

Concluding Remarks

This subject is in its infancy. The potential for growth seems large because of the well-developed natures of the two adjacent fields, namely, ground-state catalysis and photochemistry and because the concepts are likely to be useful in understanding solar photochemistry and exploiting it.

Some specific research questions that need attention can be identified. For electron hole transfer catalyses, it is not known whether an exciplex itself or a dissociated species bearing the electron hole is responsible for the observed hydrogen abstractions; there is no reason in principle why an exciplex cannot participate in the normal bimolecular photoreactions common to other excited states. We also know little about the rates and transition-state structures for proton transfers to and from excited molecules or energy-rich intermediates. Moreover, there is currently no example of protonic catalysis in which the excited molecule interacts reversibly with the catalyst, so that the conjugate acid

or base retains excitation. Indeed, it is generally true that we know little about the detailed energetics of complex photoreactions, and studies of catalysis may contribute new insights in that area. Finally, we know next to nothing about applications of catalysis in photochemistry, which might be expected to improve efficiencies and obtainable yields of products as well as to foster much new photochemistry.

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Contribution of Theoretical Chemistry to an Understanding of Electronic Substituent Effects

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Hammett substituent constants have now become an integral part of chemistry. Such σ values provide a numerical scale of the electronic effect, on a property or reactivity, of a substituent located elsewhere in the molecule. Much recent interest has centered on the origins, transmissions, and magnitudes of the various component electronic substituent effects included in such values. One difficulty is that the behavior of many substituents is dependent on the particular solvent employed, but recent developments have allowed a wide range of reactivities to be measured in the gas phase. Such measurements not only allow the establishment of unperturbed scales of substituent effects but are also directly comparable with theoretical calculations.

It is now possible to use theoretical methods to obtain reasonable values for some molecular properties, particularly using ab initio molecular orbital theory where the necessary programs are readily available. For certain processes, such as proton-transfer equilibria, the energy can often be calculated to within 1-2 kcal of the experimental gas-phase results. Likewise, theoretical electron-density distributions have been shown to be in reasonable accord with experimental electron-distribution maps.

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The level of agreement obtained between theory and experiment gives sufficient confidence to allow a theoretical approach to related model systems that may not be available or amenable to experiment. The discussion below shows that such results can greatly help our understanding of the mechanisms and magnitudes of substituent electronic effects.

Ab Initio Molecular Orbital Theory^{1,2}

Theoretical calculations of substituent effects using ab initio molecular orbital theory have mainly employed the models² developed by Pople and co-workers. For very small organic molecules, such computations involve a compromise between computational cost and accuracy while for somewhat larger molecules, the number of orbitals involved limits the level of calculation that can be employed.

The simplest level (the so-called minimal basis) represents each atom by just those functions that are necessary to accommodate all of its electrons while maintaining overall spherical symmetry. Thus, at the STO-3G level,^{3,4} hydrogen is represented by a 1s orbital and the elements Li to F by five orbitals (1s, 2s, 2p_x,

(1) See, for example, ref 2 and "Methods of Electronic Structure Theory", H. F. Schaefer III, Ed., Plenum, New York, 1977; "Applications of Electronic Structure Theory", H. F. Schaefer III, Ed., Plenum, New York, 1977.

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

(3) W. J. Hehre, R. F. Stewart, and J. A. Pople, *J. Chem. Phys.*, 51, 2657 (1969).

(4) Each orbital is approximated by a 3-G expansion to Slater-type functions.

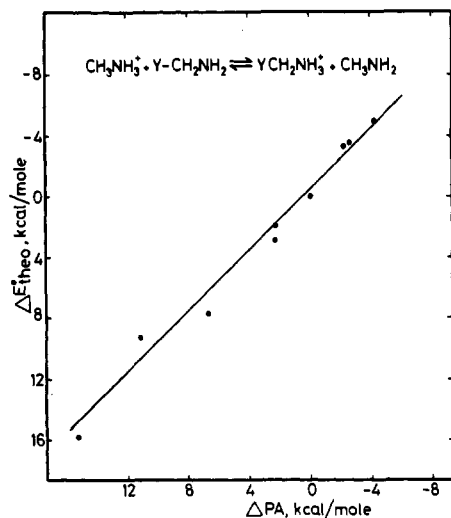
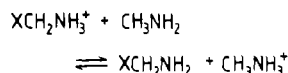
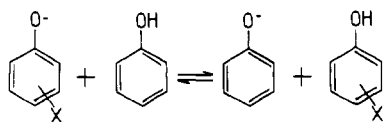


Figure 1.

and $2p_z$). Available programs will accommodate 70–90 orbitals and thus are limited to about 14 atoms other than hydrogen. It is thus possible to make calculations on simple disubstituted benzenes, systems of much interest to physical organic chemists. At this STO-3G level, equilibrium geometries are generally in good agreement² (for example ± 0.03 Å in bond lengths) with experiment for many simple organic molecules including substituted benzenes. Such calculations also usually give energies for equilibria in good accord with experiment provided that the numbers of each kind of formal chemical bond are maintained (so-called isodesmic processes). This is not so great a restriction as it might appear since many equilibria of interest to physical organic chemists are taken relative to a parent compound and can thus be expressed as isodesmic processes. As an example, Figure 1 shows⁵ a plot of the calculated ΔE° values vs. experimental proton affinities for the proton-transfer equilibria of substituted methylamines:



