

Substituent Effects. 7. Phenyl Derivatives. When Is a Fluorine a π -Donor?

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The effect of substituents on the energies of phenyl derivatives was examined with the aid of group-transfer reactions with ethane to give toluene and a substituted methane. The energies of these reactions were linearly related with a slope of 1 to those found for a corresponding set of vinyl derivatives. A comparison of the bond dissociation energies of the phenyl and vinyl derivatives gave the same result, indicating that substituents interact with benzene and ethylene in the same fashion and to the same degree. Further information was provided by rotational barriers and electron-density difference plots. The protonated forms of benzene, toluene, fluorobenzene, and chlorobenzene were examined, and the MP3/6-311++G** calculated proton affinities were in good agreement with the experimental data that found the halobenzenes to be slightly more basic than benzene in the gas phase. The para positions were the more basic, and the *m*-positions were less basic by 8–9 kcal/mol. The question of when fluorine is a π -donor was examined.

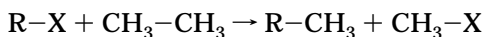
1. Introduction

The interaction of a benzene ring with substituents has been of considerable interest to organic chemists for many years and has been the subject of many theoretical studies.^{2,3} The work through 1980, based on STO-3G wave functions and standard geometries, has been summarized by Pross and Radom, and they have presented a detailed analysis of the results in terms of PMO theory.⁴ Streitwieser and Vorpapel² have made use of projection density plots to study the shifts in electron density caused by substituents.

Despite the many studies that have been carried out, it still was not clear to us just how the substituents interacted with the benzene ring. We have recently carried out studies of the interaction of substituents with vinyl groups,⁵ and we thought a comparison between a vinyl and a phenyl group might be instructive. We wished to compare the energetics of the interactions and to study the changes in charge distribution that result from the substituents. We were particularly interested in the question of σ/π polarization that we found to be a common feature of substituent effects.^{5,6} The question of how fluorine interacts with a benzene ring was also of interest to us since we had not found evidence of π -donation by fluorine toward a carbonyl group⁷ or a vinyl group.⁵

2. Substituent Interaction Energies

In our studies of acetyl and vinyl derivatives, we found it useful to examine bond separation reactions of the type



They will show if the substituent, X, prefers to be attached to the group R or to a methyl group. Thermo-

Table 1. Isodesmic Reaction Energies

Reaction	ΔH	$\Delta H(\text{calc})^a$		
		obs	MP2	MP2* MP3*
+ H ₃ C-CH ₃ → + H ₃ C-H	-5.5±0.3	-7.0	-6.9	-5.4
+ H ₃ C-CH ₃ → + H ₃ CLi	na	0.4	-0.7	-0.6
+ H ₃ C-CH ₃ → + H ₃ C-NH ₂	+5.7±0.4	5.6	5.9	5.8
+ H ₃ C-CH ₃ → + H ₃ C-OH	+6.8±0.3	4.7	4.8	5.3
+ H ₃ C-CH ₃ → + H ₃ C-F	+3.8±2.0	1.0	1.7	3.3
+ H ₃ C-CH ₃ → + H ₃ C-SiH ₃	na	-3.0	-3.5	-3.7
+ H ₃ C-CH ₃ → + H ₃ C-PH ₂	na	-0.4	-0.4	-1.2
+ H ₃ C-CH ₃ → + H ₃ C-SH	-0.4±0.3	1.0	1.2	0.0
+ H ₃ C-CH ₃ → + H ₃ C-Cl	0.0±0.4	1.4	1.7	0.9
+ H ₃ C-CH ₃ → + H ₃ C-CN	-1.8±0.5	-1.2	-1.2	-2.4
+ H ₃ C-CH ₃ → + H ₃ C-NO ₂	-1.8±0.2	-0.8	-0.8	-0.8

^a MP2 = MP2/6-31+G*, MP2* = MP2/6-311++G**, MP3* = MP3/6-311++G**.

chemical data for many phenyl derivatives are available, allowing these energies to be obtained (Table 1). In some cases of interest, the experimental data were not available, and therefore, the energies have been calculated.

Although the energies of many of these compounds have previously been calculated using modest basis sets, it is known that inclusion of diffuse functions (+) is needed in order to properly describe lone pairs⁸ and that

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Table 2. Calculated Energies, Hartrees^a

compd	MP2/6-31+G*	MP2/6-311++G**	MP3/6-311++G**	ZPE ^b
benzene	-231.472 03	-231.593 33	-231.620 63	60.3
toluene	-270.644 17	-270.795 17	-270.831 20	76.7
phenyllithium	-238.316 58	-238.434 39	-238.456 06	53.5
aniline	-286.670 85	-286.827 30	-286.855 22	70.4
aniline (rot.)	-286.664 07	-286.820 22	-286.848 83	70.2
phenol	-306.512 11	-306.678 76	-306.699 80	62.9
phenol (rot.)	-306.507 44	-306.674 15	-306.695 74	62.5
fluorobenzene	-330.501 10	-330.676 90	-330.695 65	55.6
phenylsilane	-521.631 99	-521.799 16	-521.838 99	69.3
phenylphosphine	-572.871 14	-573.034 34	-573.071 99	65.2
phenylthiol	-629.103 96	-629.262 33	-629.295 85	59.9
phenylthiol (rot.)	-629.104 51	-629.263 08	-629.296 72	59.9
chlorobenzene	-690.506 12	-690.654 86	-690.685 45	54.8
benzonitrile	323.490 64	-323.635 83	-323.646 24	59.8
nitrobenzene	-435.497 07	-435.709 49	-435.699 17	62.6
methane	-40.334 08	-40.380 37	-40.399 69	26.8
methylithium	-47.166 82	-47.211 89	-47.227 25	19.9
ethane	-79.497 60	-79.574 19	-79.604 06	44.7
methylamine	-95.515 70	-95.597 24	-95.619 25	38.6
methanol	-115.357 84	-115.449 95	-115.464 00	30.8
methyl fluoride	-139.353 50	-139.453 91	-139.463 97	24.0
methylsilane	-330.489 05	-330.582 59	-330.616 55	36.5
methylphosphine	-381.724 56	-381.813 47	-381.846 24	32.9
methanethiol	-437.955 75	-438.039 43	-438.068 67	27.8
methyl chloride	-499.357 47	-499.431 35	-499.45704	22.8
ethyl fluoride	-178.526 64	-178.656 34	-178.677 14	41.0
acetonitrile	-132.345 36	-132.416 18	-132.422 36	27.4
nitromethane	-244.351 76	-244.489 85	-244.473 38	30.6

^a The frozen core option was used for the MP2 and MP3 calculations. The 6-311++G** calculations were carried out using the MP2/6-31+G* geometries and used six Cartesian d functions. ^b HF/6-31G* scaled by 0.893.

