

the classical and bridged structures for a given $\text{Me}_3\text{Si}\cdot\text{X}^+$. MO calculations suggest that this is the case for $\text{H}_3\text{Si}\cdot\text{C}_2\text{H}_4^+$.⁵ Another possibility might be that in comparing bridged with bridged and nonbridged with nonbridged a fortuitous cancellation of factors leaves only the methyl groups contributing to the stabilization energies. This then implies that two methyl substituents in, for example, the bridged $\text{Me}_3\text{Si}\cdot\text{TB}^+$ are equally as stabilizing as the single methyl in $\text{Me}_3\text{Si}\cdot\text{P}^+$. High-level MO calculations on these compounds would help in the elucidation of this topic. If bridged structures are present in $\text{Me}_3\text{Si}\cdot\text{X}^+$ ($\text{X} = \text{E}, \text{TB}, \text{MB}$), then the term β -silicon effect may not be the most appropriate. The silyl group in these ions has a considerable stabilizing influence, but it may not be in a position β to the carbenium carbon.

The entropy changes for the formation of $\text{Me}_3\text{Si}\text{-alkene}^+$ are unusually large; in fact, they are some of the largest that have been measured in the gas phase for bimolecular association reactions. Condensation reactions with covalent products usually have entropy changes in the range 30–40 cal/K·mol.²⁶ The significantly larger value of 49 ± 5 cal/K·mol was determined for the association of Me_3C^+ and benzene.²⁷ It was suggested that the large changes in translational entropy, because of the relatively massive particles involved, together with the considerable loss in external rotational freedom accounted for the majority of the decrease. Similar considerations should apply to the present case.

The calculated entropy changes shown in Table I are obtained by considering changes due to translation and external rotation. No changes in entropy due to vibration or internal rotation are considered with the exception that the Me_3Si group in the complex is assumed to behave as a classical free rotor. Moments of inertia are calculated assuming classical geometries for the complexes with $\text{C-Si} = 2.047 \text{ \AA}$ and a tetrahedral Si-C-C angle. Calculations are performed as described in ref 28. Because of the approximation employed, the excellent agreement between ex-

periment and calculation is obviously fortuitous, but the calculations do show that the large experimental entropy changes are consistent with expectations. In particular, there is no obvious evidence for a restriction of internal rotations of methyl groups in the complexes, which would lead to even larger decreases in entropy for the association reactions than are experimentally observed. It might be appropriate to point out here that if the entropy changes had not been so large, measurements of the temperature coefficients of the equilibrium constants for the more strongly bound alkenes would have been impossible at temperatures below 600 K.

Conclusion

The considerable stabilization afforded simple carbenium ions by a β -silicon has been quantified. Although the absolute values are somewhat uncertain due to uncertainties in the thermochemistry of silicon-containing species, especially Me_3Si^+ , the values obtained are consistent with previously published, calculated values. The results also show a consistent decrease of ~ 10 kcal/mol in the stabilization energy with each successive methyl group substituted on the carbenium carbon. The data show that even the very stable Me_3C^+ is stabilized by a further 28 kcal/mol by a Me_3Si substituent in the β -position in $\text{Me}_3\text{SiCH}_2\text{CMe}_2^+$.

MO calculations on $\text{Me}_3\text{Si}\text{-alkene}^+$ adducts such as those described in this study would be useful not only in helping elucidate the structures of the ions but also in providing insight into liquid-phase solvolytic experiments, which invariably involve molecules with substituents α to the proposed carbenium carbon. Solvent effects do attenuate the β -silicon effect in solution, but even increases in reaction rates of the order of 10^{10} observed for the extrusion of Me_3SiOH from 4-*tert*-butyl-2-trimethylcyclohexanol⁴ can be accommodated by the very large effect demonstrated by our data.

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Substituent Effects on the Electron Affinities of Perfluorobenzenes $\text{C}_6\text{F}_5\text{X}$

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Abstract: The electron attachment free energy and enthalpy ΔG_a° and ΔH_a° corresponding to the reaction $e^- + \text{B} = \text{B}^-$ was determined by measuring electron-transfer equilibria, $\text{A}^- + \text{B} = \text{A} + \text{B}^-$, with a pulsed electron high-pressure mass spectrometer (PHPMS), involving compounds A whose attachment energies are known. Values were obtained for $\text{C}_6\text{F}_5\text{X}$ ($\text{X} = \text{F}, \text{Cl}, \text{C}_6\text{F}_5, \text{CF}_3, \text{COCH}_3, \text{CHO}, \text{CN}, \text{Br}, \text{I}, \text{NO}_2, \text{COC}_6\text{F}_5$). The substituent effects for the σ -acceptor/ π acceptor substituents were found to be very similar to those observed for the electron attachment energies of substituted nitrobenzenes: $\text{NO}_2\text{C}_6\text{H}_4\text{X}$. This correspondence shows that the extra electron in both systems enters a π^* -orbital. The substituent effects for the σ -acceptor/ π -donor substituents, $\text{X} = \text{Cl}, \text{Br}, \text{I}$, were found to be very much larger for the $\text{C}_6\text{F}_5\text{X}$, relative to the nitrobenzenes, and to increase greatly in the order $\text{F}, \text{Cl}, \text{Br}, \text{I}$. These results indicate that the extra electron enters a σ^* -orbital, which is localized on the C-X atoms.

