLE 1. Ionization Energies of Fluorobenzenes (eV)

		I (adiabatic)	*I* (vertical)	Δ*I* (exp)	Δ*I* (theory)
benzene[a]		290.241	290.377	0.000	0.000
fluorobenzene	C_1	292.734	292.812	2.493	2.504
	$C_{2,6}$	290.505	290.692	0.264	0.285
	$C_{3,5}$	290.592	290.753	0.351	0.374
	C_4	290.375	290.558	0.134	0.164
1,2-difluorobenzene	$C_{1,2}$	293.002	293.129	2.761	2.784
	$C_{3,6}$	290.818	291.011	0.577	0.621
	$C_{4,5}$	290.712	290.901	0.471	0.510
1,3-difluorobenzene	$C_{1,3}$	293.082	293.181	2.841	2.885
	C_2	290.781	291.007	0.540	0.574
	$C_{4,6}$	290.624	290.843	0.383	0.445
	C_5	290.914	291.096	0.673	0.737
1,4-difluorobenzene	$C_{1,4}$	292.867	292.989	2.626	2.658
	$C_{2,3,5,6}$	290.838	291.039	0.597	0.649
1,2,3-trifluorobenzene	$C_{1,3}$	293.345	293.480	3.104	3.126
	C_2	293.228	293.402	2.987	3.061
	$C_{4,6}$	290.934	291.150	0.693	0.761
	C_5	291.046	291.251	0.805	0.853
1,3,5-trifluorobenzene	$C_{1,3,5}$	293.431	293.554	3.190	3.256
	$C_{2,4,6}$	290.895	291.155	0.654	0.729
1,2,3,4-tetrafluorobenzene	$C_{1,4}$	293.438	293.607	3.197	3.253
	$C_{2,3}$	293.592	293.765	3.351	3.399
	$C_{5,6}$	291.258	291.483	1.017	1.093
1,2,4,5-tetrafluorobenzene	$C_{1,2,4,5}$	293.453	293.625	3.212	3.272
	$C_{3,6}$	291.388	291.620	1.147	1.228
pentafluorobenzene	$C_{1,5}$	293.791	293.965	3.550	3.591
	$C_{2,4}$	293.672	293.878	3.431	3.517
	C_3	293.907	294.090	3.666	3.728
	C_6	291.493	291.745	1.252	1.344
hexafluorobenzene		293.992	294.199	3.751	3.829

[a] From ref 17.

In Figure 1, the thin line represents the previous best available carbon 1s spectrum for this molecule, measured by Banna and Shirley using X-rays from a sodium anode. It is apparent that synchrotron-based high-resolution measurements provide a significant improvement in the quality of the data.

The experimentally determined ionization energies for the molecules investigated here are listed in Table 1. Two columns of ionization energies are shown. One of these is for the adiabatic ionization energy, which corresponds to leaving the ionized molecule in its vibrational ground state. This is obtained from the fitting and calibration procedure described above. The other is for the vertical ionization energy, which corresponds to producing the ion with the same geometry as that of the neutral molecule. It is obtained by adding the average vibrational excitation, obtained from the theoretical calculations of the vibrational structure, to the adiabatic ionization energies. Also shown for reference is the previously measured value for benzene, as well as the adiabatic ionization energies relative to that of benzene.

The uncertainty in the absolute ionization energies is essentially that of the calibrant, CO_2, and is about 0.03 eV. The relative uncertainty is more difficult to estimate. Comparisons with theoretically calculated ionization energies and examination of the systematic variation of the ionization energies suggest that the relative

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uncertainty may be about 0.01 eV. To allow for the possibility that it is less than this, we quote the ionization energies to the nearest meV.

Theoretical Procedures and Comparisons between Theory and Experiment

Theoretical calculations include a prediction of the vibrational profiles, the relative carbon 1s ionization energies, and the proton affinities. For all of these, the Gaussian set of programs was used.[24]

Core Ionization. The procedures used for modeling the vibrational profiles are described elsewhere[25] and will not be repeated in detail here. 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.[26] For each molecule and for each core-ionized species, we calculate the optimized geometry, the vibrational frequencies, and the 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 with each other to produce intensities for the combination modes, and, hence, the full vibrational profile. This profile is used in the fitting procedure as described above. Calculations using this method have been found to overestimate by about 0.2 pm the shrinkage of an sp^2 CH bond that accompanies core ionization of the carbon to which the hydrogen is attached.[27] The calculated CH bond lengths have, therefore, been adjusted accordingly. See ref 25 for further details of the calculation of the vibrational structure.