Table 3. MP2/6-31+G* Structural Data for the Phenyl Derivatives

X	$r(\text{C}-\text{X})$	$r(\text{C}_1-\text{C}_2)$	$\angle\text{C}_6\text{C}_1\text{C}_2$
Li	1.9983	1.4182	114.22
H	1.0887	1.3992	120.00
CH ₃	1.5077	1.4029	118.34
NH ₂	1.4084	1.4036	119.21
OH	1.3798	1.3983 ^a	120.51
F	1.3693	1.3899	123.04
SiH ₃	1.8814	1.4082	118.04
PH ₂	1.8470	1.4052 ^a	118.61
SH	1.7753	1.4026 ^a	119.42
Cl	1.7419	1.3968	121.22
CN	1.4370	1.4051	120.62
NO ₂	1.4742	1.3947	122.78

^a Average of two bond lengths.

correction for electron correlation is needed in order to reproduce experimental structural data and to correctly reproduce relative energies.⁹ Therefore, geometry optimizations have been carried out at the MP2/6-31+G* level using the frozen core option giving the energies summarized in Table 2. Some key structural parameters are summarized in Table 3, and the full structural data are available as Supporting Information. With the linear substituents, Li, F, Cl, and CN and the planar substituents such as NO₂ and OH, the benzene ring remained planar, although with significant changes in bond angles. However, with the other compounds, there were small but significant distortions from planarity.

The structural parameters for these compounds change in the fashion expected in response to changes in electronegativity. With both the first- and second-row substituents, an increase in electronegativity leads to a

decreased C–X bond length because the valence electrons about X are more tightly bound. A more electronegative atom prefers to be bonded to an orbital with relatively high *p* character,¹⁰ and this leads to an increase in the C–C–C bond angle and a decrease in the C–C bond lengths adjacent to the substituent, corresponding to an increase in *s* character in the C–C bonds.

It has been found that the MP3/6-311++G** level of theory generally gives relative energies in good agreement with experimental data,⁷ and therefore, these energies were obtained at the MP2/6-31+G* geometries. They also are given in Table 2. The energies for the group-transfer reactions in Table 1 based on the calculated energies, including the zero-point corrections, are included in Table 1. It would, of course, be desirable to examine the energies at a higher theoretical level such as G2.¹¹ This is impractical with the present compounds because of their size.

It can be seen that the MP3/6-311++G** energy changes are in good agreement with the experimental data and that the MP2/6-311++G** energy changes are similar, but not quite as satisfactory. The energy changes are compared with those for the corresponding vinyl derivatives in Figure 1. Here, the slope is close to unity (0.996), the intercept is small (–0.2 kcal/mol), and $r^2 = 0.984$. It is clear that substituent effects are essentially the same for the phenyl and vinyl derivatives.

In both series, electron-withdrawing substituents normally prefer to be attached to the unsaturated group, whereas electron-releasing substituents prefer to be attached to the methyl group. It is interesting that both a cyano group and a nitro group prefer to be bonded to methyl rather than phenyl despite the possibility of

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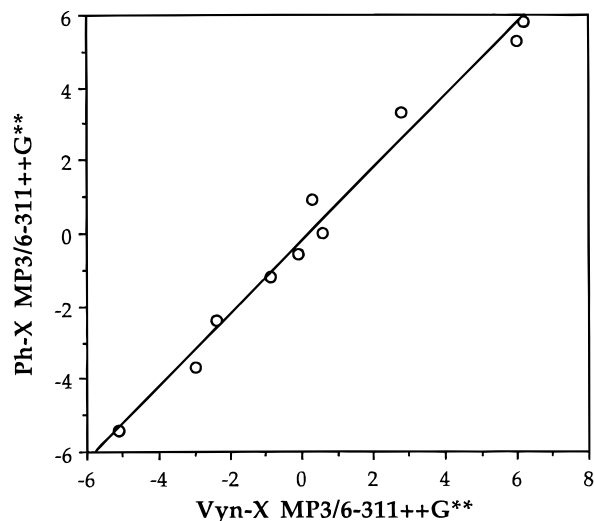


Figure 1. Comparison of MP3/6-311++G** energy changes for phenyl and vinyl derivatives.

Table 4. Comparison of Rotational Barriers, MP3/6-311++G**, kcal/mol

X	Ph-X	Vyn-X
NH ₂	3.8	4.6
OH	2.2	3.6
SH	-0.5	1.7

conjugation with the latter and despite the general tendency for electron-withdrawing groups to be attached to vinyl vs methyl. Nitro and cyano groups are clearly different than the others, and this has also been found with CX₄¹² compounds and with carbonyl groups.⁷

Another way in which the substituent effects may be examined is via a comparison of the rotational barriers for bonds to the potential π -donating substituents NH₂, OH, and SH. They are summarized for the phenyl and vinyl derivatives in Table 4. The calculated barriers for the vinyl derivatives are 1–2 kcal/mol greater than for the phenyl derivatives.¹³ The most interesting difference is found when X = SH. Here, the $\sim 90^\circ$ rotated form has a lower calculated energy than the planar form,¹⁴ whereas with vinylthiol, the planar form has the lower energy. It is apparent that conjugating effects are small for either system, but are smaller for the phenyl derivatives than for the vinyl derivatives.

