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# THE RESPONSE OF SUBSTITUENTS TO PI-ELECTRON DEMAND[1]

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Summary: The forms of responses of substituents to strongly changing pi-electron demands have been investigated using ab initio molecular orbital calculations at the STO-3G level of approximation; the non-parallel responses depend strongly upon the nature of the substituent. For example, CN, CHO, and $NO_2$ act as pi electron donors in strongly electron deficient systems.

There has been much recent interest in substituent resonance effects.[2-13] A major concern is the form of the varying substituent response as the electron demand is altered in the attached pi-system.[2-10] In applying a fixed scale of substituent resonance effects[7-10], the simplest interpretation is that there is a linear response as the demand is altered. However, non-linear enhancements are evident in the $\sigma_R^0$, $\sigma_R(BA)$, and $\sigma_R^+$ scales[9], respectively, for pi-donor substituents. There is the further question of the effect on a pi-donating substituent when it is attached to a pi-electron rich system. Some scales assume in this case that $\sigma_R^- = \sigma_R^0$, while others allow for some decrease in the substituent electron donation. A similar uncertainty arises for substituents (such as a nitro groups) which are normally pi-electron acceptors, when these substituents are placed at a very pi-electron deficient center.

Relationships based on non-linear resonance effects have been suggested. Happer[2] has proposed an exponential equation for resonance donors based on a value derived for maximum donation. He assumes that the dimethylamino group would show an approximately linear variation in $\sigma_R$ over a normal range of reactivities. Brownlee, Taft, and coworkers[4] using $C^{13}$ shifts for a wide variety of p-disubstituted benzenes have suggested that enhanced and reduced effective $\bar{\sigma}_R$ values may be obtained from the corresponding $\sigma_R^0$ value by use of equation (1), which involves a non-linear dependence upon the electron demand parameter, ($\varepsilon$).

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

However, as noted by the authors, equation (1) is limited in applicability and cannot be extended to systems with large electron demand factors ($\varepsilon$).

We wish to report evidence as to the form of the response of substituents to strongly changing pi-electron demand based upon STO-3G molecular orbital calculations of the total pi-electron transfer between a substituent and the attached pi-system. Earlier work has shown that $\sigma_R^0$ values derived[7,9] for substituents attached directly to an unperturbed benzene nucleus have a wide range of applicability including reactivity and equilibria data[9] as well as infrared[11] and NMR[12] results. It has further been shown that the calculated pi-electron transfer between a substituent and the ring in monosubstituted benzenes is a linear function of $\sigma_R^o$ both at the CNDO/2[13] and the *ab initio* STO-3G levels[12] of approximation. It has been observed[14] that approximately linear protonic energy-charge relationships are fairly general in calculations of proton affinities. These results offer support for the idea that charge transfer can be used as a measure of resonance effects.

We have investigated[15] the pi-electron transfer between the substituent, X, and a variety of systems of varying electron demand, including the following:

$^-CH_2X(-1.000)$, $^-CH_2CHCHX(-.551)$, *p*$^-CH_2C_6H_4X(-.232)$, *p*-$NH_2C_6H_4X$
$(-.120)$, $C_6H_5X(.000)$, *p*-$NO_2C_6H_4X(+.031)$, $^+NH_3C_6H_4X(+.075)$, *p*-$^+HNC_5H_4X$
$(+.201)$, *p*-$^+CH_2C_6H_4X(+.295)$, $^+CH_2CHCHX(+.558)$, and $^+CH_2X(+1.000)$

The $q_\pi$ value for X = H for the carbon atom to which the substituent is attached is taken for each system to be a measure of electron demand, equal to $1 - q_\pi(H)$. The value of this electron demand parameter is given in parenthesis for each of the above systems.

The results obtained are plotted in Fig. 1 for the planar substituents X = $NH_2$, OH, F, CN, CHO, and $CH{=}CH_2$. The following important features are noted: (a) over the whole range of demands, the response tends to be neither linear nor bilinear, and in particular is nonparallel; (b) for the $NH_2$, OH, and F substituents there is essentially no pi electron donation or acceptance for very electron-rich systems (due to the absence of effective acceptor orbitals). For electron-deficient systems, after a sharp increase in pi donation from the $NH_2$ substituent, there is a definite falling off in donation to very electron-deficient systems.[16] This non-linear behavior is increasingly less pronounced for OH and F, respectively; (c) substituents, *e.g.*, CN and CHO (also $NO_2$--not shown), act both as pi electron donors as well as acceptors. That is, these substituents show the amphielectronic behavior expected of the $CH{=}CH_2$ substituent. Between values of $1 - q_\pi(H) = +0.1$ to $-1.0$, these substituents exhibit their normally observed pi electron acceptor roles. However, for interaction with very strongly electron deficient systems, all of these substituents act by pi electron donation. The curves are not parallel, however. (d) the vinyl substituent shows approximately linear response over the whole range of electron demand.

