
ELECTRON DENSITY ANALYSIS OF SUBSTITUENT EFFECTS IN SUBSTITUTED BENZENES

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Dedicated to Dr R. Zahradnik on the occasion of his 60th birthday.

Electron projection functions and the corresponding difference functions relative to benzene are computed for π and σ electronic systems of several substituted benzenes, fluorobenzene, toluene and anilinium cation, and idealized model substituents, benzene with an external point positive charge and benzene with an external dipole. The results are plotted and integrated difference populations are compared with Mulliken populations. The later give good agreement, especially for π -systems, but obscure the underlying polarization especially evident in σ systems.

Dr. Zahradnik has had a long interest in the electronic structures of aromatic compounds. The senior author well remembers his first meeting with Rudolf in 1969, the tour of Rudolf's city of Prague which he loves so much and our wonderful discussions of chemistry.

Ab initio molecular orbital calculations have the ability to generate detailed information about electron distributions within a molecule. This approach has been used by a number of researchers to add understanding about the electronic structures of aromatic compounds and especially of substituent effects in substituted benzenes. STO-3G calculations have shown good correlations between electron populations at benzene positions and proton, fluorine and carbon-13 NMR shifts for various substituted benzenes.^{1,2} A series of 4-substituted styrenes and their comparisons with simpler substituted compounds were calculated at the STO-3G level to obtain a direct theoretical measure of the field effect of a polar substituent based on electron population differences.³ It was also possible to obtain substituent induced π effects based on the total change in π -electron populations. A detailed study of STO-3G substituent effects in benzenes has been presented by Pross and Radom.⁴ A recent review of *ab initio* treatments of substituent effects includes applications to benzene systems.⁵ π -Charge populations of substituted benzenes and phenols have also been compared with Taft's substituent constants.⁶ π -Electron populations have also been related to rates of electrophilic substitutions.⁷

All of these correlations make use of Mulliken populations,⁸ which are really basis set populations whose capabilities and important deficiencies are well known

and have been commented upon frequently in the literature.⁹⁻¹¹ Electron populations of regions within a molecule or "atomic charges" are not physical observables and therefore have no unique definition. The topological definition as formulated by Bader¹² has special appeal because it is based on a physical observable, the electron density function, and has chemical sense. Atoms in molecules are defined by Bader in terms of boundary surfaces in three-dimensional space on which the gradient of the electron density, $\nabla\rho(x, y, z)$, is zero. The integrated electron density within such a "zero-flux surface" is an integrated electron population that has important properties. We have made frequent use¹³⁻¹⁷ of an approximation to such integrations based on the projection of the electron density on a convenient plane of a molecule, the Projected Electron Density, and integrations of this function within the two-dimensional zero-flux demarkation contour.¹⁸⁻²⁰ In this paper we apply this method to electronic effects within substituted benzenes. Only a few other studies have been made of electron density functions in aromatic compounds. Hilal²¹ has studied electron density maps of five-membered heterocycles and Bader²² has demonstrated the usefulness of the Laplacian of the electron density function in aromatic compounds.

CALCULATIONS

Wave functions were calculated at the STO-3G level. Molecular geometries were chosen to approximate experimentally determined values and have been previously reported.²³ The projection functions were calculated using the PROJ program.²⁴ This program is limited to approximately 130 gaussian primitives and limits the size of the basis sets that can be used. The program is now being rewritten to be more efficient and to be unlimited in the number of basis functions that can be treated.²⁵ The projection functions were plotted with grid dimensions of 70 by 100 grids with grid spacings of 0.2 au*. We have found such grids to be small enough to be economically feasible while keeping electron density leakage to an acceptable level (<0.006 electrons). The benzene rings were chosen to be regular hexagons and demarkation boundaries were taken to be the three planes meeting at the center of the ring and bisecting the carbon-carbon bonds. This produces integrated populations of CH regions rather than individual carbon and hydrogen atoms. Moreover, this approach means that the integrated projection populations (IPP) should be almost identical to the true topological integrations of Bader.

RESULTS AND DISCUSSION

Traditionally, substituent effects in substituted benzenes have been discussed in terms of the π -system and the σ -system of the molecule. Since benzene is a flat molecule,

* 1 au = 52.917706 pm.

the π -system projection function plot is easily separable from the σ -system. Fig. 1 contains the projection function plots in contour form for the valence electrons of benzene, separated into π and σ contributions. The contour lines represent the number of electrons per square atomic unit. A stick structure for benzene has been added to show the positions of the carbon and hydrogen atoms. In the π -system, one can clearly see that most of the electron density resides close to the carbon atoms and only a small amount ($<0.15 \text{ e au}^{-2}$) can be seen between the carbon atoms. In the σ -system, much of the electron density is between the nuclei. These electron