Recent work^{1a} from this laboratory reported electron affinities of perfluorobenzene C_6F_6 and substituted perfluorobenzenes $\text{C}_6\text{F}_5\text{X}$ determined via gas-phase measurements of electron-transfer

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equilibria with a pulsed electron high-pressure mass spectrometer (PHPMS).^{1b} The electron affinity of C_6F_6 was found to be $\text{EA}(\text{C}_6\text{F}_6) = 0.52 \pm 0.1 \text{ eV}^{1a}$ and is thus some 1.7 eV higher than that of benzene, $\text{EA}(\text{C}_6\text{H}_6) = -1.15 \text{ eV}^{2}$. Since it is known that fluorine stabilizes σ -orbitals more than π -orbitals, it has been suggested³ that multiple fluorine substitution may lead to the singly

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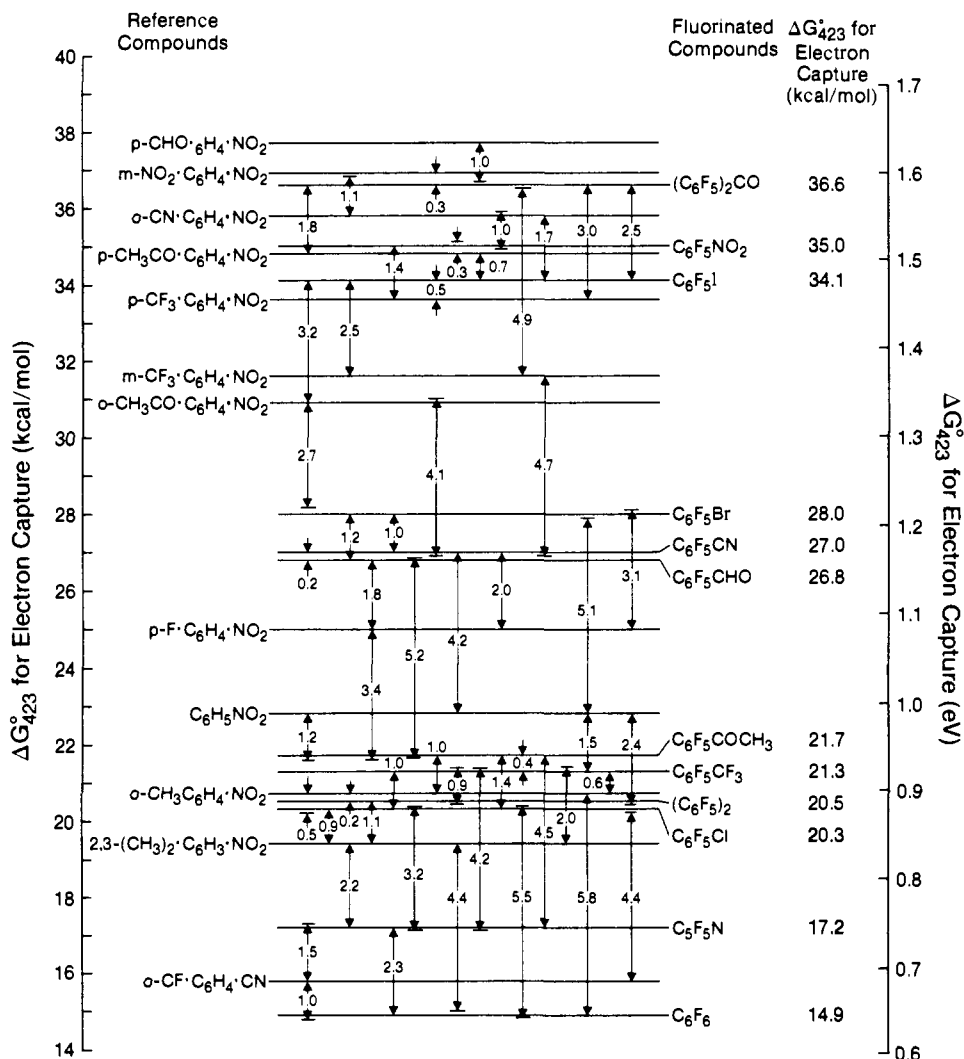