Bond dissociation energies provide one more way in which substituent effects may be examined. They are more difficult to calculate than are the group transfer energies because bond breaking causes important changes in the correlation energy. As a test of the theoretical levels used in this study, the MP2 and MP3/6-311++G** bond dissociation energies were calculated for a series of methyl derivatives for which the G2 dissociation

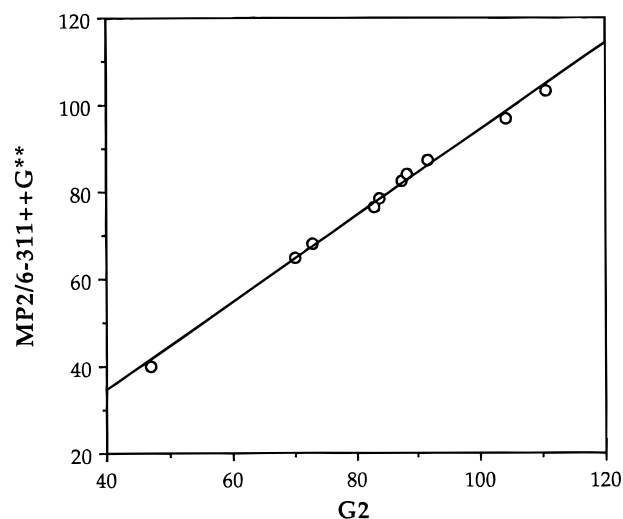


Figure 2. Comparison of MP2/6-311++G** and G2 calculated bond dissociation energies for methyl derivatives.

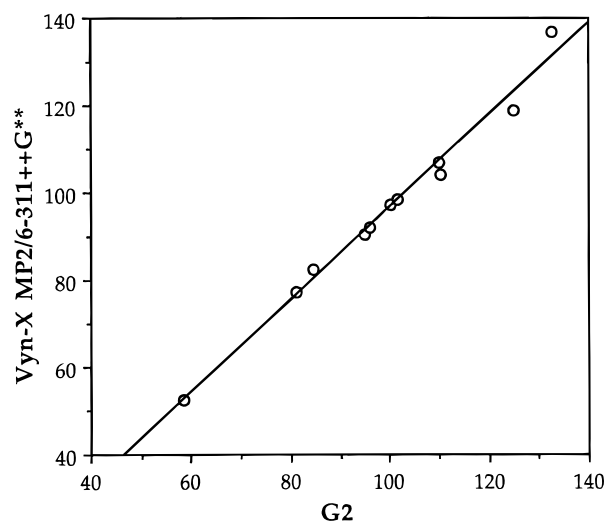


Figure 3. Comparison of MP2/6-311++G** and G2 bond dissociation energies for vinyl derivatives.

energies are available. Here, it is known that the G2 dissociation energies reproduce the available experimental BDE's with an average error of 1 kcal/mol,¹⁵ which is close to the experimental uncertainties. The MP2 energies for the methyl derivatives proved to be the more satisfactory (Figure 2).¹⁶ Here, the slope was close to unity (0.996) and the intercept was -5.4 kcal/mol ($r^2 = 0.995$). Thus, there was an essentially constant offset of 5 kcal/mol.

The MP2/6-311++G** BDE's for the vinyl derivatives are compared with the G2 values in Figure 3. Here, the slope is 1.05 and the intercept is -9.5 kcal/mol ($r^2 = 0.985$). The correlation is not quite as good as for the methyl derivatives, but the MP2 level of theory again appears to be useful for comparing BDE's.

With the phenyl derivatives, there are two questions of special interest. First, how do the phenyl derivative BDE's compare with those of the vinyl derivatives? Second, how well do the MP2/6-311++G** calculated BDE's compare with the experimental values? Unlike the vinyl derivatives where little experimental data are

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(14) The structure of thiophenol does not appear to have been precisely determined. The available data suggest that it is nonplanar (Lunazzi, L.; Bellomo, P.; Veracini, C. A.; Amanzi, A. *J. Chem. Soc., Perkin Trans. 2* **1979**, 559). Benzene-1,4-dithiol has been found to be nonplanar (Portalone, G.; Domenicano, A.; Schultz, G.; Hargittai, I. *J. Mol. Struct.* **1989**, *186*, 185).

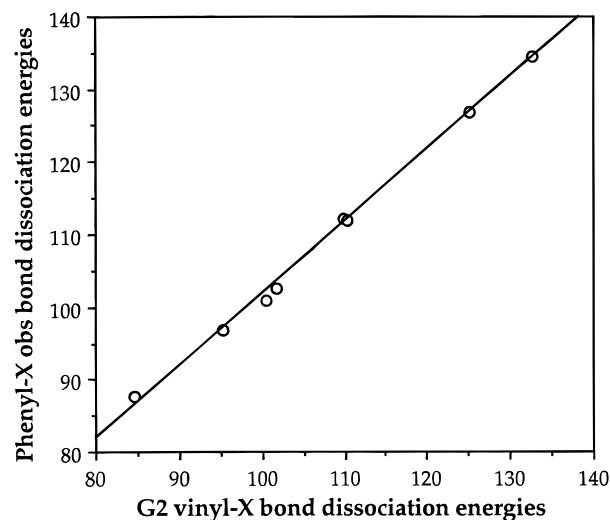
(15) Wiberg, K. B.; Ochterski, J. *J. Comput. Chem.* **1997**, *18*, 108.

(16) The MP3 data gave a slope of 0.929, an intercept of -3.4 kcal/mol and $r^2 = 0.974$.

