agreement with the calculated C_6H_6 distribution.

The polar angle distribution of C_6H_6 molecules ejected in the PDMS calculation is similar to that from the SIMS simulation (Figure 8). Both are peaked at normal ejection ($\theta = 0°$). Experimental PDMS distributions of atomic species have been fit to the $\cos^n \theta$ form where $n \approx 2.5 \pm 1$.[10] The distributions in Figure 8 follow this same general behavior, especially the C_6H_6 distribution. It is difficult, however, to uniquely determine the exponent n since the curvature of the distribution depends on the polar angle resolution of the collection scheme. The Ni polar distribution reflects the enhanced, relative to the SIMS results, normal ejection due to the forward scattering process. The peak at $\theta = 45°$ is partly due to the single-crystal nature of the substrate. As a result this curve does not follow the $\cos^n \theta$ relationship quite as well as the benzene distribution. As in the SIMS case the NiC_6H_6 clusters form from a rearrangement process of ejecting Ni atoms and C_6H_6 molecules,[18] thus their polar distribution reflects to a large degree the Ni-atom distribution. Inclusion of the image force correction results in the peak of the Ni and NiC_6H_6 distributions occurring at a larger angle. The C_6H_6 distribution, however, is not significantly altered.

Conclusions

The classical dynamics procedure has been used to model the desorption of atoms and organic molecules from surfaces due to heavy particle bombardment from the backside of the sample. For the desorption of organic molecules the predicted mass spectrum is similar to that obtained from calculations where the incident particle bombards from the frontside. The energy distribution of the C_6H_6 molecules from both calculations is Maxwell–Boltzmann-like, in agreement with the experiment, even though a thermal equilibrium is not established. The PDMS Ni energy distributions, however, exhibit a higher energy tail than those from the SIMS simulation. The azimuthal angular distributions of the Ni atoms are distinctly different from the two calculations.

We find collisional mechanisms which are important for the desorption process in this PDMS simulation which are not important in SIMS simulations. Most of the differences can be traced to conservation of linear momentum. We believe that because of the differences in the important collision mechanisms for desorption it may be possible for larger molecules to be desorbed in the PDMS experiments than in SIMS or FABMS experiments. If a molecule is bonded to a substrate at several places, desorption may require a simultaneous (within $\sim 10^{-14}$–10^{-13} s) severing of most of the bonds. It is more difficult to obtain coherent upward motion of atoms subsequent to frontside bombardment than to obtain this in-phase atomic motion from an energetic particle bombarding from the backside. The calculations presented here also offer a number of experimentally testable predictions, for example, the energy and angular distributions of monoelemental single crystals, which should help to conclusively elucidate the important desorption mechanism using PDMS.

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Nature of π-Electron-Transfer Effects in Organic Systems with Varying π-Electron Demand

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Abstract: Calculations using an ab initio molecular orbital basis (STO-3G or 4-31G) for a series of substituted probe molecules covering a wide range of π-electron demand have revealed a complex pattern of substituent resonance response to varying electron demand. The results support the suggested amphielectronic behavior of π-acceptor substituents such as CF_3, CHO, CN, and NO_2. In spite of these complexities, the resonance response patterns of individual substituents attached to aromatic molecules can be reasonably approximated by certain bilinear relationships. Comparison of calculations with experimental data for gas-phase pyridinium ion and phenol acidities offers confirmation of the recently defined $\sigma_{R}{}^{+}{}_{(g)}$ and $\sigma_{R}{}^{-}{}_{(g)}$ scales. For π-acceptor substituents (+R) in electron-rich systems, the $\sigma_{R}{}^{-}{}_{(g)}$ scale is shown to extend all the way to XCH_2^-, i.e., for the gas-phase acidities of substituted methanes. Evidence is provided for leveling effects of strong π-donor substituents (−R) under strong electron demand, e.g., for both XCH_2^+ cations and XCH_2^- anions.

It has long been recognized that the electronic effect of a substituent depends to a certain extent upon the electron demand in the system to which it is attached. In the context of the Hammett equation, this has been handled by defining different σ constant scales for systems with different electron demand (e.g., σ, σ^0, σ^+, σ^-, etc.).[2]

An alternative approach to substituent effects is to divide the total electronic effect of a substituent into field/inductive and resonance contributions, that is, to use a dual substituent parameter

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(DSP) approach.[3a] While there has been a continuing controversy concerning the relative merits of single- and dual-substituent parameter scales,[3] we strongly prefer the latter approach. The simplest DSP scale is the $\mathcal{F},\mathcal{R}$ scale of Swain and Lupton.[4] This scale assumes that both field/inductive and resonance effects vary linearly with changes in the electronic nature of the system, allowing the effect of electron demand to be estimated from the weighting factors in the DSP equation 1 (where P is the experimental parameter being correlated).[4]

$$P = P_0 + f\mathcal{F} + r\mathcal{R} \quad (1)$$

However, it is now generally recognized that this approach is inadequate,[3a] particularly because resonance response does not appear to vary colinearly as demand is changed.

The most commonly used DSP approach is that of Ehrenson, Brownlee, and Taft.[5] This assumes a linear variation of field/inductive effects with changes in the electronic nature of the system (with a resultant fixed σ_I scale) but a nonlinear variation of resonance effects. The latter variation is accommodated by having four resonance scales ($\sigma_R{}^0$, σ_R(BA), $\sigma_R{}^+$, and $\sigma_R{}^-$) for systems with different π-electron demand.[5] However, this is obviously only an approximation to the true situation since there must be a continuum of resonance scales.