Figure 1. Scale of electron capture free energies ΔG_a° based on measurement of electron-transfer equilibria (1): $A^- + B = A + B^-$. Values shown between double arrows correspond to ΔG_1° (at 423 K).

occupied molecular orbital (SOMO) of the negative ion being not a π^* -type orbital, as is the case for benzene, but a σ^* -type orbital. Experimentally measured electron spin resonance (ESR) coupling constants of C₆F₆⁻ in inert matrices indicate that C₆F₆⁻ is not planar and have been considered as evidence that the nonplanarity is due to a σ^* -character of the SOMO.^{3,4}

Our earlier determinations^{1a} included the electron affinities of only a few substituted perfluorobenzenes C₆F₅X, namely X = CF₃, COCH₃, and CN. These substituents caused electron affinity changes that were parallel to those observed for substituted nitrobenzenes: NO₂C₆H₄X. The observed correlation between the substituent effects for the perfluorobenzenes and nitrobenzenes was taken as strong evidence^{1a} that the SOMO of the perfluorobenzene anions is of π^* -character, since it is known that the SOMO of the nitrobenzene anions is a π^* -orbital.

The present work provides a much wider range of electron affinities of C₆F₅X (X = F, Cl, Br, I, CF₃, COCH₃, CHO, CN, NO₂). These more extensive data permit a more detailed examination of the substituent effects to be made. The results have turned out to be very illuminating and, to us, initially very surprising.

Method of Measurement and Results

The electron affinities were obtained from measurements of electron-transfer equilibria (1) with a pulsed electron high-pressure mass

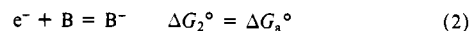


spectrometer (PHPMs), which has been described.^{1b}

The conditions used were similar to those in the earlier work^{1a} and need not be described again.

The procedures by which electron affinities are obtained from electron-transfer equilibria measurements are included in a recent review^{1c} so that only a very brief outline will be given here. Determination of K_1 leads to $\Delta G_1^\circ = -RT \ln K_1$. When a series of compounds are used, a scale of ΔG_1° values, obtained at the same temperature (150 °C), is constructed. The scale obtained in the present work is shown in Figure 1. All the ΔG_1° values shown were obtained in the present work. The scale includes a number of multiple (redundant) thermodynamic cycles, and inspection shows that these are generally consistent to ~0.1 kcal/mol. This is significantly better than that of the earlier more limited work.^{1a} Problems had been encountered in the earlier work due to reactions of the perfluorobenzene radical anions with traces of O₂, and in the present work vigorous measures in sample preparation and gas-handling plant procedures^{1b} were taken in order to exclude traces of oxygen. Only with C₆F₅NO₂ was an intense ion (OC₆F₄NO₂⁻) observed, which could be attributed to the presence of O₂.

The scale in Figure 1 includes a number of reference compounds, predominantly substituted nitrobenzenes, whose electron attachment free energies ΔG_a° (2) were determined in earlier work.^{1c} The primary



standard used^{1c,d} was SO₂, whose ΔG_a° could be evaluated from literature data.⁵ The usual stationary electron convention (neglect of translation energy and entropy of the electron) was applied.^{1d} Due to the similarity

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Table I. Electron Attachment Energies and Electron Affinities of Perfluorobenzenes and Perfluoropyridine^a

compd		$-\Delta G_a^0$ ($-\Delta H_a^0$) ^d		
decafluorobenzophenone	(C ₆ F ₅) ₂ CO	36.6	37.1 ^b	35.1
pentafluoronitrobenzene	C ₆ F ₅ NO ₂	35.0		33.5
pentafluoroiodobenzene	C ₆ F ₅ I	34.1		32.6
pentafluorobromobenzene	C ₆ F ₅ Br	28.0		26.5
pentafluorobenzonitrile	C ₆ F ₅ CN	27.0	27.0 ^b	25.5 (25) ^b
pentafluorobenzaldehyde	C ₆ F ₅ CHO	26.8		25.3
pentafluoroacetophenone	C ₆ F ₅ COCH ₃	21.7	21.7 ^b	20.2
octafluorotoluene	C ₆ F ₅ CF ₃	21.3	21.6 ^b	19.8
decafluorobiphenyl	(C ₆ F ₅) ₂	20.5	20.9 ^b	19.0
pentafluorochlorobenzene	C ₆ F ₅ Cl	20.3		18.8
pentafluoropyridine	C ₅ F ₅ N	17.2		15.7
hexafluorobenzene	C ₆ F ₆	14.9	14.8 ^b	(12.0) ^b
pentafluorobenzene	C ₆ F ₅ H	c		