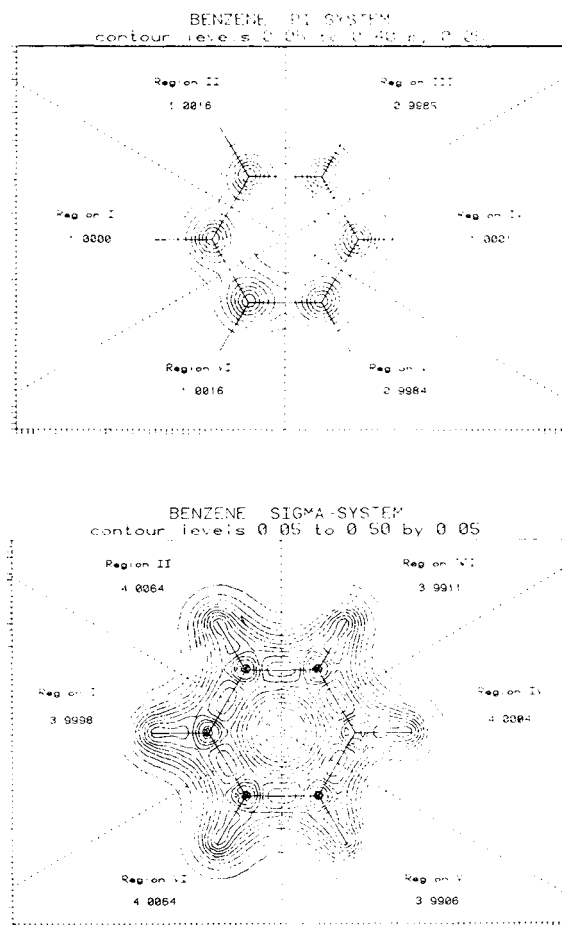


FIG. 1

Projection function plots for benzene; top: π -system; bottom: σ -system. Contour levels are 0.05 to 0.50 by 0.05 e au^{-2} . Results for numerical integrations in the different regions are shown

densities correspond to the electron distributions in benzene at the potential energy minimum, where all atomic motion has ceased. Comparisons between electron densities obtained from X-ray diffraction data and vibrationally averaged calculated densities²⁶ show that calculated electron densities are reasonable and may be used to understand the changes in electron density induced by various substituents.

Dissection of the molecule into six regions and integrating allows comparisons to be made with Mulliken population analysis results (Table I). The differences among the six equivalent positions in benzene gives a measure of the accuracy of the numerical integrations and the interpolation between grid points. The numerical integrations are based on grid spacings of 0.2 au, a value which we have found to be sufficiently fine for most purposes. The carbon and hydrogen atoms have been included together to avoid some of the inherent deficiencies in the Mulliken scheme (vide supra). That is, by combining the C and H populations we treat the "regional" populations of different positions. Mulliken analysis gives a total of 24.0435 elec-

TABLE I

Net charges at different positions for several perturbed and substituted benzenes from integrated projection population differences relative to benzene, STO-3G. Mulliken charges are included in parentheses for comparison

Electronic system	Population changes at position							
	<i>ipso</i>		<i>ortho</i>		<i>meta</i>		<i>para</i>	
(+) benzene								
π	-0.158	(0.174)	0.021	(0.027)	0.023	(0.022)	0.072	(0.075)
σ	-0.094	(.106)	.017	(.016)	.028	(.035)	.004	(.002)
(dipole) benzene								
π	-0.070	(-.078)	.018	(.022)	.004	(.002)	.028	(.029)
fluorobenzene								
π	.003	(-.008)	-.036	(-.038)	.012	(.015)	-.012	(-.018)
σ		(.212)	.020	(.023)	.003	(.000)	.008	(.012)
toluene								
π	.016	(.027)	-.018	(-.017)	.004	(.006)	-.014	(-.012)
σ		(.051)	.002	(.006)	-.002	(-.005)	.006	(.005)
anilinium cation								
π		(-.158)	.003	(.012)	.030	(.031)	.069	(.072)
σ		(1.230)	.011	(.018)	.030	(.028)	.008	(.000)

trons, while the integrated projection function gives a total of 23.9947 electrons. The Mulliken analysis gives too large a number because in a minimum basis set calculation, some of the 2s function is used to describe the core. This is not taken into account in the simple Mulliken population analysis used here and produces an excess electron population in the valence electron description. The slight deficit in the integrated result is due to leakage of electron density off the grid. A larger grid would decrease this error but the loss of $<0.006e$ is relatively small.

The major advantage to using the projection function analysis is seen in difference maps. That is, difference maps represent a direct measure of the amount of charge redistribution between two molecules. Fig. 2 shows the difference plots for the valence electrons of benzene perturbed by a positive point charge minus benzene. The charge is located 1 \AA^* away from a hydrogen atom as shown. It is instructive to use such simple, though unreal systems, so that real substituents can be understood using the concepts gleaned from the simple systems. This approach was used earlier to model Hammett σ effects.^{2,3} The molecule has been divided into regions as before such that Regions I, II, III and IV correspond to *ipso*, *ortho*, *meta* and *para*, respectively. The changes in integrated electron populations relative to benzene are given in the figure. These are converted to the corresponding net charges in Table I and compared with the corresponding Mulliken population charges (in parentheses). The Mulliken charges compare well with the integrated charges in this case. A similar calculation was made for a benzene ring perturbed by a negative charge; the results were similar to the positive charge case but of opposite sign.

Two important features emerge from the projection function difference maps. In the π -system, the projection function changes at the different positions are simple and there is no difficulty in assigning regions of demarcation such as the bond bisectors used. Even for the *ipso* carbon, the zero contour, which is the solid contour that meanders between the *ipso* and *ortho* carbons, is close to the bond bisector. The π -charges therefore have a simple and straightforward significance. For the σ -system, however, the situation is much more complex. Bond polarizations are now the dominant feature and are characterized by positive and negative contours on opposite sides of bond midpoints. The integration about a CH group now adds together positive and negative regions to give resulting net "charges" that completely obscure the underlying complex polarizations. Such obscuring of polarization is inherent in any scheme that integrates a spherical region about an atom or simply adds together the populations of basis functions centered on atoms as in the Mulliken procedure.