The electronic structure calculations give energies for the various core-ionized species. Because these involve the approximation of the effective core potential, they cannot be viewed as absolute energies. However, from these we can obtain the predicted ionization energies relative to benzene. These are listed in Table 1. The root-mean-square (rms) deviation between the experimental and the theoretical shifts is 50 meV. However, this value is misleading, because a closer inspection of the data shows that theory systematically overestimates the shifts. Figure 2 illustrates the extent of agreement between experiment and theory. Here we have plotted the difference between the predicted and the measured ionization energies versus the measured ionization energies. Two features are apparent. First, the data fall into two groups, one for CH carbons and one for CF carbons. Second, the discrepancy between theory and experiment increases with the number of fluorines. The lines represent straight-line fits through the two groups. These have slopes of 6% for the CH carbons and 4% for the CF carbons. The rms deviation of the points from the lines is only 12 meV for the CH carbons and 17 meV for the CF carbons. These deviations (represented in Figure 2 as the length of the error bars) represent the combined effects of errors in the theory and in the experiment. Because these two kinds of errors are uncorrelated, we can conclude that they represent upper limits for the uncertainties in the relative experimental values. Moreover, there is good agreement between experiment and theory as to the order of the ionization energies. Thus, this comparison between theory and experiment supports the analysis we have done of the experimental spectra to obtain ionization energies.

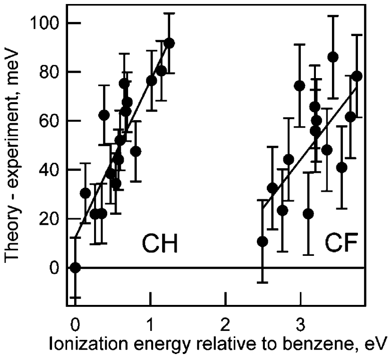

FIGURE 2. Difference between theoretically calculated and experimentally measured ionization energies plotted against the experimental ionization energy. All energies are relative to that of benzene. Solid lines show straight line fits to the two groups of data.

Proton Affinities. We are interested in correlations between proton affinities and carbon 1s ionization energies. For the latter, we have measurements for every position in the molecule, whereas for the former there are measurements 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 Maksić et al.[5,6] This involves finding the optimum geometry and zero-point corrections using a Hartree−Fock calculation and the 6-31G(d) basis set. With this geometry, the energy is then calculated with the MP2 method and the 6-31G-(d,p) basis set. The energy of the molecule is taken to be the MP2 energy plus the zero-point energy corrected by the empirical factor of 0.89.[28]

We have tested this method by comparing calculated and experimental proton affinities for benzene, 12 fluorobenzenes, and 5 methylbenzenes. For 1,2,4,5-tetrafluorobenzene and 1,2,3,5-tetrafluorobenzene, experiment and theory differ by 0.6 and 0.2 eV. It is possible that these two experimental values are in error.[29,30] Omitting these, we find that the rms difference between the experimental and the theoretical proton affinities is only 50 meV, which is significantly less than the suggested uncertainty of 90 meV in the experimental values. It appears that the method proposed by Maksić et al. provides an efficient method for calculating accurate proton affinities, and we have used this method to calculate all of the proton affinities discussed here.

Discussion

Core-Ionization Energies and Proton Affinities. Core ionization and protonation are electrically similar processes in

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[30] In ref 29, 1,2,4,5-tetrafluorobenzene is shown to have the same proton affinity as pentafluorobenzene, and 1,2,3,5-tetrafluorobenzene is shown to have the same proton affinity as 1,4-difluorobenzene. If we assign the value for pentafluorobenzene from ref 4 to 1,2,4,5-tetrafluorobenzene and the value for 1,4-difluorobenzene from ref 4 to 1,2,3,5-tetrafluorobenzene, then there is good agreement between experiment and theory for all 18 compounds.