Two basic modifications of the Taft equation have been suggested to generate a variable resonance scale. The first is to use a bilinear resonance scale with different weighting factors ($\rho_R{}^+$ and $\rho_R{}^-$) for π acceptors and π donors.[6] One equation of this type is the most recent form of the Tsuno–Yukawa relationship[7] (eq 2). A similar equation has been suggested by Weeks and Horāk on the basis of $\sigma_R{}^+$ and $\sigma_R{}^-$.[8]

$$P = P_0 + \rho_I\sigma_I + \rho_\pi{}^+\sigma_\pi{}^+ \text{ and } \rho_\pi{}^-\sigma_\pi{}^- \quad (2)$$

The second approach is to use a nonlinear resonance scale. For example, Brownlee, Taft, and co-workers have suggested that $\bar{\sigma}_R$ scales can be generated from $\sigma_R{}^0$ by using eq 3 (where ϵ is an electron demand parameter[9]).

$$\bar{\sigma}_R = \sigma_R{}^0/(1 - \epsilon\sigma_R{}^0) \quad (3)$$

Happer and Wright have suggested a more complex exponential equation for predicting $\bar{\sigma}_R$ values.[10] Finally, More O'Ferrall has proposed a quadratic version of the original Hammett equation to allow for nonlinear variation in substituent effects.[11]

One fundamental problem with all of these approaches is that there is no solid experimental or theoretical evidence concerning the precise nature of the nonlinear dependence of substituent resonance effects upon π-electron demand. Another problem is that all of these approaches assume that substituents can be rigorously divided into π-electron donors or acceptors, regardless of electron demand (although the Tsuno–Yukawa approach does specifically recognize the amphielectronic nature of the phenyl group[7]). However, recent experimental[12] and theoretical evidence[13,14] has shown that the cyano group and possibly the formyl and trifluoromethyl groups can stabilize adjacent carbocation centers by resonance, indicating that these groups can become π-electron donors in systems with strong electron demand.

Ab initio molecular orbital calculations have proved to be of great value for interpreting substituent interactions in aromatic systems.[15] Consequently, we have carried out a series of these calculations for a representative set of substituents in a variety of systems. These systems were chosen to provide general information about the dependence of substituent resonance effects over a wide range in π demand. In addition, it was hoped to obtain more specific information about the ability of individual substituents to act as both π-electron acceptors and donors, i.e., to show amphielectronic resonance effects. The results of the investigation are reported below.

Results and Discussion

As an initial survey, calculations were performed for a set of ten substituents, X, with a wide range of electronic characteristics (NH_2 (planar), OCH_3, OH, F, CH_3, $CH{=}CH_2$, CF_3, CN, CHO, and NO_2) for 13 systems (including 9 aromatic systems) ranging in π-electron demand from $XCH_2{}^-$ to $XCH_2{}^+$.[16] Calculations were first performed at the STO-3G level by using standard substituent geometries[17] and fixed geometries for the probe systems (see Details of Calculations for a full description of probe geometries). Such fixed geometry STO-3G calculations have already proved to be very useful for predicting electronic substituent effects in aromatic systems[15,18–27] and have been shown to predict the major trends in substituent effects on proton-transfer energies.[15,21–27] The actual π-electron transfer between the substituent and the probe molecule, Σq_π, was used as a measure of substituent resonance effects, since it has been previously shown that Σq_π is approximately linearly related to σ_R scales in aromatic systems.[18,20,21] In order to separate rigorously σ and π effects and estimate Σq_π accurately, we have used, as far as possible, planar probe molecules. In particular, although the $CH_2{}^-$ group is undoubtedly pyramidal in many $XC_6H_4CH_2{}^-$ and $XCH_2{}^-$ derivatives,[15,28] we have carried out calculations for the planar derivatives. This seemed reasonable since we were more interested in examining specific model systems with strong π-donor capabilities than in precisely reproducing substituent effects in benzyl and methyl anions. Finally, as a measure of π-electron demand in each system, we used the π charge density, $\Delta q_\pi{}^H$ ($\equiv 1 - q_\pi{}^H$) in the parent compound (X = H) at the carbon to which the substituent is attached. The tendency for substituent π-electron interactions should be governed by the π electron density at this carbon. In

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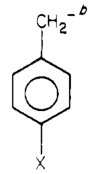
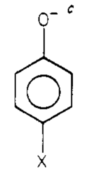
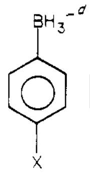
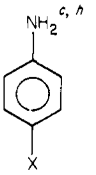
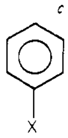
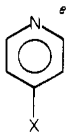
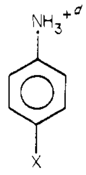
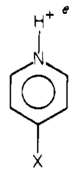
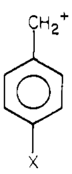
Table I. π-Electron-Transfer Parameters, Σq_π ($\times 10^3$),[a] for a Variety of Substituted Probe Molecules Estimated by Using Standard Geometries and Minimal Basis Set (STO-3G) ab Initio Molecular Orbital Calculations

X	XCH_2^-	$XCH{=}CHCH_2^-$	 [b]	 [c]	 [d]	 [c, h]	 [c]	 [e]	 [d]	 [e]	 [f]	$XCH{=}CHCH_2^+$	XCH_2^+
NH_2[b]	0	−42		−66	−88	−108	−120	−123	−162	−225	−284	−364	−514
OCH_3	+6	−36	−57	−58	*[j]		−105	−108		−197	−230	−306	−489
OH	0		−59	−60	−78	−92	−102	−104	−130	−174	−216		−427
F	0	−32	−48	−49	−63	−71	−80	−80	−95	−121	−147	−188	−303
CH_3	+52	+22	+8	+5	*	−6	−8	−10	*	−26	−32	−52	−102
$CH{=}CH_2$	+386	+231	+119[k]		+43[l]		0		−37[m]	−88[n]	−129[o]	−223	−373
CF_3	+107	+59	+36	+34	*	+15	+11	+9	*	−4	−7	−18	−52
CN	+268	+202	+103	+95	+52	+33	+22	+16	0	−27	−42	−109	−226
CHO	+394	+249	+153	+140	+73	+46	+32	+24	+7	−21	−34	−70	−176
NO_2	+383	+257	+169	+150	+72	+44	+31	+22	+14	−15	−22	−50	−137
Δq_π^{H}	−1.000	−0.481	−0.250	−0.236	−0.090	−0.057	+0.000	+0.018	+0.075	+0.201	+0.295	+0.467	+1.00

[a] Negative sign indicates electron donation by the substituent to the probe molecule. [b] Energies and geometries in ref 25. [c] Energies and geometries in ref 15. [d] Energies and geometries in ref 27. [e] Energies and geometries in ref 26. [f] Energies and geometries in ref 22b. [g] Coplanar NH_2. [h] Calculation not reported. [j] Nonplanar substituent and probe molecule. [k] $E = -341.617\,85$. [l] $E = -329.270\,71$. [m] $E = -358.571\,77$. [n] $E = -320.023\,87$. [o] $E = -341.602\,99$.