We note in connection with (c) that evidence is beginning to accumulate that unsaturated substituents which are normally resonance withdrawing substituents (+R), such as cyano[17,18] or nitro[16], can become pi-donors when the demand is high.

A recent communication[19] has examined effects on energies for such substituents when attached to a variety of cations.

We have also made calculations for $OCH_3$, $CH_3$, and $CF_3$ substituents and for additional systems including some where the geometry has been optimized. A later full publication will deal with these results including some values at the 4-31G level, and with suitable equations to describe experimental resonance effects resulting from non-parallel responses to electron demand.

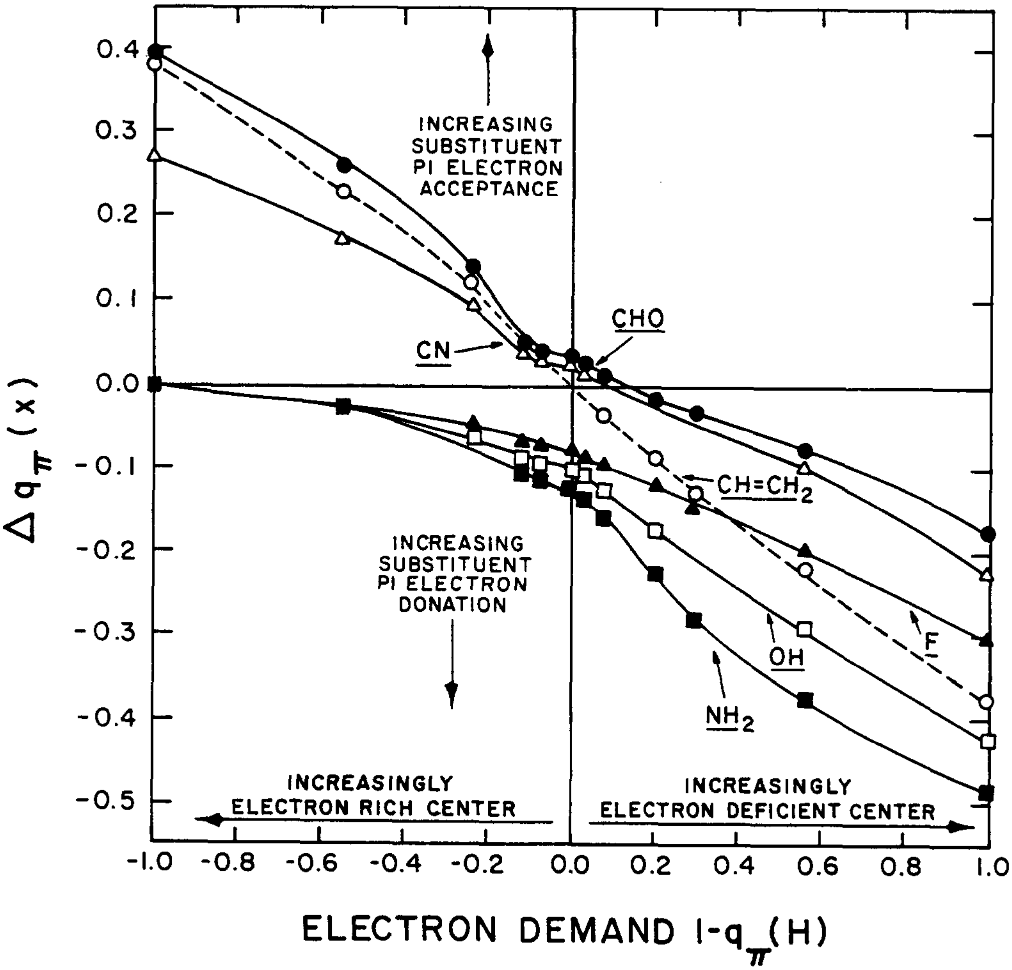
0.4
0.3
0.2
0.1
0.0
-0.1
-0.2
-0.3
-0.4
-0.5
$\Delta q_{\pi}(x)$
INCREASING SUBSTITUENT PI ELECTRON ACCEPTANCE
INCREASING SUBSTITUENT PI ELECTRON DONATION
CN
CHO
$CH=CH_2$
F
OH
$NH_2$
INCREASINGLY ELECTRON RICH CENTER
INCREASINGLY ELECTRON DEFICIENT CENTER
-1.0
-0.8
-0.6
-0.4
-0.2
0.0
0.2
0.4
0.6
0.8
1.0
ELECTRON DEMAND $1-q_{\pi}(H)$

Fig. 1.

## References and Notes

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