The concept of a "bond profile" may be useful to visualize better the observed polarizations in terms commonly used to describe substituent effects (i.e., through-bond inductive effects, field effects, etc.). The bond profile is defined as the value

* $1 \text{ \AA} = 10^{-10} \text{ m}$.

of the projection function difference densities along the C—C bonds. The distance along the carbon chain is displayed as the abscissa in atomic units while the number of electrons per square atomic unit at any point along the carbon chain is displayed as the ordinate. Points above the abscissa represent negatively charged regions while points below the line represent positively charged regions relative to benzene. Fig. 3 shows the bond profiles for the π and σ -systems of point charge perturbed benzene

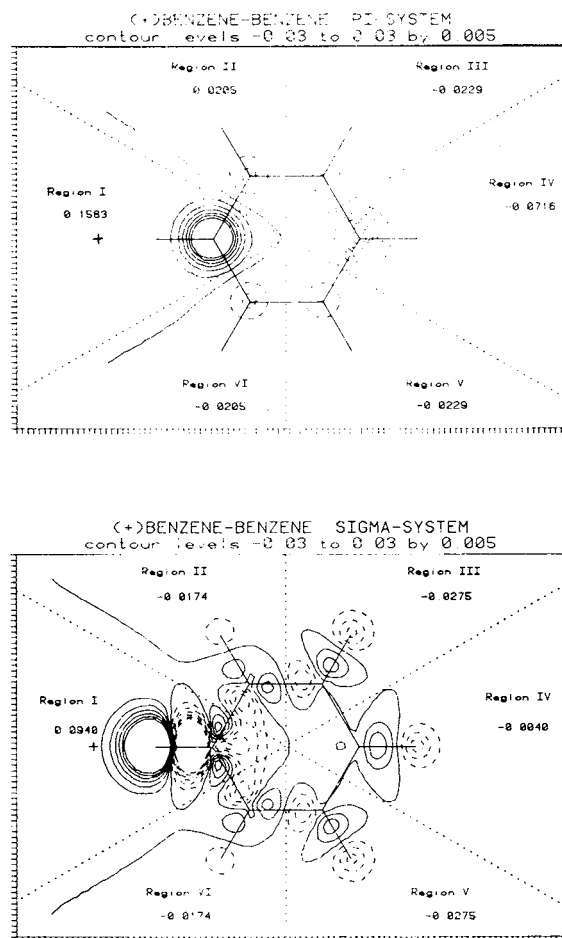


FIG. 2

Projection function difference maps for positive point charge perturbed benzene minus benzene. Contour level units are from -0.03 to $+0.03$ by 0.005 e au^{-2} . Negative contours are dashed. The zero contour is the first full contour. Integrated difference populations are given for each CH region

with respect to benzene. The π -system has a large negative charge at the *ipso* carbon and a large positive charge at the *para* carbon. This is consistent with the high degree of polarizability normally attributed to π -electronic systems. Minima between *ortho*

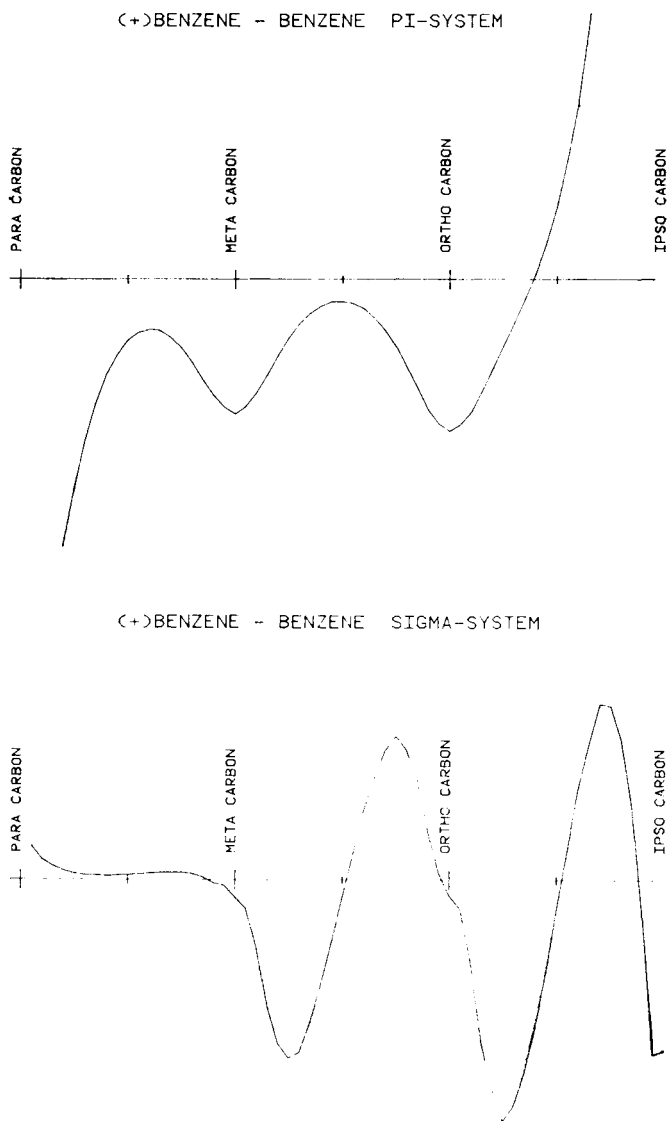


FIG. 3

Benzene bond profiles for positive point charge perturbed benzene with respect to benzene along C—C bonds

and *meta* and between *meta* and *para* carbons occur close to bond midpoints and one can "see" simple charge effects at the different ring positions. The σ -system is quite different. The trends at the *ortho* and particularly the *meta* carbon are especially intriguing. The σ -system bond profile shows a large amount of charge oscillation along the first two C—C bonds, but the charge distribution between the *meta* and *para* carbons differs little from that in benzene itself. This is probably due to a combination of effects, all of which must stem from a field effect since this is the only effect a pure point charge can have in this system. The force field "felt" by the C—C bonds decreases in the ratio 6 : 4 : 1 as one moves away from the point charge. This seems to be the case for the first two bonds; however, the σ -bonds around the *para* carbon seem to be responding to the large positive charge in the π -system near the *para* carbon. Note how the midpoints of the polarization changes at the *ortho* and *meta* carbons occur close to bond midpoints and atomic centers. These polarization changes are totally invisible in normal integration and population analyses.