Another example is the mostly satisfactory agreement found⁶ between the calculated (ΔE°) and experimental (ΔG°) values for the relative acidities of substituted phenols as shown in the following process:



The STO-3G basis also leads to dipole moments in reasonable agreement with experiment and to atomic electron populations in accord with chemical expectation for systems such as monosubstituted benzenes. Thus, a linear relationship is obtained⁷ between the carbon-13 substituent chemical shifts of the para carbon atom in a series of monosubstituted benzenes and the change in total population (Δq) at that atom.

(5) M. Taagepera, W. J. Hehre, R. D. Topsom, and R. W. Taft, *J. Am. Chem. Soc.*, **98**, 7438 (1976).

(6) A. Pross, L. Radom, and R. W. Taft, *J. Org. Chem.*, **45**, 818 (1980); A. Pross and L. Radom, *Prog. Phys. Org. Chem.*, **13**, 1 (1981).

(7) W. J. Hehre, R. W. Taft, and R. D. Topsom, *Prog. Phys. Org. Chem.*, **12**, 159 (1976).

Nevertheless, it is not difficult to find systems and results that are not well-treated with use of the STO-3G basis. Thus, molecules involving highly electronegative atoms such as fluorine are usually less well-reproduced.⁸ Substantial improvement is usually found if the number of independent functions describing the classical orbitals is increased. The usual procedure (for example the so-called 3-21G⁹ and 4-31G¹⁰ bases) is to divide the valence shell (2s and 2p) into inner and outer parts (a total of eight orbitals), while the 1s shell is still described by a single orbital.¹¹ Hydrogens are represented by a split 1s shell. While agreement with experiment is improved for most systems and properties, program limitations now restrict calculations to molecules of up to seven or eight atoms other than hydrogen.

To obtain significant further improvement in agreement with experiment, it is necessary to include functions that allow for polarization. Thus, the 6-31G* basis¹² includes a set of six orbitals to represent the d orbitals on heavy atoms in addition to having a split valence shell. Calculations are limited here to molecules containing up to four heavy atoms. The agreement with experiment of properties such as equilibrium geometries and charge density distributions is usually very good apart from molecules such as F_2 and H_2O_2 that have two or more highly electronegative atoms bonded together.

It is important to appreciate that the basic assumptions of molecular orbital theory mean that full allowance is not made for certain electron–electron repulsions. Thus absolute energies cannot be obtained, but the so-called correlation effects involved do not seem to be important in electron-density distributions or in isodesmic processes of the type considered in this Account.

Some comparisons¹³ have been made of results from ab initio molecular orbital calculations at various levels. Molecular geometries and dipole moments are overall better reproduced at the higher levels. Interestingly, atomic electron populations obtained at one basis seem¹⁴ to be linearly related to those obtained at another. Further, in spite of the inherent limitations¹⁵ of the usual analysis employed for such populations, the values obtained at the higher bases do seem¹⁴ to mirror actual electron distributions within related series of molecules. Such populations are also frequently proportional to substituent-induced changes in carbon-13 and fluorine-19 chemical shifts, which might be expected to be a function of the electron density in the

(8) This may arise (ref 2) from accommodating equal numbers of electrons in less orbitals, for example, in the series CH_3CH_3 , CH_3NH_2 , CH_3OH , CH_3F , or from the increasingly nonspherical electron distribution in the series.

(9) J. S. Binkley, J. A. Pople, and W. J. Hehre, *J. Am. Chem. Soc.*, **102**, 939 (1980).

(10) R. Ditchfield, W. J. Hehre, and J. A. Pople, *J. Chem. Phys.*, **54**, 724 (1971); W. J. Hehre and J. A. Pople, *ibid.*, **56**, 4233 (1972).

(11) Thus with the 3-21G basis set the 1s orbital of each carbon is described by a fixed sum of 3 G, while the valence orbitals are described by inner and outer functions, represented by 2 and 1 G, respectively.

(12) P. C. Hariharan and J. A. Pople, *Chem. Phys. Lett.*, **16**, 217 (1972).

(13) See, for example, ref 2, 9, and 14 and P. Pulay, G. Forgari, F. Pang, and J. E. Boggs, *J. Am. Chem. Soc.*, **101**, 2550 (1979); C. W. Bock, P. George, G. J. Mains, and M. Trachtman, *J. Mol. Structure.*, **49**, 215 (1979).

(14) S. Marriott and R. D. Topsom, *J. Mol. Struct. (Theochem.)*, **89**, 83 (1982).

(15) The Mulliken population analysis is mathematically explicit, but the method employed could result in values of little absolute significance: see ref 14 and references therein.

immediate vicinity of the atom involved.