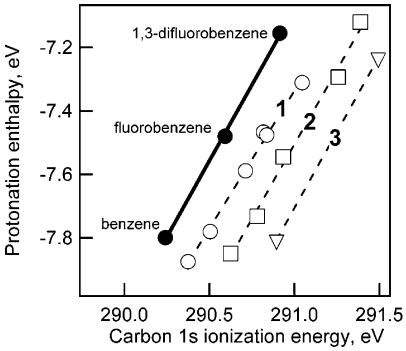

FIGURE 3. Protonation enthalpy plotted against the adiabatic carbon 1s ionization energy for benzene and nine fluorobenzenes. Solid points are for benzene and for fluorobenzenes when the site of protonation and ionization is meta to all substituents. Open points are for protonation and ionization at sites that are ortho and/or para to 1, 2, or 3 substituents. Lines represent fits of straight lines to the data.

that each involves adding a positive charge at a site in the molecule. For core ionization, the site is, in our case, the core of a carbon atom. For protonation, it is a position adjacent to a carbon atom. Although the absolute energies for these processes are quite different, we expect that the changes in energy as the result of changing a remote substituent might be similar. This expectation is indeed borne out; linear correlations between nitrogen and oxygen 1s ionization energies and enthalpies of protonation[31] are well-known.[14,15] The slopes of these linear correlations are typically of order 1, reflecting the similarity of the electrical effects in the two cases. Until recently, there has been little information on such correlations for carbon because of the difficulties of resolving carbon 1s photoelectron spectra for molecules containing several inequivalent carbon atoms. The few results that have been reported indicate that such linear correlations do exist for carbon but that the correlations are different for different classes of molecules.[32] Here we consider correlations for benzene and the fluorobenzenes that we have investigated. As noted above, we use theoretically calculated proton affinities, because experimental values are not available for all of the protonated species of interest.

In Figure 3 we have plotted the enthalpy of protonation for benzene and nine fluorobenzenes versus the adiabatic carbon 1s ionization energy (measured at the site of protonation). The solid points are for benzene and for two fluorobenzenes in which the substituents are all meta to the site of protonation and ionization: fluorobenzene protonated or ionized at C3 and 1,3-difluorobenzene protonated or ionized at C5. The open points are for fluorobenzenes with one or more substituents that are ortho and/or para to the site of protonation or ionization. The essential difference between the closed and the open points is that for the closed points there is expected to be little π donation of electrons from the substituent to the site of protonation or ionization, whereas for the open points such donation is a likely possibility.

The solid line in Figure 3 represents a least-squares fit of a straight line to the solid points. It is apparent that this line fits the points quite well. The slope of the line is 0.95, very close to 1, in keeping with the idea that protonation and core ionization are electrically similar. Thus, a single straight line fits the data for benzene, with no substituent, and for the fluorobenzenes that have an electron-withdrawing substituent meta to the site of interest. The open points, which represent molecules in which there is at least one substituent ortho or para to the site of protonation, fall below or to the right of the line for the closed points. Looking at the open points in more detail, we see that they fall into three families, each characterized by the number of fluorines that are ortho or para to the site of protonation or ionization. These groups are labeled 1, 2, and 3 in Figure 3, and we see that, in this order, each falls more to the right of or farther below the solid line. Thus, if there are fluorines ortho or para to the site of protonation or ionization, the enthalpy of protonation is more negative, and the proton affinity is greater than we would expect on the basis of the correlation when no ortho or para substituents are present.

A reasonable interpretation of the patterns that are apparent in Figure 3 is that we are seeing the effects of fluorine both as an electron-withdrawing substituent and as a π-electron donor. Focusing on the solid line and the points for benzene, fluorobenzene, and 1,3-difluorobenzene, we see the electron-withdrawing effect. Each added fluorine makes the benzene ring more positive. As a result, the enthalpy of protonation and the carbon 1s ionization energy both are shifted to more positive values. If, however, the fluorine is ortho or para to the site of protonation or ionization, then we have the possibility of π-electron donation, which will make the site less positive than it would be for a meta substituent. The net effect of this π donation is that the enthalpy of protonation and the ionization energy are shifted to more negative values when the substituent is ortho or para than when it is meta. This conclusion is not surprising. What is noteworthy, however, is the successive displacements of groups 1, 2, and 3 from each other and from the line for meta substituents. This displacement implies that π donation has an effect on the proton affinities that is larger than its effect on the ionization energies. We will return to this after we consider an approach that makes it possible to summarize all of the data rather compactly.