Table II. π-Electron-Transfer Parameters and Optimized C–X Bond Lengths for STO-3G Calculations with C–X Bond-Length Optimization

X	XCH_2^+	$XCH{=}CHCH_2^+$	$XC_6H_4CH_2^+$	XC_6H_5	$XC_6H_4CH_2^-$	$XCH{=}CHCH_2^-$	XCH_2^-
$NH_{2(p)}$[d]	−566[a]	−434	−284	−115	−53	−26	0
	(1.294)[b]	(1.321)	(1.357)	(1.408)	(1.449)	(1.481)	(1.526)
OH	−486	−334	−202	−90	−45	−23	0
	(1.276)	(1.310)	(1.349)	(1.390)	(1.422)	(1.444)	(1.475)
F	−353	−223	−134	−70	−39	−21	0
	(1.264)	(1.299)	(1.330)	(1.356)	(1.379)	(1.393)	(1.413)
$CH{=}CH_2$	−427	−243	−148	0	+105	+255	+430
	(1.394)	(1.436)	(1.494)	(1.513)	(1.491)	(1.431)	(1.383)
CH_3	−113	−58	−29	−8	+8	+23	+53
	(1.494)	(1.515)	(1.527)	(1.533)	(1.536)	(1.531)	(1.515)
CF_3	−29	−15	−4	+10	+32	+63	+120
	(1.633)	(1.598)	(1.578)	(1.560)	(1.548)	(1.522)	(1.480)
CN	−262	−105	−33	+21	+104	+200	+326
	(1.397)	(1.436)	(1.457)	(1.463)	(1.443)	(1.406)	(1.362)
CHO	−155	−77	−20	+27	+142	+274	+435
	(1.495)	(1.507)	(1.525)	(1.516)	(1.479)	(1.434)	(1.390)
NO_2	−76	−36	−10	+19	+130	+253	+398
	(1.522)	(1.513)	(1.514)	(1.506)	(1.472)	(1.427)	(1.380)
$\Delta q_\pi^{\text{H}c}$	+1.000	+0.533	+0.241	0.000	−0.250	−0.534	−1.000

[a] Σq_π ($\times 10^3$). A negative sign indicates π-electron donation by the substituent. [b] Optimum C–X bond length (Å). [c] $\Delta q_\pi^{\text{H}} = 1 - q_\pi^{\text{H}}$ where q_π^{H} is the π-electron density in the parent compound of the carbon to which the substituent is attached. [d] NH_2 is coplanar for all systems.

support of this view, there is a generally good relationship between the electron-demand parameter, ε, defined by Brownlee et al. and the ^{13}C chemical shift of the corresponding carbon in the parent compound for a series of para-disubstituted benzenes whose chemical shifts have been analyzed by using eq 3.[9,29]

The values of Σq_π from STO-3G calculations using standard geometries for different substituents for each of the different systems having different Δq_π^{H} values are summarized in Table I.

A factor that could affect the data in Table I is the use of standardized, fixed substituent geometries. To check this point, we performed a partial substituent geometry optimization at the STO-3G level for seven representative systems. In each case, the C–X bond length was optimized. In the case of $p\text{-}HOC_6H_4CH_2^+$ and $p\text{-}NCC_6H_4CH_2^+$, the $C\text{–}CH_2^+$ bond length was also reoptimized after C–X bond optimization to see if this bond was significantly affected by the geometry of the para substituent. However, the maximum bond-length change was 0.003 Å. Consequently, optimization of this bond was considered unnecessary. Furthermore, even total optimization of the aromatic ring geometry in several monosubstituted benzenes gave values of Σq_π that agreed within 1×10^{-3} electrons with those obtained with only C–X bond optimization.[30a] Consequently, this partial substituent geometry optimization should eliminate almost all of the errors associated with the use of fixed substituent geometries.

Values of Σq_π and optimized bond lengths that were obtained are summarized in Table II. A number of the π-electron-transfer parameters are significantly altered from the values in Table I, reflecting significant variations of C–X bond lengths from standard values, particularly in systems where Δq_π^{H} differs significantly from zero.[30b] Accordingly, we have based our major conclusions on the results given in Table II. In Figure 1, values of Σq_π are

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(30) (a) von Nagy-Felsobuki, E.; Topsom, R. D.; Pollack, S.; Taft, R. W. *J. Mol. Struct.* **1982**, *88*, 255. The actual value of Σq_π for OH, F, CN, and NO_2 derivatives are respectively −0.090, −0.071, +0.021, and +0.020. (b) Note in particular that the optimized bond length of NH_2 varies by almost 0.1 Å in going from the benzyl cation to anion while the bond length of NO_2 exceeds the standard value (1.40 Å) in all but $^+CH_2NO_2$. It would appear to be necessary to optimize substituent bond lengths in future theoretical investigations of substituent effects.

Table III. Comparison of Total π-Electron-Transfer between the Substituent and the Probe Molecule, Σq_π (×10³), for Substituted Methyl and Allylic Cations and Anions at the STO-3G and 4-31G Levels using Standard Geometries

	XCH_2^+		$XCH{=}CHCH_2^+$		XCH_2^-		$XCH{=}CHCH_2^-$	
X	STO-3G	4-31G	STO-3G	4-31G	STO-3G	4-31G	STO-3G	4-31G
$NH_{2(p)}$	−514[a]	−471	−364	−332	0	−15	−42	−40
OCH_3	−489	−372	−306	−232	+6	+18	−36	−20
F	−303	−194	−188	−122	0	−16	−32	−32
CH_3	−102	−103	−52	−57	+52	+59	+22	+26
CF_3	+52	+34	−18	−17	+107	+126	+59	+88
CN	−226	−168	−109	−59	+268	+238	+202	+170
CHO	−176	−96	−70	−25	+394	+412	+249	+312
NO_2	−137	−80	−50	−6	+383	+505	+257	+303
Δq_π^H	+1.000	+1.000	0.467	0.487	−1.000	−1.000	−0.481	−0.507

[a] Σq_π (×10³). A negative sign indicates π-electron donation from the substituent to the probe molecule.