One other general point is that substituent electronic effects may be considered in terms of energy or of charge. Thus, for proton-transfer equilibria, it is an energy that is measured or calculated, but it is common to view the effect of the substituent X as arising from its effect on the charge distribution in the molecule. In some measurements, such as dipole moments or NMR chemical shifts, it is the electron density that is involved. It appears that the various mechanisms of substituent electronic effect often lead to corresponding changes in energy and density, a result that has been supported by recent theoretical evidence.¹⁶

Finally, it must be kept in mind that the theoretical calculations refer strictly to isolated molecules and thus are best compared to gas-phase results, particularly as far as energies are concerned. The recent development¹⁷ of gas-phase techniques to measure the energies of proton-transfer equilibria has provided an excellent test for the computations.

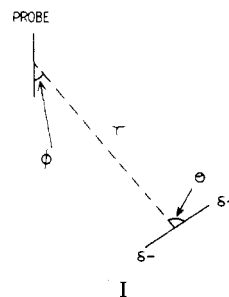
Origin and Transmission of Substituent Electronic Effects

Substituent electronic effects¹⁸ have their origin in four important processes, although a number of others have been suggested. These four are the following: the substituent dipole, leading to a field effect (F);¹⁹ the electronegativity difference between the substituent and the atom to which it is attached, leading to a σ -inductive or electronegativity effect (χ); charge transfer between suitable orbitals of the substituent and the group to which it is attached, leading to a so-called resonance or hyperconjugative effect (R); and polarizability effects (P). The last name appear to be relatively unimportant except for large hydrocarbon substituents, either in the gas phase or in certain ions in solution. The discussion below refers to the other three effects. Numerical scales of such effects are provided by the values σ_F , σ_X , and σ_R , respectively.

Field and electronegativity effects can be investigated separately from the π -electron-transfer mechanism by studying molecules where the substituent is not able to conjugate with a π -system. It is now considered^{18,20} that the field effect, involving a direct through space electrostatic interaction, is the predominant mechanism of transmission where one or more atoms separate the reaction center from the substituent. This is considered to arise from the substituent dipole or charge as felt elsewhere in the molecule at reaction (probe) site. This can be represented as in I.

Such effect are dependent on the size and geometry of the substituent dipole with respect to the probe.

If the probe is a charged group, then the electrostatic energy arising from the interaction is given by eq 1

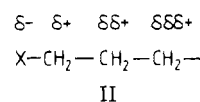


$$E = (q \mu \cos \theta) / Dr^2 \quad (1)$$

where q is the net charge at the probe and D is the dielectric constant. The equation for the effect of the dipole when the probe is the amount of polarization in a bond is given by eq 2.

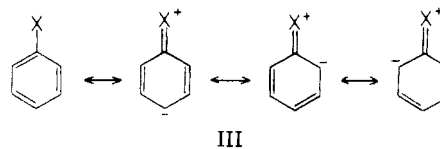
$$\epsilon_{\text{bond}} = \mu(2 \cos \theta \cos \phi - \sin \theta \sin \phi) / r^3 \quad (2)$$

The other possible mode of transmission is the progressive but diminishing relay of polar effects along a chain of carbon atoms as represented in II.



Although it is not generally appreciated, such effects originate in the electronegativity difference between the substituent X and the carbon atom to which it is attached. Thus, so-called σ -inductive effects depend on the group electronegativity of X.

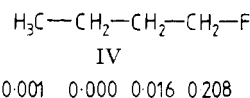
The third major effect (designated R) depends on the ability of X to accept or donate π -charge to an adjacent π -system. Thus, in monosubstituted benzenes, the effect can be represented by canonical forms such as III.



We shall consider each of the three mechanisms in turn and show how theoretical calculations can both afford evidence about their relative importance and also lead to scales of substituent parameters. It is convenient to first discuss electronegativity effects.

Substituent Electronegativity Effects (χ)

Calculations²¹ (STO-3G) on molecules such as 1-ammonio-, 1-fluoro-, or 1-cyanobutane show that the net effect of adding the substituent on the atomic electron population, compared to butane, is very small beyond the first two carbon atoms. The substituent induced changes in electron population at carbon atoms for fluorobutane are given in IV in electron units. This



suggests that transmission through a chain of carbon atoms is not important after the second atom. This is in agreement with an analysis²² of much chemical and

(16) W. H. Hehre, M. Taagepera, R. W. Taft, and R. D. Topsom, *J. Am. Chem. Soc.*, **103**, 1344 (1981).

(17) See, for example, R. T. McIver, Jr., *Science*, **243**, 186 (1980); "Gas-phase Ion Chemistry", M. T. Bowers, Ed., Academic Press, New York, 1979; "Ion Cyclotron Resonance Spectrometry", H. Hartmann and K.-P. Wanczek, Eds., Springer-Verlag, Berlin, 1978.

(18) For a review, see R. D. Topsom, *Prog. Phys. Org. Chem.*, **12**, 1 (1976).