Additivity Relationships. In Table 1 are listed 29 shifts of carbon 1s ionization energies, relative to the ionization energy in benzene. These represent the combined effects of a variety of combinations of fluorine substituents ipso, ortho, meta, and para to the site of ionization. To find a simple way to summarize these results, we consider whether they can be described by an additivity relationship in which each ionization-energy shift is described as the sum of shifts due to the fluorine atoms that are at the various positions around the ring. The equivalent mathematical expression is $\Delta I = \sum_i n_i \alpha_i$, where ΔI is the shift in ionization energy relative to benzene, n_i is the number of fluorine atoms at position i (ipso, ortho, meta, or para to the site of ionization), and α_i is a parameter characteristic of the substituent and the position. Making a least-squares fit to the data with this expression, we find that the data are well-described by such a relationship: $R^2 = 0.9998$, with an rms deviation of 20 meV.[33] Thus, the measurements can be described well with a set of four substituent parameters, one for each position. The parameters derived in this way are listed in Table 2.

The use of an additivity model to describe the enthalpies of protonation has been explored by Maksić et al.[5,6,34] Applying

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[31] The proton affinity is the negative of the enthalpy of protonation.

[32] Thomas, T. D.; Sæthre, K. J.; Børve, K. J.; Gundersen, M.; Kukk, E. *J. Phys. Chem. A* **2005**, *109*, 5085−5092.

[33] We have also considered a quadratic expression, which gives $R^2 = 0.99996$ and rms of 11 meV, but the quadratic coefficients are small and at the limit of significance.

[34] Eckert-Maksić, M.; Klessinger, M.; Maksić, Z. B. *Chem.—Eur. J.* **1996**, *2*, 1251−1257.

TABLE 2. Substituent Parameters for Carbon 1s Ionization Energies and Enthalpies of Protonation (eV)[a]

		ionization energies	enthalpies of protonation
α	ipso	2.504 (7)	0.854 (6)
	ortho	0.249 (4)	0.014 (4)
	meta	0.332 (4)	0.312 (3)
	para	0.120 (7)	−0.072 (6)
β	ortho-ortho		0.019 (4)
γ	ipso-ortho		−0.115 (4)
	ipso-para		−0.062 (7)
	meta−para		−0.027 (4)

[a] Uncertainties in the last decimal place are shown in parentheses. See the text for the definition of parameters

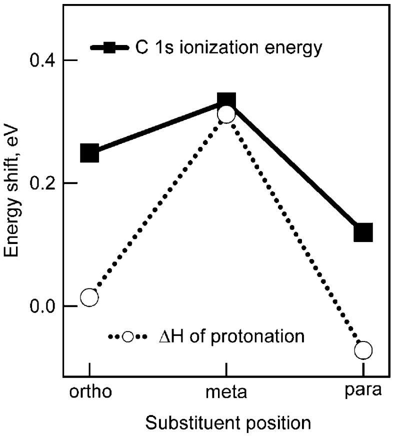

FIGURE 4. Effect of fluorine on the carbon 1s ionization energy (squares) and enthalpy of protonation (circles) relative to benzene.

this idea to the fluorobenzenes, we find that, although the simple expression used above gives a reasonable description of these enthalpies ($R^2 = 0.98$ and rms deviation = 63 meV), a much better description is obtained if we include quadratic terms that express the interaction of the substituents with each other. The appropriate expression is $\Delta H - \Delta H_{\text{benzene}} = \sum_i n_i[\alpha_i + \beta_i(n_i - 1)] + \sum_{j>i}\gamma_{ij}n_in_j$. The coefficient β exists only for ortho and meta substituents because these are the only positions where there can be two substituents of the same type. In practice, it turns out that β_{meta} and three of the γ values are negligible. When these are ignored, this expression, with 8 parameters, describes 39 proton affinities in the fluorobenzenes with $R^2 = 0.9994$ and an rms deviation of 12 meV. The parameters derived from this procedure are listed in Table 2.

Looking first at the quadratic terms, we note that the significant ones are those involving the addition of a proton to a fluorinated carbon (ipso) when there is another fluorine either ortho or para to the site of protonation. This may reflect π-electron donation by the spectator fluorine atom. There is also a small effect when there are two fluorine atoms ortho to the site of protonation.