Since most substituents are dipolar in nature, benzene was also perturbed with an external dipole of 3.5 Debye.* It has been shown²³ that this dipole "substituent" mimics the substituent effect for nitrobenzene when the nitro group is orthogonal to the benzene ring. Thus, the charge distributions for "dipole perturbed benzene" should model those arising from a pure dipolar substituent. Fig. 4 shows the projection function difference maps for benzene perturbed by a dipole minus benzene. Only the π -system has been integrated and this may be compared with the Mulliken analysis results in Table I. The corresponding bond profiles are shown in Fig. 5.

The σ -system has the same type of polarizations along the bonds though smaller in magnitude than for the positive point charge perturbed case. Note that a finer contour difference is used for Fig. 4 compared to Fig. 2. The π -system shows the type of distribution that we may refer to as a " π -inductive effect". Different definitions have been used for this term,²⁷⁻²⁹ and various charge redistribution patterns have been deduced either from experiment^{30,31} or theory.³² The confusion in definition and the resulting atomic charge redistribution appears to lie in the mechanism by which the " π -inductive effect" is transmitted to the π -system. The original definition employed by Jaffe³³ and later by Dewar and Grisdale³⁴ does not include a primary field effect from the substituent dipole for its transmission. The " π -inductive effect" defined in this way has been shown by experimental and theoretical arguments to be, at most, very small.³⁵ A second definition does include through-space electrostatic interactions as one of the three possible mechanisms^{28,29} that include the so-called π_F , π_σ , and π_{orb} effects.^{1,2} In the above treatments of charge or dipole perturbed benzenes as "substituent" effects, the charge redistribution which takes place in the π -system must have as the primary mode of transmission a direct through-space interaction (field effect).

* 1 Debye = $3.33564 \cdot 10^{-30}$ C m.

The above perturbations to the benzene ring have not changed the total number of electrons or the number of basis functions used to describe them. It is known³⁶ that comparisons between two molecules which differ in the quality of basis set can lead to erroneous conclusions, especially in minimum basis set calculations. This is a consequence of the approximate nature of any Hartree-Fock scheme which uses a finite number of basis functions. In the present context, any substituent that replaces a hydrogen atom should have the same quality basis set as the hydrogen

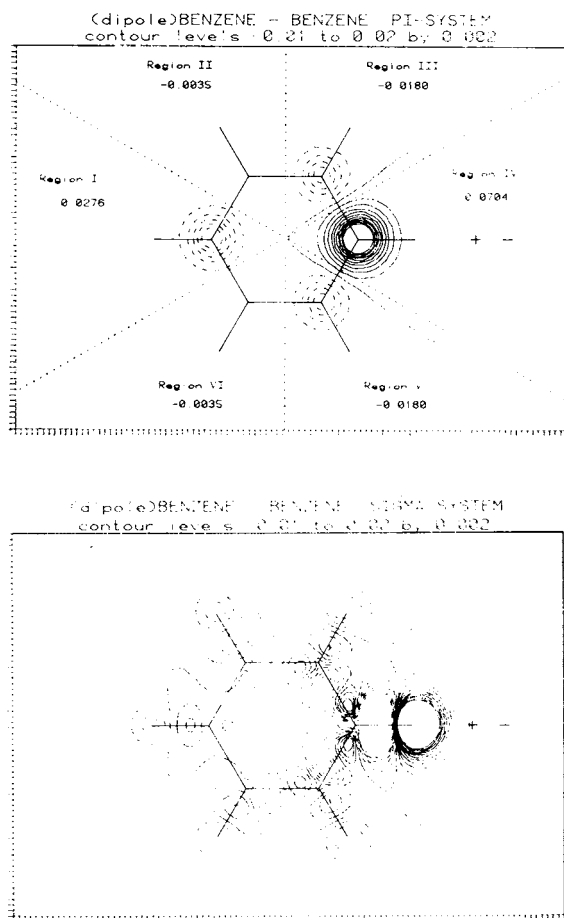


FIG. 4

Projection function difference maps for dipole perturbed benzene minus benzene as in Fig. 2. Contour level units are from -0.01 to $+0.02$ by 0.002 e au^{-2}

atom, otherwise comparisons between the two will be cluttered with computational artifacts.

In order to test for the magnitude of this effect, one of the hydrogen atoms was assigned an extended basis set which included p functions (4-31G** polarization functions on hydrogen). The results of this "phantom orbital effect" are shown as difference maps in Fig. 6. The overall effect is small compared to changes caused by various types of model and real substituents. Note that the direction of the effect