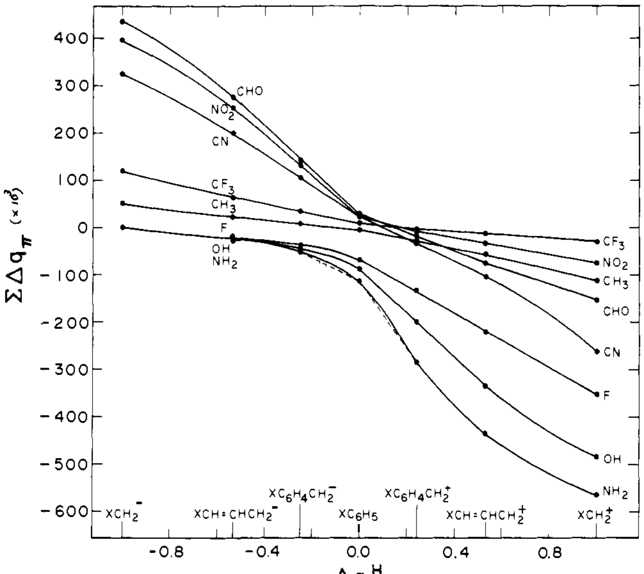

Figure 1. Plot of Σq_π (×10³) vs. π-electron-demand parameter, Δq_π^H, for substituents with optimized C–X bond lengths. Data from Table II. The dashed lines for NH_2 indicate the approximately bilinear response for this substituent in the range $-0.25 \leq \Delta q_\pi^H \leq +0.25$.

plotted vs. the electron-demand parameters, Δq_π^H, for the data of Table II.

The first key point shown by Figure 1 is that substituent π-electron properties fall into two conventional classes. Those substituents (CF_3, CN, NO_2, CHO) for which Σq_π is positive (acceptor) at $\Delta q_\pi^H = 0$ (the "no electron demand" of the XC_6H_5 system) have greater negative slopes in the electron-rich systems, i.e., as Δq_π^H goes from 0 to −1, than in the electron-deficient systems as Δq_π^H goes from +1 to 0.[31] These are the conventional +R substituents. By contrast, the conventional −R substituents (CH_3, F, OH, NH_2) for which Σq_π is negative (donor) at $\Delta q_\pi^H = 0$ have greater negative slopes in electron-deficient systems than in electron-rich systems.

The second key point displayed by Figure 1 is that the subclass of substituents (NH_2, OH, and F) act only as π donors (CH_3 cannot be included). For these substituents, Σq_π values range from zero for $\Delta q_\pi^H = -1.0$ to relatively large donation at $\Delta q_\pi^H = +1.0$ (up to more than 0.5 π electrons for NH_2). The remaining substituents are all amphielectronic, apparently via either conjugation ($CH{=}CH_2$, CN, CHO, and NO_2) or hyperconjugation (CH_3 and CF_3). The vinyl group is completely amphielectronic, as suggested by previous results.[23] However, it is noteworthy that the CN substituent results indicate that it is nearly as effective as a π-electron donor in electron-deficient systems as it is as a π-electron acceptor in electron-rich systems. This result is in accord with the fact that the CN substituent was the first +R-type substituent for which experimental evidence for π-donor capabilities was found.[12,13] The other amphielectronic substituents tend to show relatively clear preferences to act as either π donors (CH_3) or π acceptors (CF_3, CHO, NO_2) for systems with moderate π-electron demands $\Delta q_\pi^H = -0.2$ to +0.2 (the more conventionally accessible experimental regions). Additional matters of interest are discussed in the following sections.

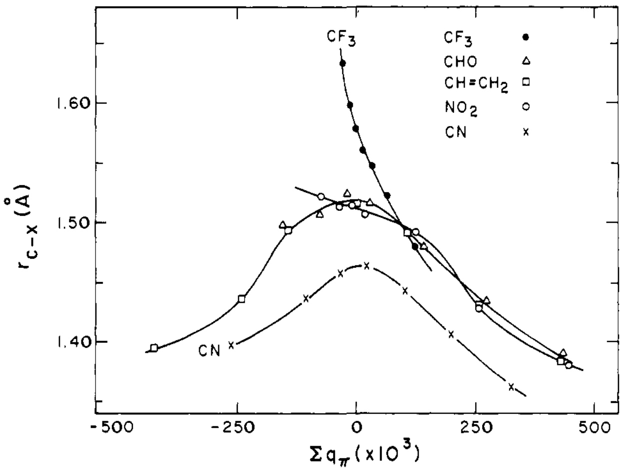

Figure 2. Plot of optimized substituent bond length vs. Σq (×10³) for amphielectronic substituents. Data from Table II.

The variations in optimized C–X bond lengths (Table II) of the amphielectronic substituents with π-electron transfer show interesting trends. The $CH{=}CH_2$, CH_3, CN, and CHO derivatives all show parabolic plots with bond-length maxima at the null resonance point (see Figure 2, noting in particular the complete coincidence of the plots for $CH{=}CH_2$ and CHO). By contrast, the CF_3 derivative shows continuously increasing bond length with increasing electron deficiency of the probe molecule while the bond length for NO_2 derivatives almost reaches a plateau in the electron-deficient region. These latter trends probably are due to electrostatic repulsion between positively charged probe groups and the relatively large positive charges on the nitrogen of NO_2 and particularly the carbon of CF_3.[31] This bond-lengthening may account for the relatively poor π-donor abilities of these two substituents in electron-deficient systems.

One criticism that could be advanced concerning the results in Tables I and II is that minimal basis set ab initio calculation may overestimate the amount of π-electron transfer in small cationic systems.[14] To check the effect of basis set size, we have made calculations for the XCH_2^+, XCH_2^-, allyl cation, and allyl anion systems using the 4-31G basis set with standard geometries.[32] Values of Σq_π for these systems are summarized in Table III. In the anionic systems, the 4-31G calculations are generally similar to the STO-3G calculations for π-donor substituents while indicating slightly greater π acceptance by CF_3, CHO, and NO_2.

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(31) The charge on N for the *p*-nitrobenzyl cation is +0.16 while the charge on the CF_3 carbon of the *p*-(trifluoromethyl)benzyl cation is +0.21. The latter value increases to +0.38 in $CF_3CH_2^+$.

(32) Hehre, W. J. *Acc. Chem. Res.* **1976**, *9*, 399.

For the two cationic systems, where all substituents act as π donors, the predicted π-donating abilities of most substituents are somewhat reduced on going from STO-3G to 4-31G calculations but are still significant for CF_3, CN, CHO, and NO_2 substituents. For this reason, the 4-31G calculations suggest that the actual null resonance point for all of the "normal" π-acceptor substituents may be shifted to a region of slightly greater π-electron demand than indicated by the STO-3G calculations (i.e., greater than $\Delta q_\pi^H \simeq +0.1$). While there may be significant quantitative differences between corresponding STO-3G and 4-31G results, there is no indication that the two key features of Figure 1 are not followed by the latter calculations.