Of more interest are the linear coefficients. The coefficients for each position, one for ionization and one for protonation, are summarized in a compact way in Figure 4. Here the solid squares represent the coefficients for carbon 1s ionization, and the open circles represent the coefficients for protonation. First to note in Figure 4 is that all but one of the shifts relative to benzene are positive, reflecting the electron-withdrawing power of the fluorine. Second is that the shifts for the meta position, where there is no contribution from π-electron donation, are essentially the same for the two processes, about 0.3 eV. Finally, we see that the shifts at the ortho and para positions, where π-electron donation may play a role, depend strongly on which process we are considering. In particular, we note in Figure 4 that the coefficients for ortho and para protonation are quite different from those for ortho and para core ionization. These differences lead to the series of more or less equally spaced parallel lines for the correlation between the enthalpy of protonation and the ionization energy seen in Figure 3.

We can understand the trends seen in Figure 4 by recognizing contributions from three sources: the electrostatic potential produced in the ground state of the molecule by the polar CF group, the modification of the potential by π-electron donation from fluorine to the ortho and para sites in the ground state, and the effect of additional π-electron donation in response to the positive charge that results from either core ionization or protonation. We will see that the major difference between the core-ionization energies and the energies of protonation arises because of differences in the effectiveness of different sites as π acceptors. In the following discussion, we consider each of these contributions.

The dominant feature of the fluorobenzenes is electron withdrawal by the fluorine from the carbon atom to which it is attached, as indicated by the large positive shifts (2.5 eV) in carbon 1s ionization energies for these carbons. An earlier analysis suggested that the amount of charge transferred in fluorobenzene is about 0.2 e.[10] To obtain a better picture of this effect, we have calculated the potentials in fluorobenzene in the direction perpendicular to the ring and originating at the ortho, meta, and para carbons.[35] Specifically, we look at the difference between these potentials in fluorobenzene and the equivalent potential in benzene, thus illustrating the change made by the substituent. We find that these can be described asymptotically by a model that puts a charge of −0.25 e at the fluorine and +0.25 e at the ipso carbon. This corresponds to a dipole moment of 1.6 D, in excellent agreement with the experimental value of 1.60 D. This dipole produces potentials of about 1.1, 0.48, and 0.40 V at the ortho, meta, and para positions, respectively. This picture is similar to that drawn by Wiberg and Rablen,[8] who concluded that “halogens act mainly via polarization of the C−X σ bond.”

The electrostatic potential due to the CF dipole is modified by π-electron donation from the fluorine to the ortho and para positions. We can see this effect by looking at the π-electron density (relative to that in benzene) in a direction perpendicular to the ring and originating at each of the carbon atoms, which is illustrated in Figure 5. This density difference reflects π-electron donation from fluorine to the ring. We see, as expected, that there is little net effect of the fluorine on the density at the meta carbon, but that there is an increase in density at the ortho and para carbons.[36] This increase in electron density leads directly to a less-positive potential in the vicinity of the ortho and para carbons. Indirectly, the negative charges at the ortho and para positions also lead to a less-positive potential at the meta position.

It is to be noted in Figure 5 that the amount of charge transferred is small, but it is also to be noted that the transfer of a small amount of charge can lead to chemically significant

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(35) Potentials and charge densities were calculated using the basis set described in the text. The calculations were done at the geometry determined in the B3LYP optimizations. The MP2 densities were used in calculating the potentials, and Hartree−Fock π wave functions were used in calculating the π-electron densities.

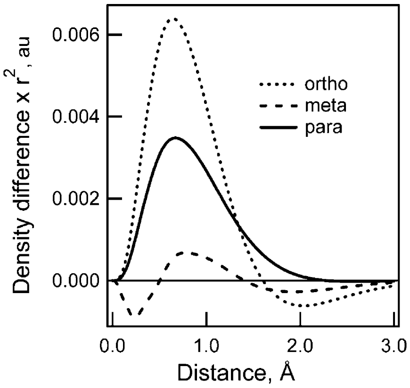

FIGURE 5. π-Electron radial density difference (fluorobenzene − benzene) in a direction perpendicular to the molecular plane and originating at the ortho, meta, and para carbons.

energy changes. A shift of 0.01 e from the fluorine to the para carbon would lead to a shift of 0.14 V in the electrostatic potential at a distance of 1 Å from the para carbon and, hence, of 0.14 eV in the potential energy of a unit charge at that position. This corresponds to 3 kcal/mol, which is significant on the chemical scale, corresponding to a change of about 300 in an equilibrium constant or rate constant.