(19) The terminology and symbols are those adopted by W. Adcock, W. J. Reynolds, R. W. Taft, and R. D. Topsom; see, for example, W. J. Reynolds, *Prog. Phys. Org. Chem.*, **14**, 165 (1983). The field effect, F , and the corresponding substituent constant σ_F , correspond to the older symbols I and σ_I .

(20) R. D. Topsom, *J. Am. Chem. Soc.*, **103**, 39 (1981), and references therein.

(21) R. D. Topsom, unreported results.

(22) W. J. Reynolds, *J. Chem. Soc., Perkin Trans. 2*, 985 (1980).

Table I
Substituent Electronegativities^a (Net Atomic Charges
on the Hydrogen Atom in HX Determined at
6-31G**//6-31G* Level)

subst	σ_X (theor)	subst	σ_X (theor)	subst	σ_X (theor)
H	0.00	CHO	0.14	NMe ₂	0.34
Me	0.17	COMe	0.14	NH ₃ ⁺	0.49
Et	0.16	CONH ₂	0.14	NO	0.33
CH ₂ NH ₂	0.16	CO ₂ H	0.18	NO ₂	0.40
CH ₂ OH	0.15	CO ₂ Me	0.19	OH	0.43
CH ₂ F	0.16	COF	0.18	OMe	0.44
CH ₂ CN	0.23	CCH	0.28	OCOMe	0.46
CF ₃	0.17	CN	0.31	O ⁻	0.21
CHCH ₂	0.18	NH ₂	0.31	F	0.52

^a From ref 29.

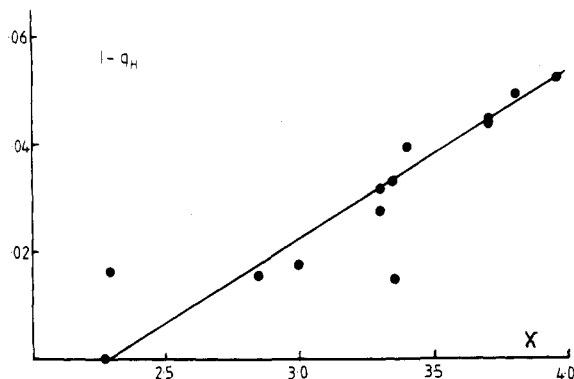


Figure 2.

physical data that failed to find any certain evidence for an effect originating in substituent electronegativity even at close range. The one possible exception was substituent-induced carbon-13 chemical shifts at the α -carbon atom. Earlier suggestions²³ of charge alternation along carbon-atom chains were based on calculations for relatively small molecules. No such effect has been detected experimentally.²⁴

The electronegativity scale has not been well-defined^{25,26} for atoms or substituent groups until recently. The electronegativities of substituents have been the subject of a comprehensive review²⁷ and more recent contributions by other authors.²⁸ However, it has now been shown²⁹ that the electron population at the hydrogen atom attached to the substituent in molecules HX provides an excellent measure of electronegativity. Table I shows the results of such calculations at the 6-31G* level with geometry optimization. The values of $1.000 - q_H$ are on the same scale as older substituent-effect scales and are thus used to define a substituent-electronegativity scale $\sigma_X(\text{theor})$. These values lead to an excellent plot vs. the electronegativity values obtained by Wells²⁷ (Figure 2), and the values for group

(23) J. A. Pople and M. S. Gordon, *J. Am. Chem. Soc.*, **89**, 4253 (1967).

(24) R. D. Stolow, P. W. Samal, and T. W. Giants, *J. Am. Chem. Soc.*, **103**, 197 (1981).

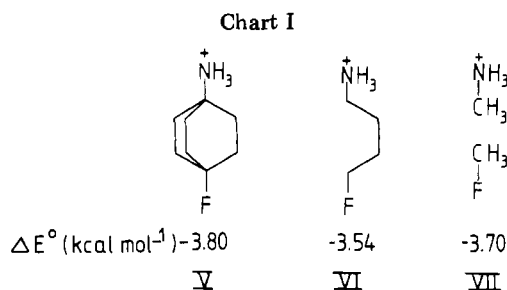
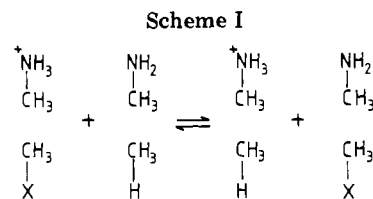
(25) R. J. Boyd and G. E. Markus, *J. Chem. Phys.*, **75**, 5385 (1981).

(26) See, for example, J. E. Huheey, "Inorganic Chemistry", Harper and Row, New York, 1975.

(27) P. R. Wells, *Prog. Phys. Org. Chem.*, **6**, 111 (1968).

(28) See, for example: R. Knorr, *Tetrahedron*, **37**, 929 (1981); J. Gasteiger and M. Marsili, *Org. Magn. Reson.*, **15**, 353 (1981); L. Ernst, V. Wray, V. A. Chertkov, and N. M. Sergeev, *J. Magn. Reson.*, **40**, 55 (1980); N. Inamoto and S. Masuda, *Tetrahedron Lett.*, **3287** (1977), 177 (1978).