Comparison of Theoretical Calculations with Experimental Results

A. π-Electron Acceptor (+R) Substituents in Electron-Rich Systems. Evidence has been recently presented[24b] that in the absence of specific substituent solvation (which invalidates the earlier σ_R^- scale),[6] a single scale of inherent $\sigma_{R^-(g)}$ substituent parameters accurately correlates resonance effects in aromatic systems for π-electron-acceptor substituents (e.g., CF_3, CN, SO_2CH_3, CO_2CH_3, NO_2, CH_3CO, and CHO) over a relatively wide range of electron demand. Specifically, the range in electron demand was found to vary from that in monosubstituted benzenes (as measured by the para carbon ^{13}C NMR shifts in hydrocarbon solvents[33]) to that involved in the gas-phase acidities of meta- and para-substituted phenols (the reaction used to define the $\sigma_{R^-(g)}$ parameters).[24b] More recently, the applicability of the $\sigma_{R^-(g)}$ parameters for the +R substituents has been shown[34] to extend to the somewhat greater electron demand (π-electron charge availability) that is involved in the gas-phase acidities of meta- and para-substituted anilines. Further, previous theoretical calculations[27] suggest that the $\sigma_{R^-(g)}$ scale will extend to correlate accurately the resonance effects involved in the gas-phase acidities of meta- and para-substituted toluenes.

The present STO-3G "optimized" π-charge-density calculations given in Table II provide a theoretical test of the applicability of the $\sigma_{R^-(g)}$ parameters over the range in electron demand from the benzene ($\Delta q_\pi^H = 0.00$) to the benzyl anion system ($\Delta q_\pi^H = -0.250$) as well as a prediction on the applicability of this scale to the much more extreme electron demands involved with the allylic anion system ($\Delta q_\pi^H = -0.534$) and the methyl anion system ($\Delta q_\pi^H = -1.00$). The test of the quantitative compatibility of the Σq_π values with corresponding $\sigma_{R^-(g)}$ values as well as a test of the applicability of this parameter scale over the range in electron demand from $\Delta q_\pi^H = 0$ to -0.250 is given by the demonstration of an approximately constant ratio of $\Sigma\Delta q_\pi/\sigma_{R^-(g)}$ in each of these systems, as shown in Table IV.

The average values of $\Sigma q_\pi/\sigma_{R^-(g)}$ are 0.066 ± 0.013 for the benzenes and 0.323 ± 0.065 for the benzyl anions. This agreement corresponds to a theoretical calculation of the $\sigma_{R^-(g)}$ values, independent of the electron demand between the benzene and benzyl anion systems, on average to about ±20% agreement. The exaltation factor with the increased electron demand for the benzyl anion system is $0.323/0.066 \simeq 5$.

Table IV. Test of the Applicability of $\sigma_{R^-(g)}$ for π-Acceptor Substituents to Different Electron-Rich Systems

i. Test of the Constancy of $\Sigma q_\pi/\sigma_R^-$ for the Different +R Substituents in Each System

		$\Sigma q_\pi/\sigma_R^{-\,b}$			
X	$\sigma_{R^-(g)}$[a]	XC_6H_5	$XC_6H_4CH_2^-$	$XCH{=}CHCH_2^-$	XCH_2^-
CF_3[c]	0.15	0.067	0.21	0.42 (0.59)	0.80 (0.84)
CN[c]	0.23	0.091	0.45	0.87 (0.74)	1.42 (1.03)
NO_2	0.41	0.046	0.32	0.62 (0.74)	0.97 (1.23)
CHO	0.46	0.059	0.31	0.60 (0.68)	0.94 (0.90)

ii. Test of the Constancy of $\Sigma q_\pi(XCH{=}CHCH_2^-)/\Sigma q_\pi(XC_6H_4CH_2^-)$ and $\Sigma q_\pi(XCH_2^-)/\Sigma q_\pi(XC_6H_4CH_2^-)$ for the Different +R Substituents

X	$\Sigma q_\pi(XCH{=}CHCH_2^-)/\Sigma q_\pi(XC_6H_4CH_2^-)$[b]	$\Sigma q_\pi(XCH_2^-)/\Sigma q_\pi(XC_6H_4CH_2^-)$
CF_3	1.91	3.76
CN	1.92	3.14
NO_2	1.95	3.06
CHO	1.93	3.06

[a] From ref 24b. [b] Σq_π from Table II. Values in parentheses are from 4-31G calculations in Table III. [c] The ratios indicate that calculations at the STO-3G level respectively underestimate and overestimate the π-acceptor abilities for CF_3 and CN. These differences appear to be decreased at the 4-31G level. However, the key observation is that the exaltation factor from one system to another is nearly the same for all four substituents as shown in (ii). Comparison of ratios of $\Sigma q_\pi/\Sigma q_\pi$ for different systems minimizes the effect of any inherent errors in the calculations for individual substituents.

The prediction of the applicability (or not) of the $\sigma_{R^-(g)}$ scale[24b] to the extremes of electron demand represented by the allylic and methyl anion systems is best made by comparing the results for "theoretical substituents" vs. "theoretical substituents" to minimize any errors inherent in the calculations.[26] This is done by using the ratios $(\Sigma q_\pi)XCH{=}CHCH_2^-/(\Sigma q_\pi)XC_6H_4CH_2^-$ and $(\Sigma q_\pi)XCH_2^-/(\Sigma q_\pi)XC_6H_4CH_2^-$ for each of the above +R substituents. The average values obtained are 1.94 ± 0.02 and 3.25 ± 0.251, respectively, by using the STO-3G results of Table II. These results suggest that the applicability of $\sigma_{R^-(g)}$ values extends at least approximately over the whole range in electron demand between benzyl and methyl anions. This may be checked by taking the ratios of $(\Sigma q_\pi)XCH{=}CHCH_2^-/\sigma_{R^-(g)}$ and $(\Sigma q_\pi)XCH_2^-/\sigma_{R^-(g)}$. The average values obtained for these ratios are 0.63 ± 0.10 and 1.03 ± 0.19, respectively, by using the STO-3G results of Table II and 0.069 ± 0.10 and 1.00 ± 0.13, respectively, by using the 4-31G results of Table III. These results correspond to an exaltation factor of about 15 for the XCH_2^- system relative to XC_6H_5.

These results indicate that the inherent $\sigma_{R^-(g)}$ scale for π-electron-acceptor substituents is at least approximately applicable to aliphatic series carbanions having very large electron demands (π-electron availability).