^aData from scale of electron-transfer equilibria free energy changes ΔG_1^0 shown in Figure 1. ΔG_a^0 and ΔH_a^0 are free energy change at 150 °C and enthalpy change for gas-phase reaction $e^- + B = B^-$ (stationary electron convention). Values are in kilocalories per mole. Estimated errors: $\Delta G_a^0, \pm 1$ kcal/mol; $\Delta H_a^0, \pm 2.5$ kcal/mol. ^bPrevious work from this laboratory.^{1a} ^cAll attempts to detect the radical anion of pentafluorobenzene failed. Rapid thermal electron detachment from C₆F₅H⁻ was probably responsible and since this ion could not be detected even at room temperature a $-\Delta G_a^0 < 10$ kcal/mol is indicated. A very rough estimate can be obtained with the assumption that each F atom introduced into C₆H₆ leads to the same decrease of $-\Delta G_a^0$. The difference between C₆H₆ and C₆F₆ is ~ 38.4 kcal/mol and $38.4/6 = 6.4$ kcal/mol. Using $-\Delta G_a^0(\text{C}_6\text{F}_6) = 14.9$ kcal/mol, one obtains $-\Delta G_a^0(\text{C}_6\text{F}_5\text{H}) \approx 8.6$ kcal/mol. ^dThe ΔH_a^0 for the substituted perfluorobenzenes were estimated from ΔG_a^0 by assuming $\Delta S_a^0 = +3.5$ cal/deg-mol, on the basis of ΔS_a^0 measured in previous work.^{1a}

of the geometries and internal motions of SO₂ and SO₂⁻, the adiabatic electron affinity,⁵ the electron attachment enthalpy,^{1d} and free energy^{1d} are very close as shown in (4).

$$\text{SO}_2^-: \text{EA} = \frac{25.3}{0 \text{ K}} \quad -\Delta H_a = \frac{25.2}{423 \text{ K}} \\ -\Delta G_a^0 = \frac{26.1}{423 \text{ K}} \quad (\text{kcal/mol}) \quad (4)$$

It should be noted that, within the approximation illustrated in (4), the $-\Delta H_a$ values correspond to the adiabatic electron affinities, since the equilibrium method involves high populations of the most stable anions, i.e., the vibrational ground-state anions.

The ΔG_a^0 at 423 K for the perfluorobenzenes obtained from Figure 1 are summarized in Table I. Also given in Table I are the ΔG_a^0 values obtained in the earlier study. The agreement observed is within ~ 0.1 kcal/mol, except for (C₆F₅)₂CO where the difference is 0.5 kcal/mol.

The temperature dependence of several electron-transfer equilibria (1) involving C₆F₆ was determined in the earlier work^{1a} and via van't Hoff plots led to ΔH_1^0 and ΔS_1^0 values. These, when connected to the primary standard, SO₂, led to electron attachment values for C₆F₆, $\Delta H_a^0 = -12$ kcal/mol and $\Delta S_a^0 = 7$ cal/deg-mol. It was assumed that the positive entropy change is due to loss of symmetry and loosening of normal vibrations on formation of the negative ion. The entropy change for the lower symmetry number C₆F₅CN was lower, $\Delta S_a = 4$ cal/deg-mol. The estimated ΔH_a for the perfluorobenzenes given in Table I were obtained from the ΔG_a^0 of Figure 1 with the simple assumption that ΔS_a^0 of all C₆F₅X is equal to $+3.5$ cal/deg-mol.

Discussion

Substituent Effects on the EAs of C₆F₅X Molecules and Other Substituted Aromatic Compounds. The magnitudes of electron affinities of a related series of compounds are often discussed on the basis of the energies of the LUMO's of the neutral molecules. The assumption is made that the electron enters the LUMO, which thus becomes the singly occupied molecular orbital SOMO. Therefore, the lower the energy of the LUMO, the higher will be the EA of the molecule (Koopmans' theorem).