(29) W. F. Reynolds, R. W. Taft, S. Marriott, and R. D. Topsom, *Tetrahedron Lett.*, 1055 (1982).



XH_n also followed the most recently derived²⁵ atom electronegativities. Such σ_X values thus provide a simple and clearly defined scale of electronegativity for a wide range of substituents. The constancy of σ_X values for substituents CH₂X shows the negligible transmission of any effect from X through a methylene group. Theoretical calculations of electron populations in more complicated molecules, such as CH₃X, do not²⁹ lead to satisfactory electronegativity scales because of the presence of hyperconjugative charge transfer.³⁰

It has also recently been shown²⁹ that $^1J_{CC}$ values for certain systems, notably $^1J_{CC}$ (ipso-ortho) in monosubstituted benzenes, are related to the calculated electronegativity scale.

Substituent Field Effects (*F*)

The influence of the substituent dipole can also be investigated theoretically. Gas-phase energies for isodesmic proton-transfer equilibria are well-reproduced by ab initio calculations. Such comparisons include aliphatic molecules, for example,⁵ for substituted methylamines and quinuclidines, where the relative energies are proportional to substituent field parameters σ_F . This gives confidence that similar calculations on various conformations of ω -substituted alkylammonium ions provide meaningful results. Such calculations for a variety of geometries have been shown²⁰ to be in general accord with eq 1 rather than depending on the number of intervening carbon atoms between the reaction site and the substituent.

Nevertheless, there is an indication that polarization of the intervening carbon-hydrogen bonds plays some indirect part in determining equilibrium energies, and the work is limited to the number of conformations possible.

The use of isolated molecule calculations much extends the range of the investigation. For example,²⁰ it is possible to use the methylammonium ion at various geometries with respect to a substituted methane. Here the relevant isodesmic process is as shown in Scheme I. A comparison²⁰ between calculations for ω -substituted alkylammonium ions and those for such isolated molecules at corresponding geometries shows that an intervening carbon atom chain does not provide a sig-

(30) Theoretical calculations have shown that σ and π interactions occur in the same fashion in monosubstituted methanes as in monosubstituted benzenes: K. B. Wiberg, *J. Am. Chem. Soc.*, **102**, 1229 (1980).

Table II
Field Parameters, σ_F , Derived from the Effect of Isodesmic Proton Exchange on NH_4^+/HX (first value listed)
or from the Polarization of H_2 by HX (second value listed)^a

subst	$\sigma_F(\text{theor})$	subst	$\sigma_F(\text{theor})$	subst	$\sigma_F(\text{theor})$
<i>t</i> -Bu	-0.03, -0.01	CH_2F	0.16, 0.14	OH	0.29, 0.33
Me	-0.02, -0.01	NH_2	0.16, 0.16	CF_3	0.45, 0.45
H	0.00, 0.00	CO_2Me	0.17, 0.21	COF	0.48, 0.46
CHCH_2	0.01, 0.04	COMe	0.21, 0.23	F	0.49, 0.49
CH_2OH	0.06, 0.01	OMe	0.26, 0.31	CN	0.51, 0.49
CCH	0.12, 0.19	CHO	0.27, 0.24	NO	0.58, 0.60
NMe_2	0.13, 0.15	CHF_2	0.28, 0.30	NO_2	0.71, 0.71

^a Calculations^b are at the 4-31G level; σ_F values are derived from eq 3 and 4, respectively. ^b From ref 31.

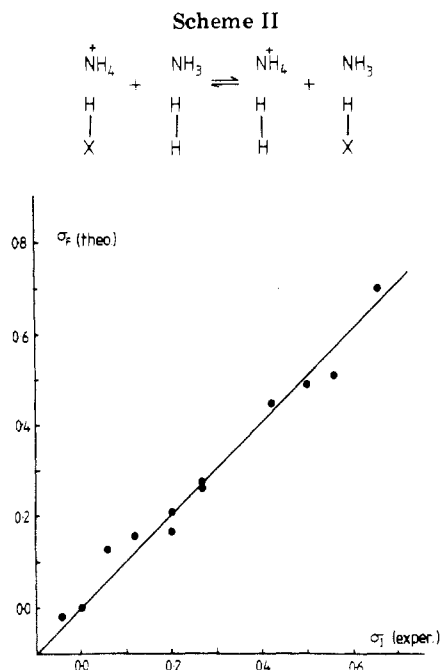


Figure 3.

nificant transmission pathway. For example, calculations (STO-3G) of the energy for the proton-transfer reactions for species V–VII are given in Chart I for corresponding substituent/probe geometries.

A similar result is found for analogous equilibria for carboxylic acids. This is strong evidence against the presence of any σ -inductive effect in these systems.