This prediction is supported by the correlation of the increased gas-phase acidities of substituted methanes, XCH_3, relative to methane,[35] by the DSP equation: $-\delta\Delta H^\circ_{acid}(298\ K) = 1.6 + (35.1)\sigma_{I(g)} + (87.6)\sigma_{R^-(g)}$; $r = 0.991$; $n = 7$. The $\sigma_{I(g)}$ and $\sigma_{R^-(g)}$ values used are taken from ref 24b. The values of $-\delta\Delta H^\circ_{acid}(298\ K)$ in kcal/mol observed and those calculated from the correlation equation are listed in Table VII.

The enhanced gas-phase acidities of the CH_3X compounds relative to methane cover a range of ca. 58 kcal/mol.[35] The average deviation between observed and calculated values is ±1.9 kcal/mol. This is quite satisfactory agreement considering that there may be small contributions to these acidities from variable polarizability[35] and substituent electronegativity effects[36] as well as the facts that an error of ±0.02 in the $\sigma_{R^-(g)}$ value gives an error of ±1.8 kcal/mol and an error of ±0.02 in the $\sigma_{I(g)}$ value gives an error of ±0.7 in the calculated value of $-\delta\Delta H^\circ$. It is also remarkably consistent that the ratio of the electron-demand parameter for the methyl anions (Δq_π^H equals -1.00) to that for phenoxide ions (Δq^H equals -0.236; cf. Table I) is 4.2—virtually identical with the ratio (4.3) of ρ_R values of 87.6 for the gas-phase CH_3X acidities and 20.0 for the gas-phase acidities of para-substituted phenols (the latter value was used for definition of the $\sigma_{R^-(g)}$ parameters).[24b]

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(33) Bromilow, J.; Brownlee, R. T. C.; Lopez, V. O.; Taft, R. W. *J. Org. Chem.* **1979**, *44*, 4766.

(34) Mashima, M.; McIver, R. T., Jr.; Taft, R. W., unpublished results.

(35) Bartmess, J. E.; Scott, J. M.; McIver, R. T., Jr. *J. Am. Chem. Soc.* **1979**, *101*, 6046.

(36) Reynolds, W. F.; Taft, R. W.; Marriott, S.; Topsom, R. D. *Tetrahedron Lett.* **1982**, *23*, 1055.

B. π-Electron Donor Substituents in Electron-Deficient and Electron-Rich Systems. In the range from benzene ($\Delta q_\pi{}^H = 0.000$) to benzyl cations ($\Delta q_\pi{}^H = +0.24$), the enhancement factors in substituent π charge donation increase in the familiar −R order F < OH < NH_2. For example, the ratios $(\Sigma q_\pi)XC_6H_4CH_2{}^+/(\Sigma q_\pi)XC_6H_5$ are F, 1.91; OH, 2.24; NH_2, 2.47. On the other hand, in the range of electron demands from benzyl cations ($\Delta q_\pi{}^H = +0.241$) to allylic cations ($\Delta q_\pi{}^H = +0.533$), the enhancement factors for these as well as for the CH_3 and $CH_2{=}CH$ substituents are nearly constant. The $(\Sigma q_\pi)XCH{=}CHCH_2{}^+/(\Sigma q_\pi)XC_6H_4CH_2{}^+$ ratios are CH_3, 1.64; $H_2C{=}CH$, 1.64; F, 1.66; OH, 1.65; NH_2, 1.53.

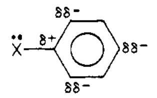
The slightly lower ratio for the NH_2 substituent indicates a leveling in the strong π-donor action of this substituent with the greater electron demand. This leveling effect is clearly evident in the results for the extreme electron demand of the substituted methyl cations ($\Delta q_\pi{}^H = 1.00$). The ratios of $(\Sigma q_\pi)XCH_2{}^+/(\Sigma q_\pi)XC_6H_4CH_2{}^+$ now increase in the unfamiliar order: NH_2, 2.01 < OH, 2.40 < F, 2.63 < $H_2C{=}CH$, 2.89 < CH_3, 3.9.

Evidence has been recently presented[26] for leveling of the strong π-donor effects of the 4-$N(CH_3)_2$ substituent in gas- and aqueous-phase pyridinium ion acidities between the relatively strong electron demand in the gaseous ion compared to that of the aquated ion. The present results suggest that leveling effects of this kind will be common in highly electron-deficient species (cf. Figure 1). Our results further suggest that in contrast to the expected failure of a single scale of π-electron-donating parameters to apply over a very wide range of electron demand, such a scale should apply for certain relatively narrow ranges of electron demand (cf. Figure 1). For example, the nonoptimized results for the pyridinium and benzyl cation systems (from Table I) indicate the latter type of behavior. The following essentially constant ratios of $(\Sigma q_\pi)XC_6H_4CH_2{}^+/(\Sigma q_\pi)XC_5H_4NH^+$ are obtained: CH_3, 1.23; F, 1.21; OH, 1.24; OCH_3, 1.17; NH_2, 1.26. Values of resonance effects (R) for −R para substituents obtained from experimental gas-phase pyridinium ion acidities[26] may also be compared with the corresponding $\Sigma\Delta q_\pi$ values to obtain confirmatory evidence. The R values (obtained as $\delta\Delta G^\circ{}_{(p)} - 20.0\sigma_I$) give the following approximately constant ratios of $R/(\Sigma q_\pi)XCH_6H_4CH_2{}^+$, for example: NH_2,[37a] 13.4/−0.284 = −47; OCH_3, 12.2/−0.230 = −53 (from nonoptimized calculations); F, 6.4/−0.134 = −48; CH_3, 3.1/−0.029 = −107, each in kcal/mol/unit π charge. The deviation for CH_3 is probably due to a contribution from a polarizability effect as well as a π resonance effect to the R value. The scale of π-electron-donor ability obtained from the R values for pyridinium ion acidities also appears to apply reasonably satisfactorily to the gas-phase acidities of para-substituted α-methyl styrenes and benzaldehydes.[37b]

As previously noted,[16] the calculations show that, under extreme electron demands, substituents that are commonly π-electron acceptors (NO_2, CN, CF_3 CHO) become π donors. There is as yet meager experimental evidence for these effects.[12,13] Calculations for all of the strongly electron-deficient cation systems in Tables I–III predict the order of π-donor ability to be CF_3 < NO_2 < CHO < CN < $CH{=}CH_2$. This order is also independent of electron demand in electron-deficient systems for the first four substituents (see Figure 1, the ratio $\Sigma q_\pi(XCH_2{}^+/\Sigma q_\pi(XC_6H_4CH_2{}^+)$ is 7.5 ± 0.5 for these four substituents). This predicted behavior is being further investigated.