Table 5. Phenyl-X Experimental Heats of Formation and Bond Dissociation Energies, kcal/mol

X	ΔH_f (298 K)	ΔH_f (0 K)	D_{298}	D_0
H	19.7 \pm 0.2	23.9 \pm 0.2	113.6 \pm 0.6	112.0 \pm 0.6
CH ₃	12.1 \pm 0.1	17.6 \pm 0.1	104.1 \pm 0.6	100.9 \pm 0.6
NH ₂	20.8 \pm 0.3	26.1 \pm 0.3	105.5 \pm 0.7	102.6 \pm 0.7
OH	-23.0 \pm 0.2	-18.5 \pm 0.2	113.6 \pm 0.6	112.1 \pm 0.6
F	-27.7 \pm 0.3	-24.0 \pm 0.3	127.9 \pm 0.7	126.8 \pm 0.7
SH	26.6 \pm 0.3	30.8 \pm 0.3	88.8 \pm 1.0	87.7 \pm 1.0
Cl	12.4 \pm 0.3	16.0 \pm 0.3	97.8 \pm 0.6	96.9 \pm 0.6
NO ₂	16.1 \pm 0.1	21.0 \pm 0.1	73.0 \pm 0.7	71.9 \pm 0.7
CN	51.6 \pm 0.5	54.9 \pm 0.5	135.1 \pm 1.3	134.5 \pm 1.3

^a ΔH_f C₆H₅ 81.2 \pm 0.6 (298 K), 84.3 \pm 0.6 (0 K).

**Figure 4.** Comparison of observed bond dissociation energies for phenyl derivatives with the G2 BDE's for vinyl derivatives.

available, the BDE's for many of the substituted benzenes may be derived from their heats of formation¹⁷ making use of the recently determined heat of formation of the phenyl radical¹⁸ (Table 5).

The experimental phenyl-X BDE's are compared with the G2 calculated BDE's for the vinyl derivatives in Figure 4. A very good correlation was obtained with a slope close to unity (0.993), a small intercept (2.5 kcal/mol), and $r^2 = 0.997$. This confirms the above conclusion that substituents affect benzene and ethylene in the same fashion. It should be noted that the substituents include good π -donors (NH₂) and strong σ -acceptors (CN).

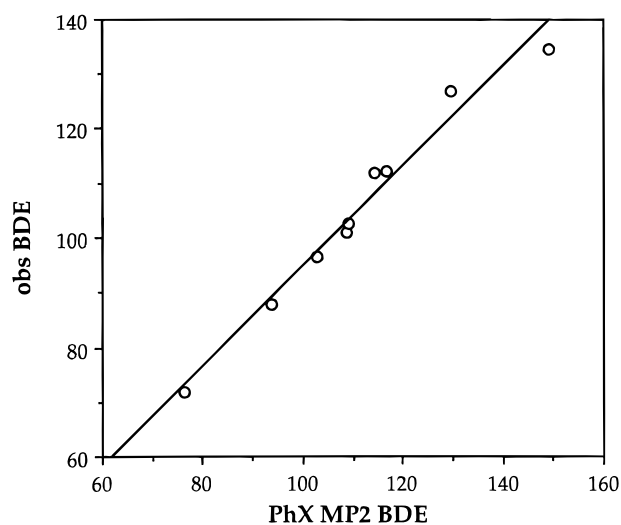
Since compounds as large as the phenyl derivatives cannot readily be examined using model chemistries such as G2, it was of interest to see how well the more computationally accessible MP2/6-311++G** BDE's (Table 6) reproduce the experimental values. They are compared with the latter in Figure 5. The comparison is generally satisfactory ($r^2 = 0.973$) with a slope close to 1 (1.065) and with a small intercept (-0.5). Thus, this level of theory is capable of reproducing the trends in bond dissociation energies in a fairly satisfactory fashion.

The C-X bond dissociation energies generally increase with increasing electronegativity of the substituent, as is commonly observed.¹⁹ The more interesting values are

Table 6. Calculated MP2/6-311++G C-X Bond Dissociation Energies, kcal/mol^a**

X	MeX	CH ₂ =CHX	C ₆ H ₅ X
H	96.6	103.9	111.4
Li	39.9	52.5	64.2
CH ₃	84.1	97.1	108.8
NH ₂ (gs)	78.5	98.4	109.3
NH ₂ (ts)		93.8	105.0
OH (gs)	87.3	106.7	116.8
OH (ts)		103.1	113.9
F	103.4	118.9	129.8
SiH ₃	82.2	92.1	103.5
PH ₂ (gs)	64.7	77.1	89.0
SH (gs)	67.9	82.3	94.5 ^b
SH (ts)		80.6	93.9
Cl	76.5	90.3	103.0
CN	125.5	137.0	149.1
NO ₂	52.3	64.0	76.3

^a The calculations are based on the PMP2 energies of the radicals. ^b The planar conformation of phenylthiol is the transition state.

**Figure 5.** Comparison of the observed bond dissociation energies for phenyl derivatives with the MP2/6-311++G** calculated BDE's.

those for nitrobenzene and benzonitrile. The high BDE for the latter presumably arises from the high s -character of both the bond from the cyano carbon (sp) and from the benzene ring (sp²). The low BDE for nitrobenzene results from the relatively high stability of the NO₂ radical.

A final way in which the substituent effects may be examined is via the use of charge-density difference plots. Projection density plots derived from STO-3G wave function have been presented by Streitwieser and Vorpahl for a few substituted benzenes.² We were interested in examining a larger group of substituents, and it is now readily practical to use larger basis sets and to include a correction for electron correlation.

The calculations provide wave functions from which the electron density, ρ , may be calculated at any point in space. A comparison does require that the atoms of interest have the same coordinates for the two compounds being examined. Here, the structure of the phenyl ring was maintained as that of benzene, but the geometry of the substituent was optimized. A cubic array of electron density was constructed for the substituted benzene and that for benzene was subtracted from it. The electron-density change associated with the substituent itself was eliminated as previously described.⁵ 3D plots were constructed and are shown in Figure 6.