More significant than the amount of charge transferred is its effect on the energy changes of interest: core-ionization energies and proton affinities. For the carbon 1s ionization energies, the net effect of the charge distribution can be estimated either from the potential at the carbon nucleus or from the orbital energies of a Hartree−Fock calculation (Koopmans theorem). Because both of these methods have their drawbacks, we use instead the extended Koopmans theorem suggested by Børve and Thomas.[37] With this approach, the electrostatic contributions to the carbon 1s ionization energies in fluorobenzene (relative to benzene) are 0.30 eV (ortho), 0.39 eV (meta), and 0.22 eV (para). First, it is apparent that the total electrostatic contributions, especially at the ortho and para positions, as indicated by these values, are considerably less than those that are attributable to the dipole of the CF bond (1.1, 0.48, and 0.40 eV, respectively, as indicated above). Second, these values are similar to the substituent coefficients for core ionization listed in Table 2. This similarity indicates that the relative core-ionization energies are largely determined by the charge distribution in the initial state of the molecule.

To estimate the effect of the electrostatic potential on the protonation energy, we use the potential 1.15 Å above each carbon atom. Calculations show that this is approximately where a proton would add if the benzene or fluorobenzene molecule is forced to remain planar. The potential energy of a proton at this point reflects the energy of placing a proton there, without any electronic or geometric relaxation of the system. These energies are calculated to be 0.29 eV (ortho), 0.29 eV (meta), and 0.19 eV (para) for fluorobenzene relative to benzene. We note that the value for meta is very close to the substituent coefficient for protonation at the meta position, 0.312 eV, suggesting that the relative energy for meta protonation is determined primarily by the initial-state charge distribution. By contrast, the substituent coefficients for ortho and para protonation, 0.014 and −0.072 eV, are considerably less than the potential energies, suggesting that there is a considerable effect of geometric and electronic relaxation on the protonation energy.

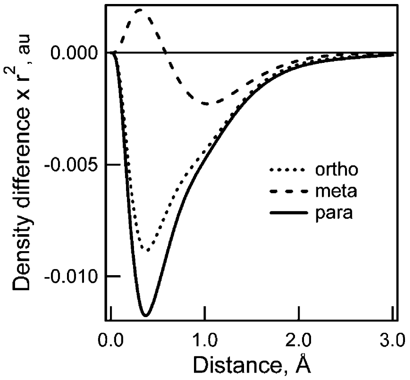

FIGURE 6. π-Electron radial density at the fluorine in protonated fluorobenzene (relative to fluorobenzene) in a direction perpendicular to the plane of the molecule for different sites of protonation.

This relaxation energy arises because of the π-acceptor ability of the protons at the site of protonation. In the equilibrium protonated molecule, there is one hydrogen above the molecular plane and one below. The s orbitals on these hydrogens combine to give one orbital of σ symmetry and one of π symmetry. This new π orbital allows the π electrons to delocalize to the site of the added proton, thus lowering the energy of the protonated state and increasing the proton affinity. No such orbital is available for core ionization (or for any process that leaves the molecule planar, such as acidity of benzoic acid), and, as a result, the influence of relaxation through the π system is much less in such cases. As an example, we have calculated the enthalpy changes to form protonated fluorobenzene with all of the protons confined to the molecular plane. In this case, the hydrogen atoms are not good π acceptors, and, in agreement with this, the relative proton affinities for the three possible sites of protonation are about the same as the relative ionization energies.

The effect of the protons as efficient π acceptors can be seen in Figure 6, where we have plotted the π-electron density in protonated fluorobenzene (relative to that in fluorobenzene) in a direction perpendicular to the plane and originating at the fluorine. These three curves show the change in π-electron density at the fluorine when a proton is added at different sites. We note that the relative density at the ortho and para positions is negative, indicating that protonation leads to a withdrawal of π electrons from the fluorine. Second, we note that there is little effect when protonation takes place at the meta position, in keeping with views based on resonance structures. Finally, we see that, although there is a slightly bigger effect for para protonation than for ortho, the two effects are comparable.