The frontier orbital perturbation molecular orbital (PMO) theory applied by A. Pross and L. Radom⁶ to even electron systems is very well suited also for qualitative predictions of the relative energies of the LUMO's of molecules and relative electron affinities. This approach was used recently in a discussion⁷ of the

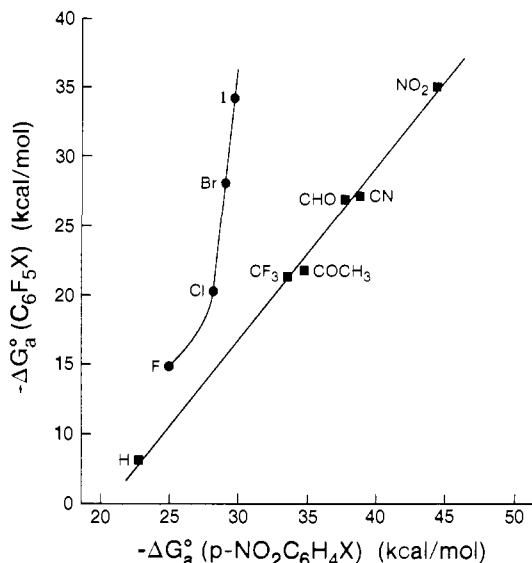


Figure 2. Plot of electron capture free energies ΔG_a^0 for substituted perfluorobenzenes and substituted nitrobenzenes: ■, σ -acceptor/ π -acceptor substituents; ●, σ -acceptor/ π -donor substituents. Value for $-\Delta G_a^0(\text{C}_6\text{F}_5\text{H}) \approx 8$ kcal/mol is an arbitrary estimate; see Table I.

electron affinities of substituted nitrobenzenes NO₂C₆H₄X and will be used also in the present considerations.

The substituents included in this study may be classified into two categories:⁸ (i) σ -acceptor/ π -acceptor substituents (NO₂, CHO, COCH₃, CN, CF₃); (ii) σ -acceptor/ π -donor substituents (F, Cl, Br, I). In Figure 2 a comparison is made of the EAs ($-\Delta G_a^0$) of the C₆F₅X molecules versus the EAs ($-\Delta G_a^0$) of the corresponding para-substituted nitrobenzenes. It is seen that with σ -acceptor/ π -acceptor substituents there is a straight line relationship between the two sets of EAs with a high degree of correlation (coefficient of correlation 0.998) and a slope slightly greater than one (1.25). It is clear that these substituents influence the EAs of C₆F₅X and p-NO₂C₆H₄X molecules in a very similar manner. In contrast, with σ -acceptor/ π -donor substituents, there is a dramatic divergence between the two sets of EAs, indicating that π -donor substituents influence the EAs of C₆F₅X and p-NO₂C₆H₄X molecules by distinctly different mechanisms. For this reason, the two substituent classes will be discussed separately.

(i) σ -Acceptor/ π -Acceptor Substituents. With frontier orbital PMO the energy of the LUMO of a benzene carrying a σ -acceptor/ π -acceptor substituent is derived from the interaction of the LUMO of the substituent and the LUMO of the benzene, the two being considered initially as separate entities.⁶ This interaction leads to the LUMO of the substituted benzene, which is of lower energy than either of the above LUMO's. The energy difference between the lower of the above LUMO's and the new LUMO is the stabilization energy. The stabilization energy is the frontier orbital counterpart of the delocalization or resonance energy.⁶⁻⁸ Further stabilization of the LUMO is induced by a "deshielding" effect⁶ where electrons in the aromatic system are drawn to the substituent due to the local dipole produced by the substituent, which generally contains electronegative atoms. The deshielding effect is the PMO counterpart of the "field-inductive" effect.⁸ Both of these effects stabilize the LUMO and increase the EAs of molecules bearing σ -acceptor/ π -acceptor substituents. These effects have been discussed in more detail in the examination of substituent effects on the EAs of substituted nitrobenzenes.⁷ Given the similar influences of σ -acceptor/ π -acceptor substituents on the EAs of C₆F₅X and p-NO₂C₆H₄X molecules demonstrated by Figure 2, much of the previous discussion⁷ is directly applicable to the C₆F₅X molecules and need not be repeated. The important point to note is that electron capture by the C₆F₅X molecules

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Table II. Substituent Coefficients Determined by Multiple Regression Fits to $-\delta\Delta G_a^\circ$ Values for Substituted Benzenes, Para-Substituted Benzonitriles, and Para-Substituted Nitrobenzenes to (5)

substituted syst	substituent coeff		coeff of correlatn
	ρ_R	ρ_F	
C_6H_5X	149.6 ± 14.6	31.2 ± 4.9	0.996
$p\text{-CNC}_6\text{H}_4X$	89.4 ± 16.1	20.9 ± 5.1	0.982
$p\text{-NO}_2C_6\text{H}_4X$	46.0 ± 5.0	19.0 ± 1.6	0.996

bearing σ -acceptor/ π -acceptor substituents most likely occurs into a π^* -LUMO, as happens with $p\text{-NO}_2C_6\text{H}_4X$ molecules.