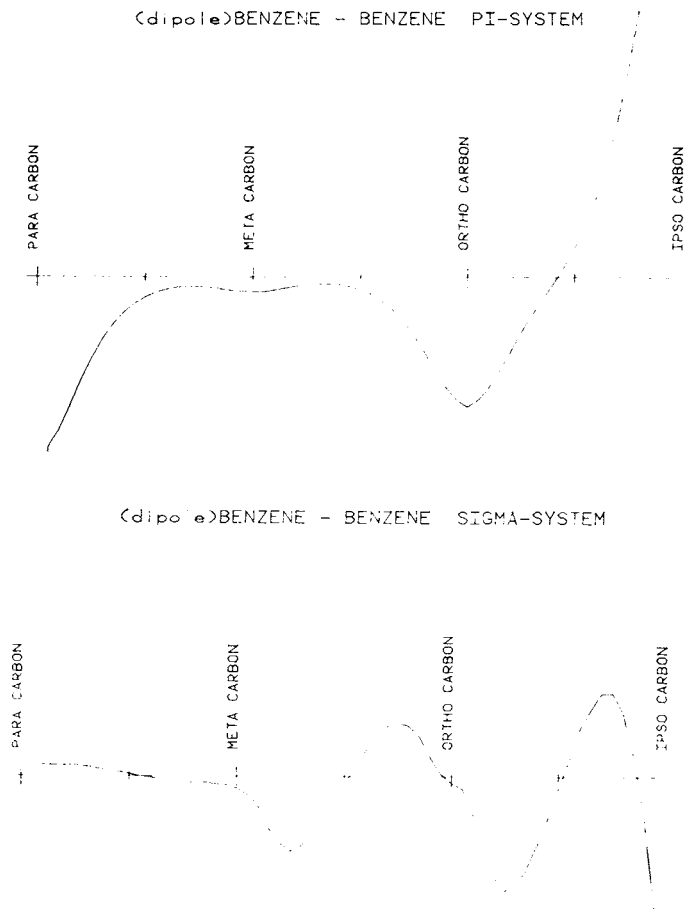


FIG. 5

Benzene bond profiles for dipole perturbed benzene with respect to benzene along the C—C bonds

is expected. The additional basis functions on the H* hydrogen make it effectively electron-withdrawing; electrons concentrate in regions where more mathematical functions are available for their description.

We next turn to several real substituents for comparison. Fluorobenzene is important because of extensive work done with ^{19}F NMR^{1,2,37} and because it is a typical π -donating σ -withdrawing substituent. Fig. 7 shows the projection difference plot. Several important features should be noticed. In the π -system, "atomic charges" correspond well with Mulliken charges (Table I) for most carbon atoms except for the *ipso* carbon. The simple Mulliken scheme assigns some of the electron density at fluorine to the carbon atom. The π -electron charge redistributions can be interpreted as a combination of a π_{F} effect stemming from the C—F bond dipole and the π -donating conjugating effect of the fluorine substituent. From the atomic charge assigned to the fluorine atom in Region IV, the amount of charge donated to the ring is 0.06e. The conjugation effect increases the electron density at the *para* and *ortho* carbons while the π_{F} effect decreases electron density at the *para* and *meta* carbons and increases electron density at the *ortho* carbon. The σ -system is much more complex than the Mulliken analysis reveals and is probably best understood in terms of the bond profile given in Fig. 8. Polarizations across the C—C bonds are clearly important. The oscillations can probably be best interpreted as a combination of field effects induced by the C—F bond dipole and a response of the σ -system to charges in the π -system (σ_{π} effect). If the π -system were not present, the polarizations along the C—C bonds would slowly damp out as the distance from the perturbing dipole increases.³⁹ However, with the π -system present, any oscillation which would increase electron density in a region where a large electron density exists in the π -system is decreased or reversed. This phenomenon has already been mentioned in the point charge and dipole perturbed benzenes where polarization in the *meta* carbon-*para* carbon bond region is affected. In fluorobenzene it is the *ortho* carbon-*meta* carbon bond region that is primarily affected in this manner.

In the extensive study of Hehre, Taft and Topsom^{1,2} an attempt was made to correlate theoretically calculated Mulliken populations with NMR substituent shifts. They generally found excellent correlations with *para* substituted systems but poor correlations in the *meta* substituted systems. This result can be readily understood with the aid of the bond profile of fluorobenzene. Recall that Mulliken schemes tend to average the electron populations and obscure any underlying polarization. At the *para* carbon all of the electron density changes between that carbon and midway to the *meta* carbons are of the same sign. However, this is not the case for the *meta* carbon. On one side the change is negative and on the other side it is positive. The result is that the net change in electron density induced at the *meta* carbon by different substituents will tend to be cancelled in the Mulliken scheme.

Another molecule of interest is toluene since the methyl substituent is an important donating group. The projection function difference plots are shown in Fig. 9. In this

figure several smaller subregions have been integrated in order to get a better understanding of the total charge involved in these systems. The zero contours are now represented by dot-dash lines. The π -system charge redistribution pattern is similar to that of fluorobenzene but smaller in magnitude. Extensive theoretical calculations have shown that the redistribution pattern of the π -system is due not to any significant net π -donation to the ring but by polarization that can be rationalized by second order perturbation theory.⁴⁰ The total amount of charge donated to