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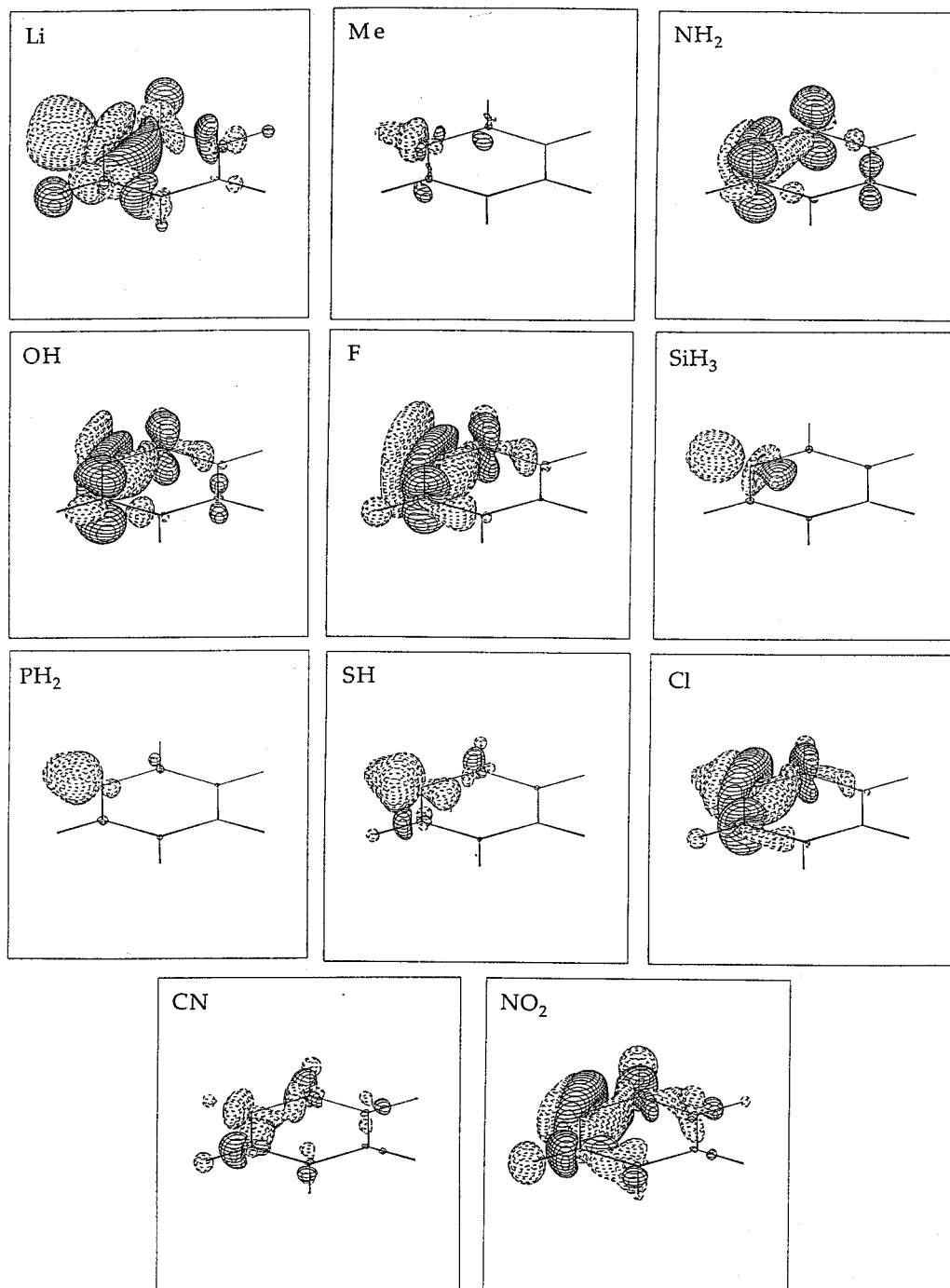


Figure 6. Electron density difference plots for phenyl derivatives vs benzene. The contour level is $2.0 \times 10^{-3} e/\text{au}^3$. Solid contours indicate a gain in electron density, and dashed lines indicate a loss.

As a substituent, lithium is only able to act via polarization of the Li–C σ -bond, and the change in electron density caused by this substituent is what might be expected. Electrons are repelled from the carbon bearing the lithium and appear in a band between the ortho carbons, and also at the *o*-hydrogens.

The F and Cl substituents lead to similar changes in electron density, which are the reverse of that found for the Li substituent. This suggests that the halogens also act mainly via polarization of the C–X σ -bond. Such polarization would lead to changes in both the σ - and π -systems, which results from the commonly observed σ/π -polarization. This leads to opposite shifts of the two types of electrons in order to minimize repulsion between

them. The polarization mechanism for fluorobenzene may be further studied by examining a model of a purely polar effect: a phenyl cation plus a negative charge where the hydrogen was lost from benzene. The electron-density difference plot for going from benzene to the above model is shown in Figure 7. The similarity between the plot for phenyl cation with a minus charge and that for fluorobenzene is striking.

Only two substituents, OH and NH₂, lead to significant electron-density transfer to the para position, and in most cases there is little electron density transfer to either the meta or para positions. With, CH₃, SiH₃, PH₂, and SH, there is also little transfer to or from the *o* positions.

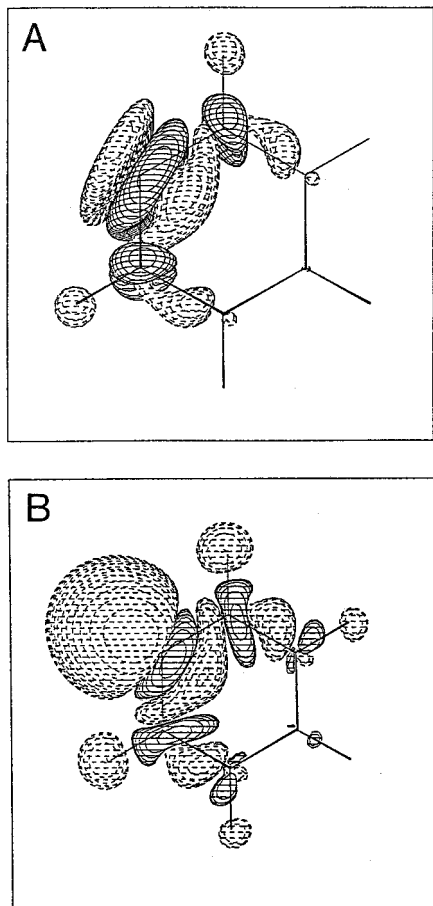


Figure 7. Comparison of the electron density difference plot for (A) fluorobenzene minus benzene with (B) phenyl cation with a nearby negative charge minus benzene. The contour level is $2.0 \times 10^{-3} \text{ e/au}^3$. Note the similarity of the electron density difference in the benzene rings.