The relatively strong π-donor substituents NH_2, OH (or OCH_3), and F show strongly leveled π-donating properties in electron-rich systems. The $XCH_2{}^-$ ions represent the extreme where there is no π donation observed for any of these. In other less electron-rich systems, the calculations show similar π-donating properties for these substituents, but the familiar order F < OH < NH_2 is preserved. These latter results are at least in part (if not entirely) due to an assumption made in the calculations. The OH (or OCH_3) and NH_2 substituents have been taken as coplanar with the molecular framework, an assumption that is very likely to be incorrect for electron-rich systems (since twisting from coplanarity will relieve electron repulsion). It has been recently indicated[24b] that resonance effects are in the order $N(CH_3)_2$ < NH_2 < OCH_3 < F for the acidities of phenols both in the gas and aqueous phases. This could reflect strong π-orbital repulsion,[38a] possibly in combination with saturation of resonance[38b] in electron-rich systems.[24b]

Orbital repulsion between a lone pair or a σ bond of a substituent and the π-electron system at the *ipso* carbon leads to π-electron redistribution as shown in **1**.[4b] It has been suggested that this is an important interaction for π-donor substituents such as F and CH_3.[38] If so, then it should be particularly significant in systems such as para-substituted benzyl and phenoxide anions due to the strong π-donor tendencies of the $CH_2{}^-$ and O^- groups and consequent increase in π-electron density at the carbon *ipso* to the substituent (note the significant negative $\Delta q_\pi{}^H$ values for these derivatives in Table I). Orbital repulsion does not involve actual π-electron transfer between the substituent and the probe molecule and therefore does not contribute to Σq_π values. However, it will cause destabilizing energetic interactions for substituents such as CH_3, OH, NH_2, and F in para-substituted anionic systems and therefore will appear in the "experimental" R values,[24b] possibly leading to an R order different from that expected from Σq_π values. Further, experimental and theoretical investigations are being carried out in an attempt to determine the importance of orbital repulsion effects in electron-rich systems.



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Possibility of a Universal Resonance Scale for Aromatic Systems

The complex patterns of substituent resonance response in Figure 1 indicate that none of the existing resonance scales discussed in the introduction are able to fully reproduce organic substituent effects, even if one restricts the range of electron demand only to that covered by aromatic systems (ca. $-0.25 \le \Delta q_\pi{}^H \le +0.25$). However, within this restricted range, the substituent resonance response curves can be reasonably approximated by individual bilinear relationships covering the ranges $-0.25 \le \Delta q_\pi \le 0$ and $0 \le \Delta q_\pi{}^H \le +0.25$ (this is illustrated in Figure 1, for example, by NH_2.[39] Much of the experimental data discussed in the previous section is consistent with the idea of near-linear resonance response over restricted regions of π-electron demand. The only serious problem may occur for −R substituents in electron-rich systems due to orbital repulsion and related factors.

After further experimental work, it should be feasible to produce a new bilinear resonance response curve for aromatic derivatives anchored on the existing $\sigma_R{}^\circ$ scale ($\Delta q_\pi{}^H = 0$), an expansion of the recently proposed $\sigma_R{}^-{}_{(g)}$ scale[24b] based on gas-phase phenol acidities ($\Delta q_\pi{}^H \sim -0.25$) and a new $\sigma_R{}^+$ scale based on the R values estimated for pyridinium ion[26] and benzyl cation[37a] systems ($\Delta q_\pi{}^H \sim +0.25$). This would have the advantage of replacing four fixed scales ($\sigma_R{}^-$, $\sigma_R{}^0$, $\sigma_R(BA)$, and $\sigma_R{}^+$)[6] by three, covering a wider range of electron demand. Resonance scales for systems corresponding to intermediate-demand situations could then be generated by linear interpolation between $\sigma_R{}^0$ and one of the new $\sigma_R{}^+$ and $\sigma_R{}^-$ scales. For example, preliminary results indicate that a resonance scale almost identical with $\sigma_R(BA)$ can be generated by linear interpolation between $\sigma_R{}^0$ and a $\sigma_R{}^+$ scale based on pyridinium ion acidities ($\Delta q_\pi{}^H \simeq 0.2$), indicating that $\sigma_R(BA)$ simply represents one point along a continuum of resonance scales.

Further experimental work is being carried out to better define $\sigma_R{}^+$ and $\sigma_R{}^-$ and to test the applicability of this proposed bilinear resonance scale.

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(37) (a) Gal, J. E., unpublished results. (b) Abboud, J. L. M.; Wolf, J. F.; Taft, R. W., unpublished results.

(38) (a) Murrell, J. N. "The Theory of Electronic Spectra of Organic Molecules"; Methuen: London, 1963. (b) Hoefnagel, A. J.; Hoefnagel, M. A.; Wepster, B. M. *J. Am. Chem. Soc.* **1976**, *98*, 6194.

(39) This differs very significantly from previously proposed bilinear resonance scales[7,8] in having a separate bilinear relationship for each substituent rather than just different slopes for π donors and π acceptors in general.

Table V. Energies (in hartrees) for XCH_2^+, XCH_2^-, $XCH=CHCH_2^+$, and $XCH=CHCH_2^-$ at the STO-3G and 4-31G Levels

	XCH_2^+		XCH_2^-		$XCH=CHCH_2^+$		$XCH=CHCH_2^-$	
X	STO-3G	4-31G	STO-3G	4-31G	STO-3G	4-31G	STO-3G	4-31G
NH_2	-93.215 54	-94.229 23	-93.053 41	-94.275 21	-169.181 67	-171.025 40	-169.105 69	-171.129 29
OCH_3	-151.289 92	-152.945 96	-151.195 98	-153.072 11	-227.247 06	-229.720 75	-227.217 29	-229.882 75
OH	-112.691 90		-112.604 93					
F	-136.263 52	-137.888 96	-136.245 44	-138.104 91	-212.271 04	-214.735 78	-212.280 48	-214.944 74
CH_3	-77.403 46	-78.193 33	-77.386 29	-78.326 66	-153.406 49	-155.018 53	-153.406 59	-155.160 89
$H=CH_2$	-114.801 21		-114.821 81		-190.778 88		-190.797 94	
H	-38.775 40	-39.175 09	-38.795 97	-39.388 79	-114.802 39	-116.020 51	-114.822 68	-116.214 01
CF_3	-369.726 25	-374.310 17	-369.829 72	-374.637 62	-445.753 33	-451.121 14	-445.823 27	-451.440 97
CN	-129.317 22	-130.730 03	-129.471 17	-131.071 11	-205.332 01	-207.576 73	-205.442 69	-207.862 86
CHO	-150.017 67	-151.708 86	-150.125 22	-152.033 14	-226.027 66	-228.556 81	-226.098 20	-228.824 29
NO_2	-239.415 89	-242.226 14	-239.644 98	-242.676 36	-315.454 26	-319.064 74	-315.604 79	-319.401 77