The system HNH_3^+/HX completely avoids any problem of CH polarization, and calculations³¹ (4-31G) for the isodesmic process in Scheme II are found to give an excellent fit vs. previously published σ_F values as shown in Figure 3. Furthermore, they provide values of σ_F for other substituents according to eq 3, which

$$\sigma_F(\text{theor}) = 0.079\Delta E^\circ \quad (3)$$

applies for a nitrogen to hydrogen distance³² of 4.5 Å where the N and HX are colinear. Some results are given in Table II.

As mentioned above, the polarization of bonds in isolated molecule calculations also follows eq 2. For a system of fixed geometry, the polarization of a bond should change as the substituent dipole. Once again, polarization of adjacent bonds can complicate the situation. However, the electron distributions in simple molecules, such as the polarization of H–H³¹ or the

(31) S. Marriott and R. D. Topsom, *Tetrahedron Lett.*, 1485 (1982).

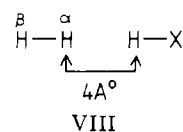
(32) A distance of 4.5 Å is enough to avoid intramolecular charge-transfer effects.

Table III
Calculated (STO-3G) π -Electron Transfer from the Substituent (negative values) or to the Substituent in Monosubstituted Benzenes (values are in 10^3 electrons)

subst	$\Sigma \Delta q_\pi^a$	subst	$\Sigma \Delta q_\pi^a$	subst	$\Sigma \Delta q_\pi^a$
NMe_2	-134	Me	-8	CF_3	11
NHMe	-126	CH_2OH	-7	CONH_2	20
$\text{NH}_2(\text{pl})$	-120	CH_2F	-6	CN	22
NHOH	-119	Et	-5	COMe	28
NHNH_2	-116	CH_2NH_2	-5	NO_2	31
OMe	-105	NH_3^+	0	CHO	32
OH	-102	CCH	5	CO_2H	34
OF	-90	CHCH_2	6	COF	36
F	-80	CHF_2	10	NO	37

^a From ref 35.

π -system of ethylene^{33,34} by an isolated HX molecule, give an excellent measure of the substituent field effect. Table II shows q_H values at the hydrogen in the system VIII as determined³¹ at the 4-31G level. These again



give an excellent relationship to established σ_F values according to the eq 4, where Δq_H is $q_H(\text{X}) - q_H(\text{H})$.

$$\sigma_F(\text{theor}) = 38\Delta q_H \quad (4)$$

Average values of $\sigma_F(\text{theor})$ obtained from eq 3 and 4 are given in Table IV. These results illustrate the fact that eq 1 and 2 lead to a proportionality of field effects on energy and on charge for a series of molecules of approximately constant substituent to probe geometry.

The availability of both a scale of σ_X and σ_F values should allow an analysis of polar effects in nonconjugated systems.

Substituent Resonance Effects

Calculations^{7,35} (STO-3G) have shown that the atomic electron populations in monosubstituted benzenes are in qualitative agreement with the concepts of resonance. Thus, in phenol, the OH group acts as a π -electron donor, leading to an increase, compared to benzene, in the π -electron population (Δq_π) at the ortho and para

(33) S. Marriott and R. D. Topsom, manuscript submitted for publication.

(34) It was earlier shown that the polarization of the π -system of isolated ethylene by CH_2X molecules follows the field effect of the substituent X as measured by a parameter T_F . The geometry was based on the relative positions of the ethylenic linkage and X in para-substituted styrenes: W. F. Reynolds, P. G. Mezey, and G. K. Hamer, *Can. J. Chem.*, 55, 522 (1977). The use of HX avoids the hyperconjugation interaction that can occur in methyl derivatives.

(35) W. J. Hehre, L. Random, and J. A. Pople, *J. Am. Chem. Soc.*, 94, 1496 (1972).

Table IV
Theoretical Substituent Parameters for Some
Common Substituents

subst	σ_X (theor)	σ_F (theor)	σ_R^0 (theor)
NMe ₂	0.34	0.14	-0.58 ^a
NH ₂	0.33	0.16	-0.48 ^b
OMe	0.44	0.29	-0.45
OH	0.43	0.31	-0.44
F	0.52	0.49	-0.34
Me	0.17	-0.02	-0.03
CH ₂ OH	0.15	0.04	0.03
CHCH ₂	0.18	0.03	0.03
CCH	0.28	0.16	0.02
CF ₃	0.17	0.45	0.05
CN	0.31	0.50	0.10
COMe	0.14	0.22	0.12
CO ₂ Me	0.19	0.19	0.14
NO ₂	0.40	0.71	0.13
CHO	0.14	0.26	0.14
COF	0.18	0.47	0.16
NO	0.33	0.59	0.16

^a Planar. ^b Nonplanar (experimental) geometry.

positions in accord with representation III. Similar results (4-31G) are found³³ for the β -position in mono-substituted ethylenes.