Further information may be obtained from the changes in electron density that result when the substituents NH_2 , OH , and SH are rotated (Figure 8). With aniline, rotation from the conjugated conformation leads to loss of the π -like electron density at the ortho and para positions, and the same is true for phenol, but to a smaller extent. Thiophenol is calculated to prefer the unconjugated conformation.

The changes in electron density seen in Figure 6 may be integrated to yield an estimate of the charge transfer to or from the benzene ring that is caused by the substituents (Table 7). Here, ΔE is the change in energy on going from the fully optimized geometry to one having the phenyl carbons in the geometry found for benzene. Except for phenyllithium, all of the energy changes are small. The column labeled "positive" is the integral of all of the positive regions in the difference density plots²⁰ and corresponds roughly to the π -space for the first row substituents. The column marked "negative" is the integral of all the negative regions. The "bond" column gives the integral of the negative region in the vicinity of the C-X bond. The difference between these two columns ("difference") corresponds roughly to the σ -space for the first row substituents. In the above, it should be noted that "positive" and "negative" have different connotation for phenyllithium than for the other substituents.

(20) The integrations were extrapolated to a zero value of ρ as previously described (ref 5).

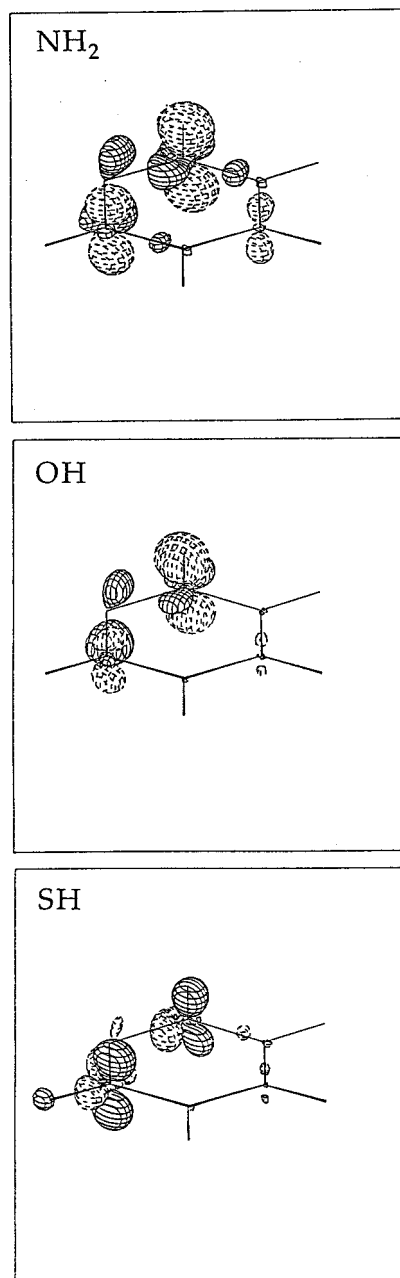


Figure 8. Electron density difference plots for the rotation of NH_2 , OH , and SH groups attached to a benzene ring. The contour level is $2.0 \times 10^{-3} \text{ e/au}^3$.

With the substituents CH_3 through F , the "negative" integrals increase in magnitude from -0.023 to -0.216 , and when corrected for the differences in the vicinity of the C-X bonds, they increase in magnitude from -0.003 to -0.079 . A similar trend is found for the second row substituents. These changes are expected in the σ -system for the changes in electronegativity through the series.

The π -interactions are best seen in Figure 8, which shows the effect of rotation of the substituent. With NH_2 , there is clearly π -electron transfer to the para position, and the transfer is much smaller with OH . This is also seen in the integrals in Tables 8 and 9b. There is a larger π -transfer to the ortho positions. This is reasonable since transfer to this position will lead to less charge separation than for the para position.

Even with the substituents that lead to π -charge transfer to the benzene, the amount of transfer is

Table 7. Integration of Substitution Difference Densities, Electrons

compd	ΔE^a	positive ^b	negative ^c	bond ^d	difference ^e
Ph-Li	1.96	+0.119	-0.523	-0.409	-0.114
Ph-CH ₃	0.18	+0.018	-0.023	-0.020	-0.003
Ph-NH ₂	0.29	+0.102	-0.080	-0.034	-0.046
Ph-OH	0.48	+0.120	-0.131	-0.068	-0.063
Ph-F	0.63	+0.109	-0.216	-0.137	-0.079
Ph-SiH ₃	0.29	+0.012	-0.176	-0.163	-0.014
Ph-SH	0.07	+0.011	-0.149	-0.128	-0.021
Ph-Cl	0.13	+0.088	-0.186	-0.129	-0.057
Ph-NO ₂	0.51	+0.104	-0.164	-0.051	-0.113
Ph-CN	0.11	+0.025	-0.061	-0.013	-0.048

^a Energetic cost, kcal/mol, of using the benzene ring geometry for the substituted compounds. ^b Integration of all positive regions in the difference density plots. This corresponds roughly to the π -space for most first row substituents. ^c Integration of all negative regions in the difference density plots. ^d Integration of the negative region in the vicinity of the C-X bond. ^e The difference between the "negative" and "bond" columns. This corresponds roughly to the σ -space for most first row elements.

Table 8. Integration of Bond Rotation Difference Densities, Electrons

compd	barrier ^a	distortion ^b	positive ^c	negative ^d
Ph-NH ₂	4.3	0.49	+0.032 (σ)	-0.048 (π)
Ph-OH	2.9	0.66	+0.021 (σ)	-0.028 (π)
Ph-SH	0.8	0.44	+0.023 (π)	-0.023 (σ)

^a Bond rotation barrier (kcal/mol), calculated at MP2(fc)/6-31+G* without zero-point energy correction. Note that for Ph-SH, the planar geometry is the transition state. ^b Energetic cost (kcal/mol) of maintaining the ground-state geometry for the aromatic ring in the transition state for bond rotation. ^c Integration of all positive regions in difference density plots. The table indicates for each compound whether this corresponds roughly to the σ - or π -space. ^d Integration of all negative regions in difference density plots.