In a manner similar to that described for the substituted nitrobenzenes⁷ and following the example of Taft and co-workers,^{8,9} the relative EAs of the C_6F_5X molecules bearing σ -acceptor/ π -acceptor substituents were fitted to (5) by a multiple regression

$$-\delta\Delta G_a^\circ = \rho_R\sigma_R + \rho_F\sigma_F \quad (5)$$

procedure. In (5), $-\delta\Delta G_a^\circ = 0$ kcal/mol for $X = H$, σ_R , and σ_F are system-independent substituent parameters, which have been compiled by Taft et al.^{8,9} and which rank the resonance (R) and field (F) capacities, respectively, of the various substituents; ρ_R and ρ_F are system-dependent substituent coefficients, which give a measure of the magnitude of resonance and field effects on $-\Delta G_a^\circ$ in a given system such as C_6F_5X or $p\text{-NO}_2C_6\text{H}_4X$ molecules. From the multiple regression procedure, it was determined that the EAs of the C_6F_5X molecules relative to $-\delta\Delta G_a^\circ = 0$ kcal/mol for C_6F_5H may be described with a high degree of correlation (coefficient of correlation 0.989) by (6). This rela-

$$-\delta\Delta G_a^\circ = (55.9 \pm 10.2)\sigma_R + (23.5 \pm 3.2)\sigma_F \quad (6)$$

tionship confirms that the influence of σ -acceptor/ π -acceptor substituents on the EAs of C_6F_5X molecules may be accounted for well in terms of the established resonance and field effects of the substituents. In this system, the interaction between the substituent LUMO and the aromatic LUMO is the primary determinant of the EAs, but field stabilization of the LUMO is also substantial.

It is informative to compare the ρ_R and ρ_F values obtained from the above analysis with the substituent coefficients obtained from a similar analysis of the EAs of other substituted benzene systems. Table II lists the ρ_R and ρ_F values determined from the EAs of substituted benzenes,^{1,2} para-substituted benzonitriles,^{1,11} and para-substituted nitrobenzenes^{1,7} bearing σ -acceptor/ π -acceptor substituents. While the uncertainties in ρ_R and ρ_F are somewhat large in some cases due to small data sets, up to $\pm 25\%$ in the worst instances, the important trends are still clearly evident. In particular, it is seen that ρ_R is quite system dependent, varying from 150 in substituted benzenes to 46 in para-substituted nitrobenzenes, whereas ρ_F is much less system dependent.

The variation of ρ_R amongst the four series of substituted aromatic molecules is inversely related to the EA of the unsubstituted ($X = H$) member of each series, as shown in Figure 3. Thus, ρ_R is highest for the series where the unsubstituted molecule has the lowest EA, i.e., the monosubstituted benzenes. This trend may be understood readily in terms of the stabilization energy expected from the interaction of the substituent LUMOs and the aromatic LUMO, the latter staying constant in a given series. Schematic representation is shown in Figure 4, where the nitro group has been chosen to represent a typical π -acceptor substituent and $-\Delta G_a^\circ$ has been taken as an approximate guide to the energy levels of the various orbitals. This figure shows that the nitro group LUMO lies at a much lower energy than the LUMO of benzene, so that when a nitro group is added to benzene and the two LUMOs are combined, the nitro group will make the dominant contribution to the new nitrobenzene LUMO. That is, much of

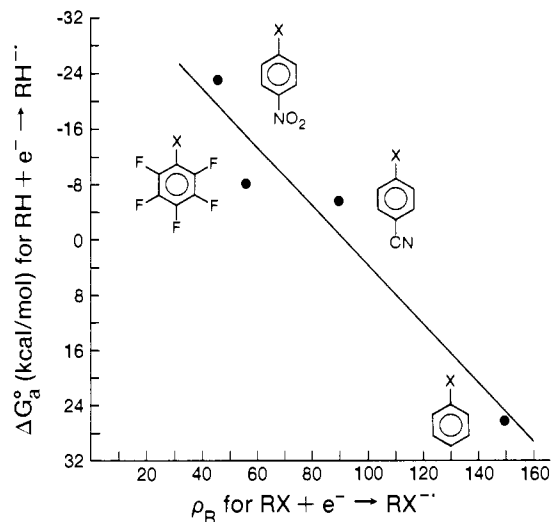


Figure 3. Values of ΔG_a° for substituted perfluorobenzenes, nitrobenzenes, cyanobenzene, and benzene versus resonance parameter, ρ_R , obtained with (5).