It was pointed out³⁶ some years ago using CNDO/2 calculations that the π -charge transfer to or from the substituent ($\sum \Delta q_\pi$) for monosubstituted benzenes followed closely the σ_R^0 scale. Such σ_R^0 values are a measure of the π -charge transfer to or from the substituents in the absence of significant perturbation, for example, in monosubstituted benzenes. These values have been well-established,³⁷ particularly by physical methods such as infrared³⁸ and carbon-13 NMR spectroscopy.^{7,36} It has also been shown that the STO-3G values of $\sum \Delta q_\pi(X)$ follow σ_R^0 closely. A dual substituent parameter analysis of the STO-3G figures shows that there is no significant dependence on field effects. The derived formula²¹ is given in eq 5. Table III lists

$$\sigma_R^0(\text{theor}) = 4.3 \sum \Delta q_\pi \quad (5)$$

values for $\sum \Delta q_\pi$ for common substituents, and σ_R^0 - (theor) values are in Table IV. Similar results have been obtained³³ (4-31G) from monosubstituted ethylenes. In both systems, the use of π -electron transfer is straightforward compared to interaction energies that include both field and π -electron effects, which are not readily separated.

It is also possible to examine substituent π -charge transfers under a variety of conditions of electron demand. The systems investigated³⁹ varied from the extremes of $^+\text{CH}_2\text{X}$ and $^+\text{CH}_2\text{CH}=\text{CHX}$ through to $^-\text{CH}_2\text{CH}=\text{CHX}$ and $^-\text{CH}_2\text{X}$. As shown in Figure 4, the substituent π -electron response to varying demand (as measured by the π -electron population at the relevant carbon atom in the parent compound, i.e., X = H) is continuous and does not appear to be accurately linear or bilinear. The responses for various substituents are also not parallel. Nevertheless, for the usual ranges of

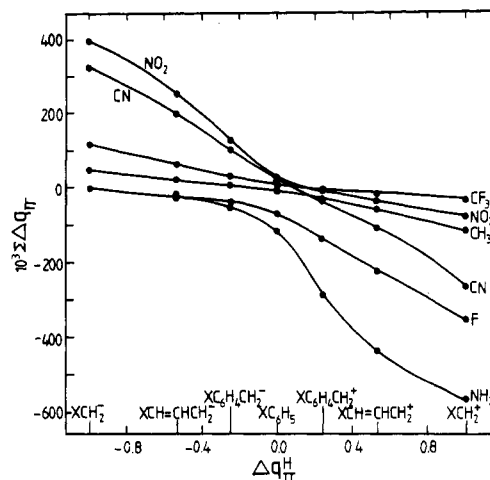


Figure 4.

chemical significance (say from $p\text{-}^+\text{CH}_2\text{C}_6\text{H}_4\text{X}$ to $p\text{-}^-\text{CH}_2\text{C}_6\text{H}_4\text{X}$), the error in treating the substituent induced enhancement or diminution in π -electron responses as bilinear, with $\text{C}_6\text{H}_5\text{X}$ as the point of inflection, seems not to be great. Thus, the use of σ_R^+ , σ_R^0 , and σ_R^- scales is seen to be a reasonable approach. The actual values of the π -electron response under various conditions have been related to σ_R^+ and σ_R^- scales⁴⁰ but are not yet developed³⁹ to such an extent as to generate suitable theoretical scales. Nevertheless, it is clear that some current scales are in error. This is particularly true⁴¹ for σ_R^+ values for substituents such as NO_2 , CN , CF_3 , and CHO . The σ_R^+ values in the literature were taken to be the same as the σ_R^0 values. The theoretical calculations (STO-3G and 4-31G) clearly show that these substituents withdraw less π -charge as the system becomes electron deficient and indeed can act as π -donors under extreme conditions. Experimental evidence⁴² now appears to substantiate this. The null point for most π -electron-withdrawing substituents occurs at about the demand change in the pyridine-pyridinium ion equilibrium, explaining why some workers⁴³ have suggested a lack of resonance effects by such substituents here. Values of σ_R^- for π -electron-donating substituents under conditions of π -electron response are less easy to assess, as substituents such as NH_2 and OMe can change their geometry, and hence π -electron response. Investigations are continuing here.

Summary

The nature of the electronic effect of a substituent on a remote probe can be quite complex. Nevertheless, theoretical calculations have greatly helped to assess the relative importance of the primary mechanisms involved. It is clear that effects deriving from the sub-

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(40) The σ_R^+ scale represents the response of π -electrons in a substituent to a situation of strong demand, for example, in para-substituted benzyl cations, while the σ_R^- scale represents the response in a situation of high π -electron availability, such as in para-substituted benzyl carbanions.

(41) This has also been concluded from theoretical calculation (STO-3G) of the energies of monosubstituted benzenes in the presence of positive charges: E. R. Vorpapel, A. Streitwieser, and S. D. Alexandratos, *J. Am. Chem. Soc.*, **103**, 3777 (1981).

(42) P. G. Gassman and J. J. Talley, *J. Am. Chem. Soc.*, **102**, 1214 (1980); D. A. Dixon, P. A. Charlier, and P. G. Gassman, *ibid.*, **102**, 3957 (1980).