Table 9. π -Charge Transfer to the Para Positions

(a) Net Transfer			
X	transfer	X	transfer
Li	+0.012	PH ₂	0.000
CH ₃	+0.002	SH	0.000
NH ₂	+0.012	Cl	+0.005
OH	+0.010	CN	-0.004
F	+0.003	NO ₂	-0.002
SiH ₃	-0.001		
(b) Charge Shift on Rotation			
X	shift	X	shift
NH ₂	-0.011	SH	+0.005
OH	-0.006		

relatively small. This is expected since such charge transfer leads to charge separation that is energetically unfavorable. The large effects of substituents in electrophilic substitution reactions is not due to ground-state charge transfer, but rather to the stabilization of the charge in the transition state.

3. Energies of Protonation of Benzene Derivatives

The factors that control the rates and regiochemistry in electrophilic aromatic substitution have been the subject of a number of studies.^{3,21} We have examined the protonation of benzene, toluene, fluorobenzene, and chlorobenzene via geometry optimizations at the MP2/6-31G* level followed by MP2 and MP3/6-311++G** energy calculations at the MP2/6-31G* geometry (Table 10).

These data allow the calculation of the gas-phase proton affinities, and they are compared with the experimental values²² in Table 11. The MP3 energies give the best fit to the observed proton affinities and agree with the experimental observation that in the gas phase both chlorobenzene and fluorobenzene are more basic than benzene. In addition, they indicate that the para positions of the halobenzenes are the more basic positions and, as expected, the meta positions are the least basic.

The data also allow one to estimate the ratio of ortho/meta/para attack that would occur if an electrophile responded only to the difference in energy between the protonated forms (Table 12). Here, $1/K$ relative to the para position is given because it is convenient to have values greater than unity. Large values correspond to low reactivity. There is a significant preference for the para position rather than ortho, and the meta position is strongly disfavored. The strong preference for the para position in fluorobenzene may result from the need to add the proton to a position that would not be disfavored by the σ -electron withdrawal by fluorine.

The energy differences are for the gas phase and would probably be significantly reduced in solution. The experimental data for electrophilic aromatic substitution (nitration) indicates that a fluorine substituent leads to a very strong preference for the para position.²⁴ Thus, there is good agreement between the calculations and the experimental data. The smaller preference for para substitution found with chlorobenzene is also mirrored by the calculations.

4. When Is a Fluorine a π -Donor?

The interaction of fluorine lone pairs with adjacent groups has frequently been proposed to explain properties of fluorine-substituted compounds. Examples include the stabilization of carbon tetrafluoride by negative hyperconjugation (double bond: no bond resonance),²³ the ortho,para directing effect of fluorine in electrophilic aromatic substitution,²⁴ and the small σ -value for fluorine attached to a benzene ring.²⁵

Examples of the effect of fluorine substitution on energies may be illustrated by bond separation reactions such as for the processes shown in Table 13. We have calculated the energy changes for these reactions at the MP3/6-311++G**//MP2/6-31G* level using the data presented in Table 10. The data clearly show that fluorine substitution may have large effects on relative energies. It now remains to consider its origin.

We have presented data indicating that the preference of fluorine for multiple substitution on carbon is due to Coulombic interactions and not negative hyperconjugation.⁷ Using three different methods of estimating atomic charges, we found that the positive charge at carbon increases steadily as the number of fluorines increase. Additional support for a constant fluorine charge was obtained in a study of infrared intensities for the halo-methanes.²⁶ The CF bond in methyl fluoride has a larger

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Table 10. Energies of Protonated Phenyl Derivatives and Related Compounds (6D)

compd	MP2(fc)/6-31G*	MP2(fc)/6-311++G**	MP3(fc)/6-311++G**	ZPE ^a
benzene-H ⁺	-231.750 31	-231.880 21	-231.917 74	66.5
toluene- <i>p</i> -H ⁺	-271.932 91	-271.094 08	-271.141 47	83.0
toluene- <i>m</i> -H ⁺	-270.926 25	-271.087 47	-271.133 46	83.0
toluene- <i>o</i> -H ⁺	-270.931 22	-271.092 17	-271.139 05	83.0
fluorobenzene- <i>p</i> -H ⁺	-330.772 40	-330.966 44	-330.994 56	62.1
fluorobenzene- <i>m</i> -H ⁺	-330.757 36	-330.951 41	-330.979 53	61.6
fluorobenzene- <i>o</i> -H ⁺	-330.768 73	-330.960 26	-330.989 42	62.1
chlorobenzene- <i>p</i> -H ⁺	-690.782 87	-690.944 49	-690.984 66	61.1
chlorobenzene- <i>m</i> -H ⁺	-690.770 43	-690.931 13	-690.971 79	60.8
chlorobenzene- <i>o</i> -H ⁺	-690.780 56	-690.941 87	-690.981 75	61.1
benzene	-231.457 73	-231.593 33	-231.620 63	60.3
toluene	-270.628 43	-270.795 14	-270.831 22	76.7
fluorobenzene	-330.477 00	-330.676 90	-330.695 65	55.6
chlorobenzene	-690.490 60	-690.654 84	-690.685 45	54.8
methane	-40.332 55	-40.380 88	-40.399 69	26.8
ethane	-79.494 74	-79.574 19	-79.604 05	44.7
propene	-117.455 54	-117.550 69	-117.583 18	47.9
methyl fluoride	-139.335 86	-139.454 07	-139.464 32	24.0
ethyl fluoride	-178.508 72	-178.656 49	-178.677 49	41.0
difluoromethane	-238.364 05	-238.546 73	-238.547 39	20.2
vinyl fluoride	-177.303 41	-177.433 68	-177.446 83	26.7
ethyl cation	-78.552 31	-78.617 05	-78.643 70	36.5
fluoromethyl cation	-138.368 97	-138.466 10	-138.470 79	16.4
acetone	-192.523 91	-192.663 56	-192.686 52	50.4
acetyl fluoride	-252.398 66	-252.572 06	-252.572 98	29.7