It is useful to compare these conclusions with those reached by Wiberg and Rablen.[8] First, they concluded that the effect of fluorine in fluorobenzene is dominated by the polarization of the CF bond and the “preference for the para position in fluorobenzene may result from the need to add the proton to a position that would not be disfavored by the σ-electron

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(36) The positive density difference at the para carbon shown in Figure 5 is in contrast to the results reported by Wiberg and Rablen (ref 8), which showed no enhancement of density at the para position of fluorobenzene. This apparent contradiction may arise because Wiberg and Rablen used a contour level of 0.002 e/au^3 to define the surfaces that they displayed. In our calculations it is found that the highest density difference for the electrons on the para carbon is just above this level. The difference between their results and ours may lie in the small details of the calculations that are made apparent by their choice of this contour.

(37) Børve, K. J.; Thomas, T. D. *J. Electron Spectrosc. Relat. Phenom.* **2000**, *107*, 155−161.

withdrawal by fluorine." This picture is certainly partially correct but cannot be completely so, because it cannot account for the observation that the proton affinity of fluorobenzene is greater than that of benzene and that the rates of some electrophilic reactions are greater at the para position of fluorobenzene than those for benzene.[3] Also, as we have noted above, the electrostatic potential at the ortho and para positions of fluorobenzene is significantly less positive than that arising from the CF dipole. Second, they concluded that "the only cases in which fluorine was found to be a π donor are those where a positive charge may be stabilized, such as protonated fluorobenzene." We have seen above that the effectiveness of the added proton as a π acceptor greatly enhances the ability of fluorine as a π donor. However, added positive charge by itself is not sufficient to bring about this degree of enhancement; the effect of π donation is much smaller for core ionization and planar protonation than it is for formation of the protonated molecule with hydrogen atoms above and below the molecular plane. Thus, there appear to be two aspects of π donation by fluorine, a relatively small but significant donation in the neutral molecule and a larger one when an effective π acceptor is added to the molecule.

Finally, it is interesting to note that the additivity parameters for carbon 1s ionization, $\alpha_p = 0.120$ eV and $\alpha_m = 0.332$ eV, have about the same relationship to one another as the corresponding Hammett parameters $\sigma_p = 0.15$ and $\sigma_m = 0.34$, indicating that the carbon 1s ionization energies respond to the same factors that affect many other chemical properties. For protonation, on the other hand, the corresponding parameters, -0.072 and 0.312 eV, correlate better with σ_p^+ (-0.07)[38] and σ_m. While it is not surprising that the protonation energy correlates with σ_p^+, it *is* surprising that the core-ionization energy does not because both involve adding a positive charge to the molecule. The difference can be understood in terms of the foregoing discussion; the protonated species provides a better π-electron acceptor than does the core-ionized species.

Conclusions

The carbon 1s ionization energies and protonation enthalpies of the fluorobenzenes (relative to those of benzene) can be summarized accurately and compactly by a linear additivity relationship that assigns a substituent constant for each position in the ring. The shift in ionization energy or proton affinity is thus given by a sum of contributions from all of the fluorine substituents that are attached to the ring. Closely related to this additivity relationship are the linear correlations that are observed between the core-ionization energies and the enthalpies of protonation.

For substitution at the meta position, both the ionization energies and the protonation enthalpies are shifted from the values for benzene by about +0.3 eV. This shift can be understood as arising primarily from the potential produced at the meta carbon by the dipole of the CF bond. This potential is secondarily affected by π-electron donation from the fluorine to the ortho and para carbons.

By contrast, the shifts at the ortho and para positions are not the same for ionization as those for protonation. The differences reflect the different role played in the two processes by π-electron donation in response to the added positive charge. Because protonation involves hydrogen atoms symmetrically above and below the plane of the benzene ring, there is an expanded π system that does not exist in the core-ionized species. As a result, the hydrogens on the protonated molecule form an efficient π-electron acceptor, and the protonation energies are more strongly affected by fluorination than are the core-ionization energies.

When the effects of ortho and para substituents are compared, both protonation and carbon 1s ionization are more favorable at the para position than at the ortho position by about 0.1 eV (0.13 eV for ionization and 0.09 eV for protonation). This difference arises from the initial-state charge distribution; the contribution from π-electron donation, though significant, is essentially the same for protonation at the two different sites.

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Supporting Information Available: Experimental photoelectron spectra and fits. This material is available free of charge via the Internet at http://pubs.acs.org.

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(38) Exner, O. In *Correlation Analysis in Chemistry*; Chapman, M. B., Shorter, J., Eds.; Plenum: New York, 1975; pp 439−546.