(43) See, for example: A. Fischer, W. J. Galloway, and J. Vaughan, *J. Chem. Soc.*, 3591, 3596 (1964); C. D. Johnson, I. Roberts, and P. G. Taylor, *J. Chem. Soc., Chem. Commun.*, 897 (1977).

stituent dipole and π -electron-donating properties are of primary importance, with substituent electronegativity most likely being of little significance for most systems. It is now possible to generate theoretical scales for all three effects for common substituents, and some values are summarized in Table IV.

Future work is likely to extend preliminary investigations into polarizability effects,⁴⁴ the influence of

(44) See, for example: ref 31 and R. W. Taft, M. Taagepera, J. L. M. Abboud, J. F. Wolf, D. J. DeFrees, W. J. Hehre, J. E. Bartmess, and R. T. McIver, Jr., *J. Am. Chem. Soc.*, **100**, 7765 (1978); J. E. Douglas and P. A. Kollmann, *J. Am. Chem. Soc.*, **102**, 4295 (1980).

substituent dipoles on remote π -systems,⁴⁵ and the role of solvent molecules.⁴⁶

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From Charged to Super-Charged¹ Systems: The Problem of "Aromaticity" in Polycyclic Ions

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Among the fundamental concepts upon which chemistry is based, the notion of aromaticity seems to play a particular and, in a sense, a rather disturbing role.² A variety of chemical and physical phenomena are interpreted as caused by, or directly related to, the aromatic nature of substances. The predisposition to electrophilic substitutions vs. low proclivity toward additions, the unusual tendency of species to release a positive or negative group (e.g., cyclopentadiene, cycloheptatriene), and the existence of significant dipole moments due to uneven electron distribution over different moieties of the molecule are some known examples of how significantly aromatic character and the tendency of species to acquire such a character influence chemical behavior.³

Important physical properties such as enhanced magnetic susceptibilities and characteristic electronic transitions, as expressed by NMR and UV patterns,⁴ are also interpreted as originating from the aromatic nature prevailing in the system under observation. Aromaticity and antiaromaticity (vide infra) play a crucial role in determining properties of species not only in their ground but also in their excited states. Consideration of the relative extent of aromatic or antiaromatic contributions to the transition states was shown to be fully equivalent to consideration of orbital

symmetry in predicting allowed chemical reactions.⁵ Thus, the importance of aromaticity in determining reaction paths is made clear.

In view of the fundamental significance of aromatic character, the general interest in it, and the fact that the first quantum mechanical explanation to this phenomenon was provided as early as 1931,⁶ it is surprising that the concept is still far from being defined and understood. The confusion associated with this subject is mainly due to the fact that neither aromaticity nor ring current phenomena, which are taken as directly related to aromatic nature, is a physically observable property.⁷ Thus, the question whether all the previously mentioned chemical and spectroscopic phenomena are really due to aromaticity is by no means a trivial one, and should be seriously considered.

The numerous definitions suggested to characterize aromaticity point to the heart of the problem. The most comprehensive definition is based on the energy content of systems.^{2a} Aromatic molecules are defined as systems that sustain cyclic π -electron delocalization

(1) The term super-charged systems was introduced by us in order to describe quadruply charged hydrocarbon systems (see ref 26b).

(2) For general series, see: (a) E. D. Bergmann, B. Pullman, Eds., "Aromaticity, Pseudoaromaticity and Antiaromaticity", Jerusalem Academic Press, Jerusalem, 1971; (b) P. J. Garratt, "Aromaticity", McGraw-Hill, London, 1971; (c) A. Streitwieser, "Molecular Orbital Theory for Organic Chemists", Wiley, New York, 1961; (d) I. Agranat and A. Barak, "MTP International Review of Science", Butterworth, London, 1976, Vol. 3; (e) R. Breslow, *Chem. Eng. News*, **43**, 90 (1965); (f) M. Rabinovitz, Ed., "Non Benzenoid and Homoaromatic Systems", *Israel J. Chem.*, **20**, 213-321 (1980); (g) M. J. S. Dewar, "The Molecular Orbital Theory for Organic Chemistry", McGraw-Hill, New York, 1969.

(3) T. Nakajima in "Molecular Orbitals in Chemistry, Physics and Biology", P. O. Löwdin, B. Pullman, Eds., Academic Press, New York, 1964.

(4) NMR: (a) H. Günther, "NMR Spectroscopy: An Introduction", Wiley, New York, 1980; (b) R. C. Haddon, V. R. Haddon, and L. M. Jackman, *Fortschr. Chem. Forsch.*, **16**, 103 (1970/1971); UV: E. Clar, "Polycyclic Hydrocarbons", Academic Press, London, 1964, Vol. 1, pp 133-160.

(5) M. J. S. Dewar, *Angew. Chem., Int. Ed. Engl.*, **10**, 761 (1971).

(6) E. Hückel, *Z. Phys.*, **70**, 204 (1931); *ibid.*, **72**, 310 (1931).

(7) R. B. Mallion, *Pure Appl. Chem.*, **52**, 1541 (1980), and references cited therein.

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