^a HF/6-31G* frequencies scaled by 0.893 kcal/mol.**Table 11. Proton Affinities, kcal/mol**

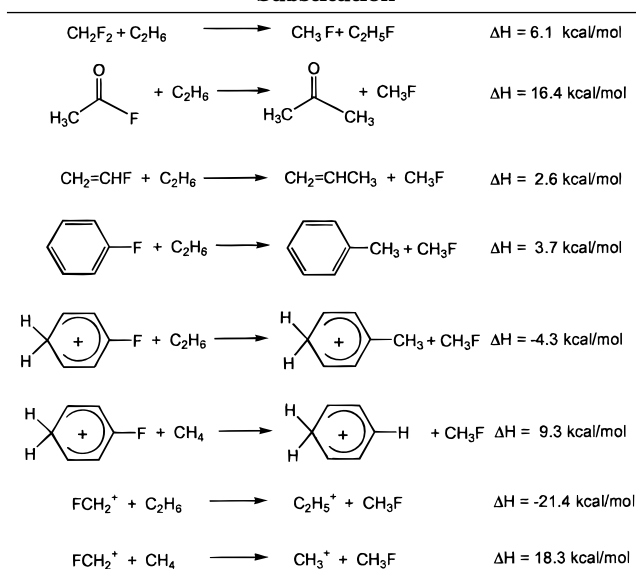
compd	position	MP2 6-31G*	MP2 6-311++G**	MP3 6-311++G**	obsd
benzene		177.4	173.8	180.2	181.3
toluene	para	184.8	181.3	188.4	187.8
	meta	180.6	177.1	183.3	
	ortho	183.7	180.1	186.9	
fluorobenzene	para	178.9	175.8	181.1	182.6
	meta	169.9	166.8	172.1	
	ortho	176.6	171.9	177.8	
chlorobenzene	para	177.1	175.5	181.5	181.7
	meta	169.6	167.4	173.7	
	ortho	175.7	173.8	179.6	

Table 12. Energy Differences among Positions for Protonated Species

X	position	$\Delta\Delta H$	1/K
F	para	0.0	1
	meta	8.9	3×10^6
	ortho	3.2	222
Cl	para	0.0	1
	meta	7.8	5×10^5
	ortho	1.8	21
CH ₃	para	0.0	1
	meta	5.0	4600
	ortho	1.5	13

bond dissociation energy than the C–C bond in ethane by 19 kcal/mol because the charge separation in the CF bond resulting from the electronegativity of fluorine leads to internal Coulombic stabilization. The introduction of a second fluorine increases the positive charge at carbon, strengthening both the new CF bond as well as the first CF bond. Thus, increasing fluorine substitution leads to increasing strength of all of the CF bonds, as is seen in the increasing bond dissociation energies. The increased Coulombic interactions also lead to a decrease in the C–F bond lengths with increasing fluorine substitution.

We also have examined the effect of substituents on acetyl derivatives.⁸ Here, the bond dissociation energies

Table 13. Isodesmic Reactions Involving Fluorine Substitution

of the acetyl derivatives were compared with those of the corresponding methyl derivatives. To eliminate π -interactions, the dissociation energies of the 90° rotated acetic acid, acetamide, and thioacetic acid were used. Now, the points for X = PH₂, SH, Cl, NH₂, OH, and F all fell on the same straight line having a slope of 1.6. Since both Cl and F fell on the line, it appears that the halogens do not have a significant π -interaction with the carbonyl group. The energy of the isodesmic reaction involving acetyl fluoride again arises from the electronegativity of fluorine. By withdrawing charge from the carbonyl carbon, it leads to a strengthened CF bond (similar to the effect for methyl fluoride) but at the same time leads to a strengthened C–O bond, which is strongly polarized C⁺–O[−] and is further polarized by the introduction of the fluorine. Thus, the energy changes for the first two isodesmic reactions have a common origin: internal Coulombic stabilization.

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Vinyl derivatives have been examined in a similar fashion.⁴ A comparison of vinyl-X and methyl-X bond dissociation energies in which 90° rotated vinyl thiol, vinylamine, and vinyl alcohol were used in order to eliminate π -interactions led to a good linear correlation with a slope close to 1. Again, since Cl and F fell on the line, there is no reason to postulate lone pair interactions in these cases. The present study of substituted benzenes indicates that the bond dissociation energies of phenyl and vinyl compounds are linearly related, showing that fluorine does not behave differently as a substituent in the vinyl and phenyl cases. As noted above, the effect of fluorine on a benzene ring appears to be mainly due to polarization.

Since no evidence for lone pair π -interactions were found with the first four cases, it now remains to examine the last two. Here, the positive charge will place a much larger electron demand on the fluorine, and a larger response might be expected. It may first be noted that there is a large difference between the reactions with ethane where a methyl group replaces the substituent and the reactions with methane where a hydrogen replaces the substituent. The data show that fluorine stabilizes a positive charge better than hydrogen, but not as effectively as a methyl group. Thus, when there is a strong electron demand, fluorine is a weak π -donor. This may also be seen in the data in Table 12, where a fluorine leads to a considerable difference in energy between protonation at the para and meta positions.

5. Conclusions

The effect of substituents on a benzene ring is closely related to their effect on ethylene. The only significant difference is found with X = SH, where the planar (conjugated) form is favored for ethenethiol, whereas the rotated form is preferred for thiophenol. Many of the substituents such as Li, F, and Cl lead to changes in

electron density via a polarization mechanism. π -Donating substituents such as NH₂ and OH do donate π -electron density to the para position, but the amount of transfer is rather small.

The calculated energies of protonation of benzene rings are in good agreement with the experimental values. The strong preference for para substitution in electrophilic reactions with fluorobenzene is reproduced by the calculations and appears to be due to the strong inductive effect of the fluorine.

The only cases in which fluorine was found to be a π -donor are those where a full positive charge may be stabilized, such as protonated fluorobenzene and the fluoromethyl cation.

6. Calculations

The ab initio calculations were carried out using Gaussian-94.²⁷ The electron density difference plots were made using CASGEN.²⁸

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Supporting Information Available: Tables of calculated structural data in Z-matrix format (26 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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