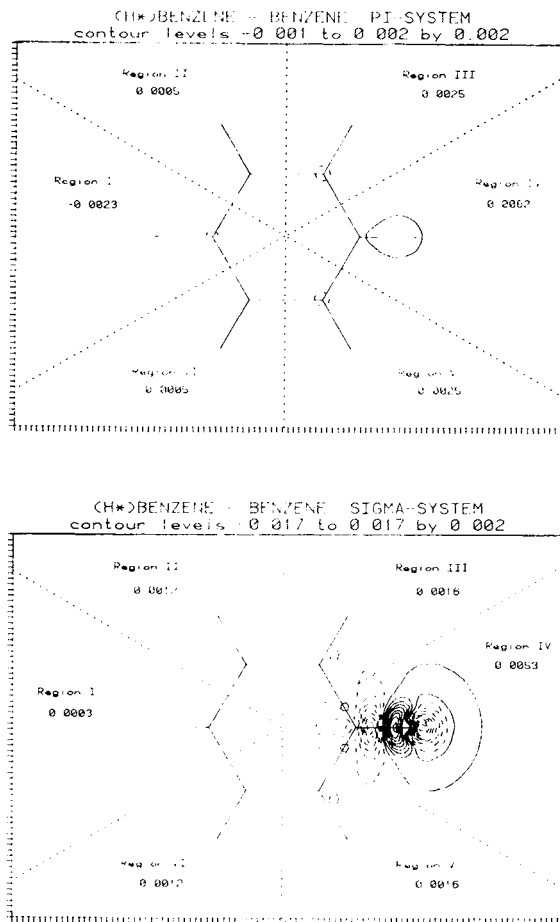


FIG. 6

Projection function difference maps for benzene with an extended basis set on one hydrogen atom (4-31G**) minus benzene. Contour levels are -0.001 to 0.002 by 0.002 e au^{-2} in the π -system (top) and -0.017 to 0.017 by 0.002 e au^{-2} in the σ -system (bottom)

the π -system is $0.02e$, about one third that in fluorobenzene. The σ -system has very little charge redistribution. From the bond profile in Fig. 10, one can see that polarization oscillations are small. In fact, they are almost totally dominated by charges in the π -system. This is not surprising because of the small magnitude of the sp^2-sp^3 bond dipole.

Protonated aniline is the final molecule considered in this series. The C—N bond length used in the calculation was the same as the C—C bond length in toluene

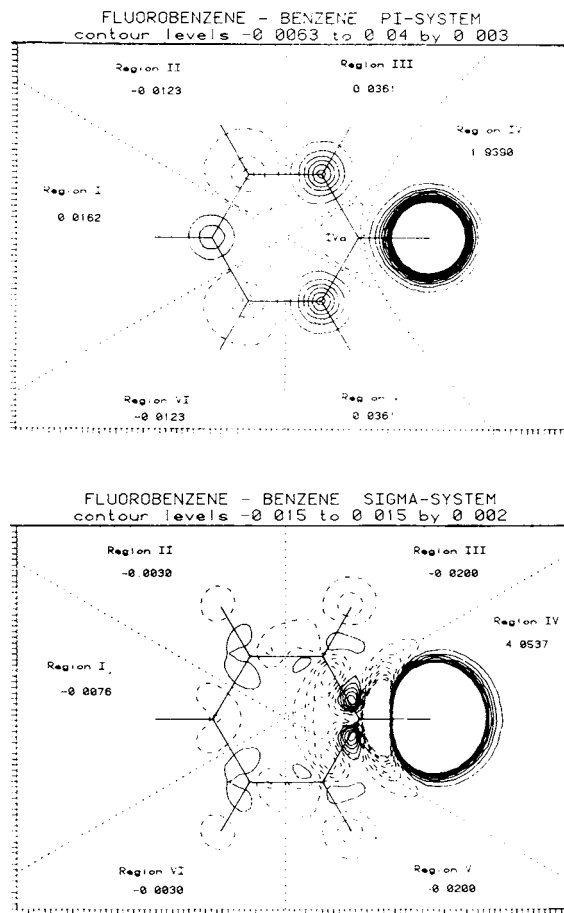


FIG. 7

Projection function difference maps for fluorobenzene minus benzene. Contour intervals are $0.003 e au^{-2}$ for the π -system (top) and $0.002 e au^{-2}$ for the σ -system (bottom). The integrated value of Region IVa = $-0.0027e$

(the optimized C—N bond length differs by only 0.0077 Å) in order to provide a direct comparison with toluene. The difference maps with respect to benzene are shown in Fig. 11. The π -system redistribution of electrons looks similar to that shown earlier for the point charge perturbed benzene but with the *meta* and *ortho* distributions reversed. In fact, if one compares the bond profiles for the π -system electron density distribution in toluene (Fig. 10) and the positive point charge perturbed benzene (Fig. 3), their sum is close to the π -bond profile for anilinium ion (Fig. 12). It is important to notice that there is no significant transfer of π -electrons to or from the ring. The σ -system resembles that of the positive point charge perturbed benzene. Indeed, the entire difference projection functions for anilinium ion closely resemble the sum of those for toluene and the point positive charge.