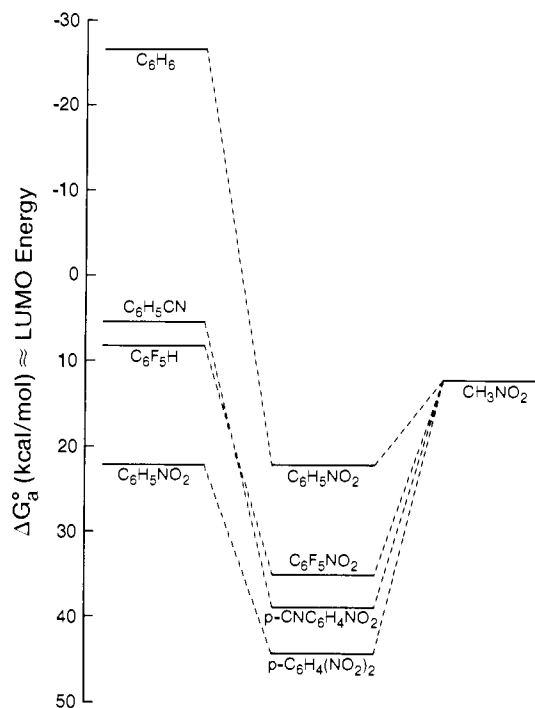


Figure 4. Schematic plot of LUMO energies of aromatic compounds (on the left side) and NO_2 substituent (on the right side) and new LUMO (middle) resulting from interaction of aromatic LUMO and substituent LUMO. Energy for NO_2 substituent LUMO approximated by EA of CH_3NO_2 (Kearlarle¹⁶).

the LUMO will be located on the nitro group.

Upon passing from benzene to pentafluorobenzene, benzonitrile, and nitrobenzene, the aromatic LUMO becomes progressively more stable and therefore makes a progressively greater contribution to the combined LUMO in $C_6F_5\text{NO}_2$, $p\text{-CNC}_6\text{H}_4\text{NO}_2$, and $p\text{-NO}_2C_6\text{H}_4\text{NO}_2$, respectively. Conversely, the contribution of the added nitro substituent to the combined LUMO will decrease as the aromatic LUMO becomes more stable. The same trend will occur with the other π -acceptor substituents as well. In other words, the resonance effects of the substituents will be attenuated as the aromatic LUMO becomes more stable, and this is reflected in the decreasing ρ_R values. This type of effect has been observed previously with substituted naphthalenes and anthracenes.¹²

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In contrast, the field effects of the substituents on the LUMO are attenuated only moderately upon passing from substituted benzenes to para-substituted nitrobenzenes. Indeed, ρ_F is almost the same for the C_6F_5X , $p\text{-CNC}_6H_4X$, and $p\text{-NO}_2C_6H_4X$ series. This is a consequence of the similar size of these molecules. The field effect of the substituents is primarily a through-space electrostatic effect, which diminishes as a function of distance from the substituent.⁸ Hence, as each of these series of molecules are of comparable size, the field effects of the substituents are also comparable from series to series. The largest field effect is observed with the substituted benzenes because the substituent interacts directly with the aromatic LUMO. Conversely, in the para-substituted nitrobenzenes, much of the LUMO is located on the nitro group away from the substituent, and hence the lowest field effects are observed with this series.

It is the different rates of attenuation of resonance and field effects that is responsible for reversals in the EA of cyano- and acetyl-substituted systems, which has been noted previously.¹² The cyano group is a moderate-resonance, high-field substituent ($\sigma_R = 0.10$, $\sigma_F = 0.60$) whereas the acetyl group is a high-resonance, moderate-field substituent ($\sigma_R = 0.17$, $\sigma_F = 0.26$).^{3,4} Thus, when attached to systems such as benzene with a high-lying LUMO where resonance effects are most pronounced, the acetyl-substituted molecule has a higher EA than the cyano-substituted molecule. However, upon passing to systems with a more stable LUMO where the resonance effect of the substituents is attenuated, the field effect becomes more important and the cyano group becomes the more stabilizing substituent: $-\Delta G_a^\circ$ (kcal/mol); C_6H_5CN (5.5), $C_6H_5COOCH_3$ (7.7), $p\text{-NO}_2C_6H_4CN$ (38.7), $p\text{-NO}_2C_6H_4COCH_3$ (34.8).