Table VI. Total Energy (in hartrees) for Various Molecules from STO-3G Calculations with C-X Bond-Length Optimization

X	XCH_2^+	$XCH=CHCH_2^+$	$XC_6H_4CH_2^+$	XC_6H_5	$XC_6H_5CH_2^-$	$XCH=CHCH_2^-$	XCH_2^-
NH_2	-93.230 51	-169.201 63	-319.992 26	-282.205 19	-319.966 76	-169.115 23	-93.067 85
OH	-112.701 26	-188.691 06	-339.499 85	-301.730 38	-339.503 88	-188.658 79	-112.618 79
F	-136.269 05	-212.279 50	-363.106 36	-325.351 02	-363.131 62	-212.290 51	-136.253 38
CH_3	-77.403 90	-153.413 39	-304.237 96	-266.474 91	-304.250 55	-153.412 61	-77.386 31
H	-38.775 70	-114.807 33	-265.646 51	-227.891 24	-265.670 16	-114.829 07	-38.795 79
CF_3	-369.732 25	-445.760 89	-596.600 53	-558.857 59	-596.653 92	-445.832 89	-369.830 84
CN	-129.319 58	-205.340 65	-356.179 22	-318.444 20	-356.259 28	-205.455 83	-129.478 04
CHO	-150.018 40	-226.035 48	-376.868 31	-339.118 625	-376.919 50	-226.110 66	-150.129 92
NO_2	-239.422 99	-315.466 42	-466.318 62	-428.593 01	-466.417 55	-315.618 85	-239.645 38
$CH=CH_2$	-114.805 11	-190.790 26	-341.594 35	-303.827 83	-341.617 11	-190.810 49	-114.827 41

Conclusions

1. Calculations for a series of substituted probe molecules covering a wide range of π-electron demand have revealed a complex pattern of substituent resonance response to π-electron demand. The most striking feature is the predicted amphielectronic nature of CF_3, CN, CHO, and NO_2, all of which become π donors in systems with strong π-electron demand.[16]

2. In spite of the complexity, the calculated resonance response for a significant number of substituents can be approximated to corresponding experimental results based upon gas-phase acidities of pyridinium ions, phenols, anilines, and substituted methanes. For example, conventional π-electron-acceptor substituents (CF_3, CN, CHO, NO_2) are found to closely follow the $\sigma_R^-{}_{(g)}$ scale[24b] of π-electron-acceptor abilities over an extremely wide range in π-electron availability. A major requirement is the absence of specific substituent solvation-assisted resonance effects, especially for the CHO and NO_2 substituents.[24b]

3. π-Donor abilities in electron-deficient systems are found to differ very significantly from the σ_R^+ scale of Ehrenson, Brownlee, and Taft.[5] Strong leveling of the effects of the strongest π-donor substituents (i.e., $N(CH_3)_2$ and NH_2) is indicated with relatively large increases in π-electron demand. Further, substituents, e.g., CF_3, NO_2, CHO, and CN, are indicated to be amphielectronic and to become π-electron donors (in this order) in systems with relatively extreme π-electron deficiency.

4. Orbital and other π-electron repulsions and related geometric problems are indicated to be involved with strong π-donor substituents in electron-rich systems. Further experimental and theoretical studies are in progress concerning these and related matters.

5. The substituent resonance response curves in Figure 1 can be reasonably approximated by bilinear relationships for each substituent covering the ranges $-0.25 \leq \Delta q_\pi^H \leq 0$ and $0 \leq \Delta q_\pi^H \leq +0.25$. This may provide the basis for an experimental bilinear resonance scale for aromatic derivatives anchored on σ_R^0 and new σ_R^+ and σ_R^- scales based on gas-phase data for pyridinium ion, benzyl cation, and phenoxide ion. Resonance scales for intermediate demand situations could then be generated by linear interpolation between σ_R^0 and σ_R^+ or σ_R^-. This possibility is being actively investigated.

Details of Calculations

Energies and geometries for most of the series in Table I have been reported previously.[15,22b,25-27] In the case of the methyl cation and anion species, the assumed geometries were trigonal planar with $r_{C-H} = 1.08$ Å. For the $XCH=CHCH_2^+$ species, the geometries were $r_{C=C} = 1.37$ Å, $r_{C-CH_2^+} = 1.46$ Å, and $r_{C-H} = 1.08$ Å with each carbon trigonal planar and with the substituent trans to CH_2^+. All substituent geometries were standard[17] except for OCH_3, where ∠C-O-C = 118°.[40] Energies obtained in the STO-3G and 4-31G calculations are summarized in Table V.

Table VII

+R substituent, X	$\sigma_{I(g)}$	$\sigma_R^-{}_{(g)}$	$-\delta\Delta H^0{}_{(obsd)}$	$-\delta\Delta H^0{}_{(calcd)}$
H	0.0	0.0	(0.0)	1.8
CN	0.58	0.23	44.4	42.1
CO_2CH_3	0.17	0.41	45.6	43.5
CH_3CO	0.22	0.43	47.8	47.0
CHO	0.31	0.45	50.2	51.9
CH_3SO_2	0.59	0.30	50.0	48.6
NO_2	0.65	0.42	57.9	61.2

In the case of the C-X bond-length optimization calculations, the geometries for methyl cations and anions were identical with those given above while the phenyl geometry in C_6H_5X was standard.[17] In other systems, the geometry of the parent probe molecule was partially optimized. For allyl cations and anions, trigonal-planar carbons were assumed ($r_{C-H} = 1.08$ Å) and each structure was optimized to give a symmetric ion ($r_{C\cdots C} = 1.3851$ Å for the cation, $r_{C\cdots C} = 1.3783$ Å for the anion). The optimized benzyl anion structure was identical with that previously reported[24a] while the benzyl cation had $r_{C-CH_2^+} = 1.3746$ Å, $r_{C-H} = 1.095$ Å, ∠C-C-H = 122.2°, and standard phenyl geometry. Energies obtained in the calculations are summarized in Table VI.

Ab initio calculations were performed by using the programs GAUSSIAN80,[41] GAUSSIAN77/UCI,[42] and MONSTERGAUSS81.[43]

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