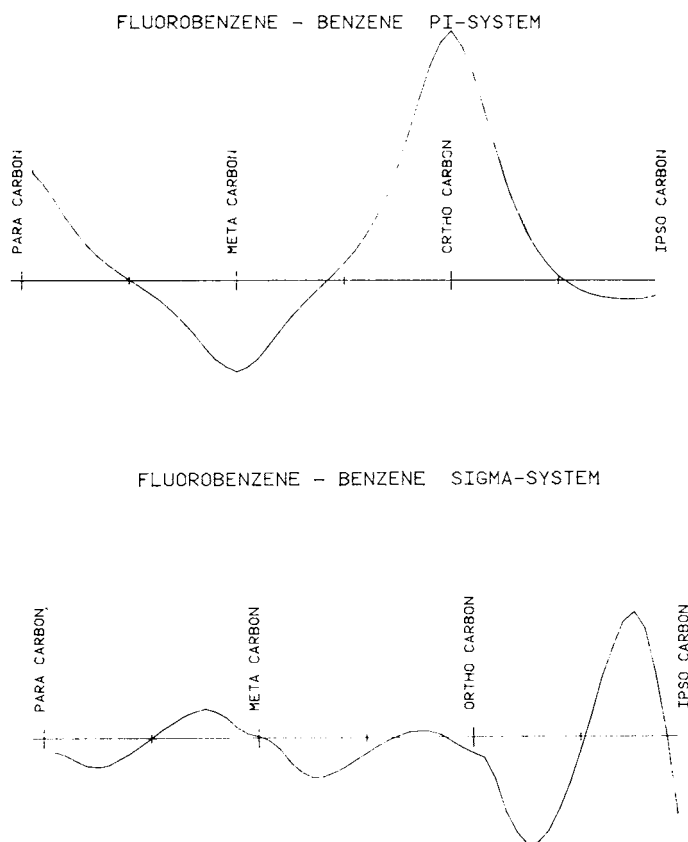


FIG. 8

Bond profiles for fluorobenzene relative to benzene along the C—C bonds

The polarized regions along the *meta* C—H bond, the C—C bond and the *ortho* C—H bond were integrated to determine the actual charge associated with these regions. The values are quite large and have the same order of magnitude as the charge differences in the π -system of fluorobenzene. These large polarizations may

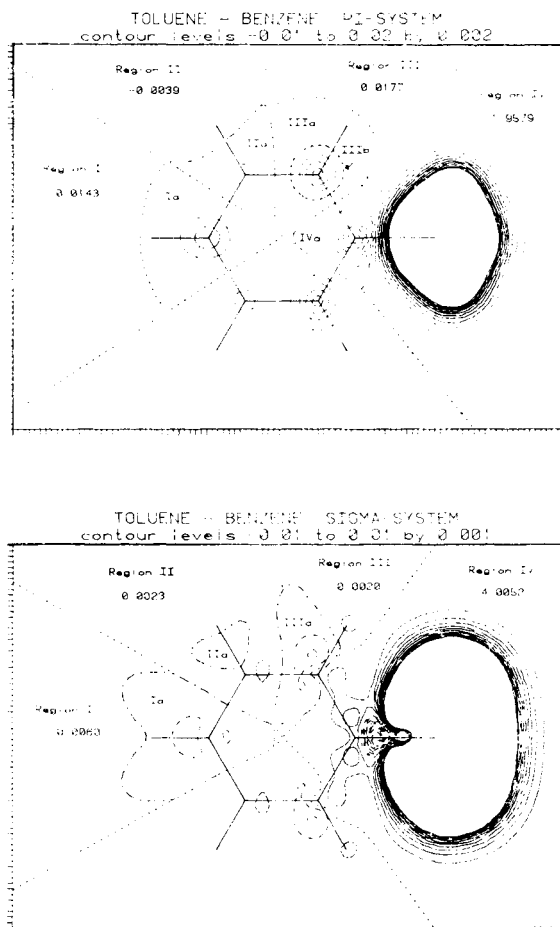


FIG. 9

Projection function difference maps for toluene minus benzene. Contour levels are -0.01 to 0.02 by 0.002 e au^{-2} in the π -system (top) and -0.01 to 0.01 by 0.001 e au^{-2} in the σ -system (bottom). Integrations for the addition regions indicated are: π -system: region Ia = $0.0137e$, region IIa = $0.0042e$, region IIIa = $0.0174e$, region IIIb = $0.0124e$, region IVa = $-0.0163e$; σ -system: region Ia = $-0.0061e$, region IIa = $-0.0004e$, region IIIa = $-0.0039e$

affect the "breathing mode" vibrations (ν_{16a} and ν_{16b}) of anilinium ion in the infrared absorption spectrum. This effect could be the reason for the apparent resonance donor activity attributed to charged substituents by Katritzky and Topsom.⁴¹

CONCLUSIONS

Mulliken population analysis schemes used to assign "atomic charges" in substituted benzenes are meaningful for π -benzenoid systems at the *para*, *meta* and *ortho* positions. Polarization effects of the σ -system are totally obscured in any Mulliken type scheme or integration procedure that averages polarization effects about an atom.

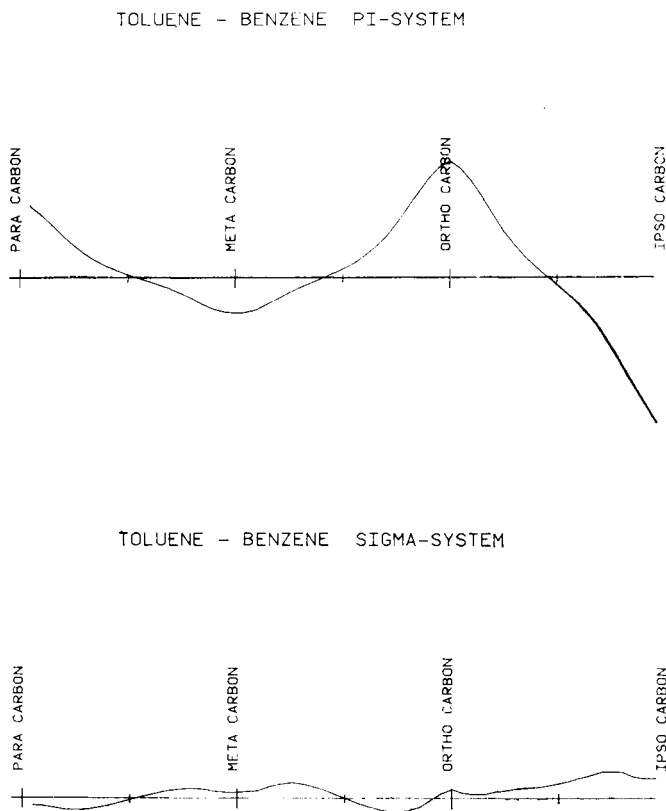


FIG. 10

Benzene bond profiles for toluene with respect to benzene along the C—C bonds

The major feature for the substituent effect in the σ -system is longitudinal polarization along bonds. These polarizations appear to be caused by direct field effects and are strongly dependent on the π -system. The ammonium group does not donate electron density to the benzene ring. Changes in "breathing mode" vibrations seen