It is noteworthy that Taft and co-workers have identified qualitatively similar trends in the effects of substituents on the gas-phase acidities of aromatic acids such as phenols and anilines.⁹

The causes for the close similarities between the substituent effects on the even-electron systems studied by Taft and co-workers and the odd-electron radical ions resulting from electron capture were examined from the standpoint of PMO theory in our recent discussion of the electron affinities of substituted nitrobenzenes.⁷

(ii) σ -Acceptor/ π -Donor Substituents. The substituents in this group are characterized by the presence of a lone pair of electrons, which may be donated to aromatic systems. It has been shown^{6,7} that when attached to nitrobenzene, these substituents destabilize the LUMO by donation of the lone-pair electrons to the aromatic π -system, especially when located ortho or para to the nitro group, but also stabilize the LUMO through their field effect. Depending on whether the resonance donation or the field withdrawal of electrons is dominant, these substituents may decrease or increase the EA relative to nitrobenzene.^{1,7} It is apparent from the plot of $-\Delta G_a^\circ(C_6F_5X)$ versus $-\Delta G_a^\circ(p\text{-NO}_2C_6H_4X)$ in Figure 2 that halogen substituents *do not* influence the EAs of C_6F_5X molecules in the same way. In $p\text{-NO}_2C_6H_4X$, replacement of $X = F$ with I leads to a small increase in $-\Delta G_a^\circ$ of 4.6 kcal/mol,^{7,11} whereas the same substitution in C_6H_5X leads to a giant $-\Delta G_a^\circ$ increase of 19.2 kcal/mol.

It has been shown, using ESR spectroscopy,^{3,13} that electron capture by the perhalogenated C_6F_5X compounds (i.e., $X = F, Cl, Br, I$) in *solid matrices* at *low temperature* (77 K) leads to addition of an electron into a σ^* -orbital rather than a π^* -orbital. This produces a σ^* -anion where the electron is *localized* on the C-X bond.¹³ Theoretical support for this has been provided by semiempirical (MNDO-UHF) calculations,¹⁴ indicating that although the LUMO of the C_6F_5X ($X = Cl, Br, I$) molecules is

a π^* -orbital, upon electron capture a reorganization of the orbitals occurs causing the added electron to reside in a σ^* -SOMO strongly localized on the C-X bond. This theoretical study also indicated that the SOMO density at X decreases in the order $I > Br > Cl$. The reliability of the MNDO-UHF results may be questioned, and it would be very interesting to await predictions based on ab initio calculations with large basis sets. Nevertheless, the calculations,¹⁴ taken together with the unequivocal ESR results¹³ for the localized character of the SOMO of $C_6F_5X^-$ in the C-X bonds, are strong indications that the "anomalous" substituent effects of the π -donor substituents observed in the present work (Figure 2) are due to a localization of the SOMO in the C-X bond. An important component in the stabilization of these localized negative ions will be the polarizability of X, which increases greatly from F to I.

When we recall that the dihalogens ($F_2, Cl_2, Br_2, I_2, ClI, BrI$) all have relatively high electron affinities¹⁵ of ~ 2.5 eV where the SOMO is σ^* , a certain analogy may be seen with the electron affinities of the C_6F_5X molecules where the C-X carbon heavily "desielded" by the neighboring F atoms acts as a quasi halogen atom.

The position of C_6F_5X ($X = F$) in the substituent effect plot (Figure 2) does not provide a clear indication whether the $C_6F_6^-$ SOMO is of π^* - or σ^* -character. The spin coupling constants obtained in the ESR studies⁴ of $C_6F_6^-$ in condensed-phase matrices indicated a SOMO that was delocalized over a nonplanar $C_6F_6^-$. Symons⁴ assumed a σ^* -orbital and a nonplanar carbon structure similar to the chair form of cyclohexane. However, later theoretical work by Shchegoleva et al.¹⁶ pointed out that a planar carbon structure with C-F bonds bent in and out of the plane fits the coupling constants better. Such a structure can be considered to indicate a π^* -SOMO for $C_6F_6^-$. Bending of the C-F bonds reduces greatly the destabilization of the negative ion due to π -donation while the stabilizing σ -withdrawal is reduced only a little, and this leads to a more stable π^* -SOMO. Since bending of these bonds amounts to a π/σ mixing, the π^* -SOMO will acquire some σ^* -character.

The low EA(C_6F_6) ≈ 12 kcal/mol (see Table I) obtained from the electron-transfer equilibria provides at least a partial explanation for the "anomalous temperature dependence" of the electron attachment coefficient, β , of C_6F_6 reported by Adams et al.¹⁷ These authors observed that β decreases rapidly above 350 K, while β is found to be temperature independent for other compounds. However, the authors assumed that EA(C_6F_6) ≈ 41 kcal/mol on the basis of the then available literature values.¹⁸ Furthermore, it is obvious from the preceding discussion of the geometry of $C_6F_6^-$ that the vertical electron affinity will be appreciably lower than the adiabatic value equal to 12 kcal/mol. It is possible that the temperature dependence of β is somehow related with these low electron affinities. Adams et al.¹⁷ were unable to observe electron attachment to C_6F_5H . This result is in line with the lower EA of C_6F_5H implied by the present work (see Figure 2 and footnote c in Table I) and the fact that $C_6F_5H^-$ could not be observed in the present work also.

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