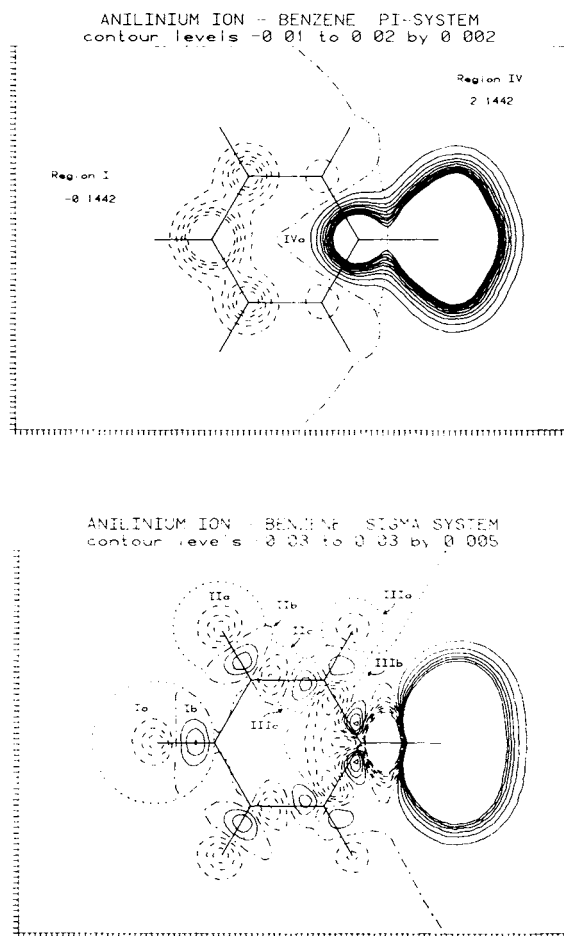


FIG. 11

Projection function difference maps for anilinium ion minus benzene. Contour levels are -0.01 to 0.02 by 0.002 e au^{-2} in the π -system (top) and -0.03 to 0.03 by 0.005 e au^{-2} in the σ -system (bottom). Integrations for the subsystems are: π -system: region IVa = $0.1474e$; σ -system: region Ia = $-0.0301e$, region Ib = $0.0173e$, region IIa = $-0.0285e$, region IIb = $0.0118e$, region IIc = $-0.0134e$, region IIIa = $-0.0139e$, region IIIb = $0.0065e$, region IIIc = $0.0080e$

in IR spectra are probably due to large polarizations in the σ -system. Phantom orbital effects (basis set superposition errors) can cause spurious results in minimum

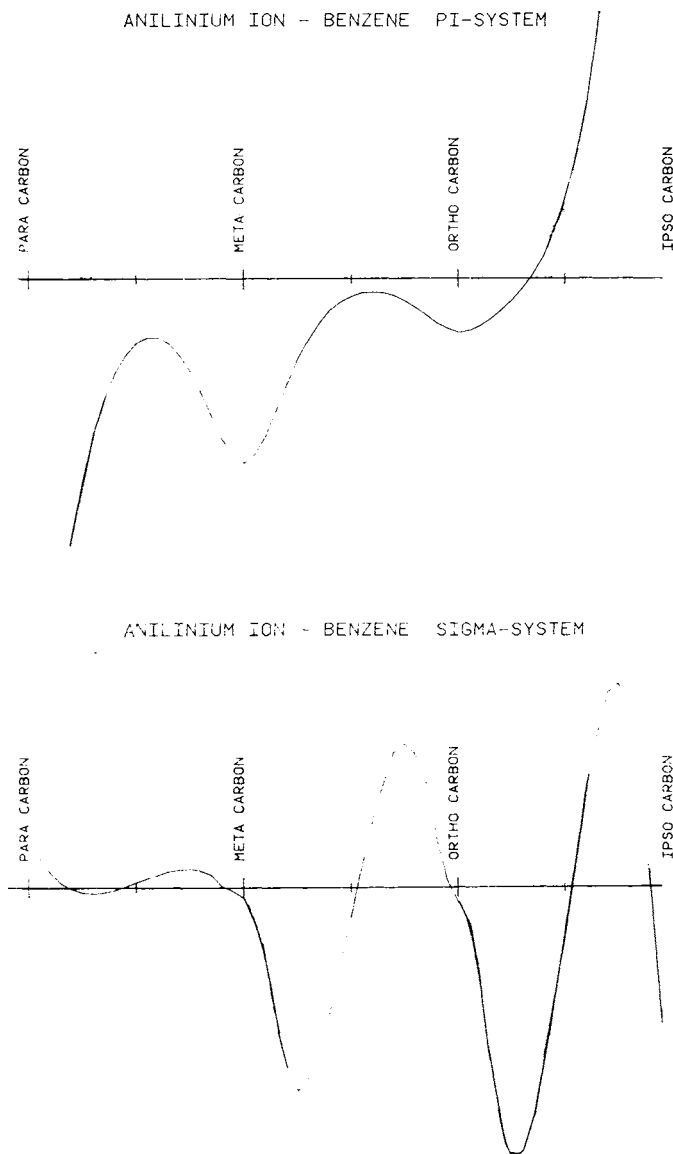


FIG. 12
Bond profiles for anilinium ion with respect to benzene along the C—C bonds

basis set *ab initio* calculations that can mimic π -inductive effects. Discretion must be used when interpreting such calculations.

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