Substituent Effects on the Physical Properties and pK_a of Aniline*

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ABSTRACT: The aniline molecule is nonplanar, with its NH_2 group lying at an angle θ of approximately 42° to the plane of the benzene ring. Substituents on the phenyl ring alter this out-of-plane angle as well as other molecular properties such as the ring bond lengths and angles, the barrier to inversion E_{inv}, and the pK_a of the amino group. Ab initio 6-311G** quantum chemical calculations have been employed to examine these substituent influences and the extent to which they are interrelated. Electron-donating substituents increase the C—N bond length R(C—N), θ, E_{inv}, and the pK_a, whereas electron-withdrawing substituents have the opposite effect. Among the molecular parameters that might serve as regression indicators for these changes, Hammett σ constants, which traditionally have been used to represent substituent electronic effects, yield fair to good correlations for R(C—N) ($r^2 = 0.797$), θ ($r^2 = 0.804$), E_{inv} ($r^2 = 0.829$), and the amino group pK_a ($r^2 = 0.931$) for aniline and 18 substituted anilines. Of several measures of atomic charge, the Mulliken and electrostatic charges on the amino nitrogen atom show essentially no correlation with these properties. In contrast, the natural charge Q_n on the amino nitrogen is well correlated with the bond length R(C—N) ($r^2 = 0.889$), θ ($r^2 = 0.932$), E_{inv} ($r^2 = 0.839$), and the amino group pK_a ($r^2 = 0.960$). This latter result suggests that the natural charge, rather than either the Mulliken or electrostatic charges, may be the preferred charge descriptor for correlation purposes. Inclusion of electron correlation at the MP2 level increases the correlations of E_{inv} with both σ ($r^2 = 0.951$) and Q_n ($r^2 = 0.892$). Int J Quantum Chem 80: 1107–1115, 2000

Key words: aniline; ab initio; substituent effects; pK_a

Introduction

The influence of substituents on the physical and chemical properties of compounds has long been an important focus of interest in chemistry. In general, substituents alter the reactivities, conformations, equilibrium relationships, spectra, and thermal properties of the substituted compounds. Most commonly, studies of substituent effects have focused on the influence of substitution on a single molecular property, and more general studies of substituent effects on a variety of molecular properties have been comparatively rare. Here we report an examination of alterations in several representative structural, energetic, and chemical

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*Dedicated to the memory of Dr. Michael Charles Zerner (1940–2000), outstanding scientist and dear friend.

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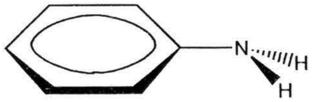
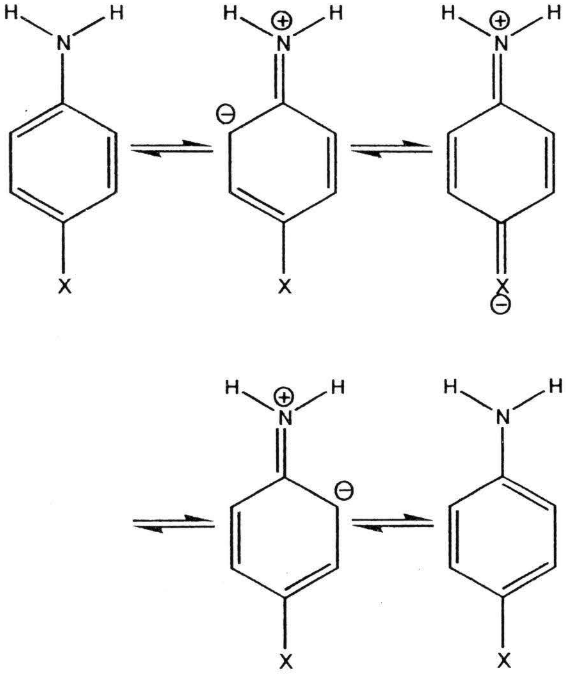
properties induced by substitution in aniline, and an examination of the extent to which these changes correlate with one another.

Aniline is an interesting candidate in which to study the influence of substituents for several reasons. On the basis of microwave [1, 2], ultraviolet absorption [3, 4], vibrational [5], and theoretical studies [6, 7] it is known that the NH_2 plane of the amino group lies at an angle of between 37° and 46° to the plane of the phenyl ring.



Substituents can be expected to alter the out-of-plane (OOP) angle θ in a characteristic manner depending on their electron-donating and -withdrawing influences. On the basis of resonance theory, electron-withdrawing substituents, especially at the para position, should favor quinoid resonance structures, which are more planar than aniline itself, decreasing both θ and the C—N bond length [7].



Conversely, electron-donating substituents should favor Kekulé-type structures with more nearly tetrahedral conformations at the nitrogen atom, and hence engender greater θ and R(C—N) values. This same reasoning suggests that electron-withdrawing substituents should decrease the energetic barrier to inversion at the amino group, E_{inv}, and the acid dissociation pK_a, whereas electron-donating substituents should have the opposite effect.

Historically, the electronic effects of substituents on reactivities have usually been examined with the aid of the substituent σ constants developed by Hammett from reactivity studies [8–11]. For the present study, it was of interest to see if additional, quantum chemical indices might also serve as helpful guides to the effects of substituents on the different molecular properties. Atomic charges, although not genuine physical properties, have a long history of employment as heuristic aids in mechanistic studies and therefore seemed natural parameters to examine. Of the several proposed calculational schemes for determining these charges, the Mulliken and electrostatic charges have historically been the most widely used [12–16]. Natural charges, derived from natural orbitals, have sometimes also been employed [17]. Accordingly, we looked at the extent to which these different atomic charge measures correlated with the conformational, energetic, and pK_a changes that occur upon substitution in aniline.

Methods

Hammett constants for the substituents were taken from the compilation of Hansch et al. [18]. The pK_a values for the aniline derivatives were taken from the review of Albert and Serjeant [19].

Quantum chemical calculations were performed using SPARTAN (v. 5.01) [20] and the Gaussian 94 suite of programs [21] on an SGI Indigo^2 workstation. Except as noted, the calculations were carried out at the Hartree–Fock (HF) 6-311G** level of theory. In aniline the amino nitrogen atom is ca. 0.05 Å above the plane defined by the six carbons of the phenyl ring. For purposes of consistency, we defined the out-of-plane angle θ as the angle between the amino H–N–H plane and the average plane formed by the six-ring carbon atoms and the nitrogen atom. The atomic charges were found as output from the SPARTAN interface. Statistical analyses were performed using the *Mathematica* (versions 3.0 and 4.0) [22] and StatMost [23] software programs.

Results

To simplify the analysis of substituent effects, we restricted attention to four representative properties: two structural features, the C—N bond length

R(C—N) and the out-of-plane angle θ; an energetic property, the amino group inversion barrier E_{inv}; and a chemical property, the acid dissociation pK_a. In relating to these properties, we examined four indices of electronic structure as potential regression descriptors: the traditional, empirical Hammett σ constants for the substituents [19], and the Mulliken (Q_M), electrostatic (Q_e), and natural charges (Q_n) on the amino nitrogen atom.

ANILINE

The results from various levels of calculation for aniline itself are summarized in Table I. Most of the methods listed yielded R(C—N) values close to the experimental value of 1.402 Å, with the semiempirical methods yielding higher values and the ab initio methods lower values. For the out-of-plane angle θ, it is apparent that the MNDO/d and PM3 calculations yield rather high values, and the HF 3-21G* calculation shows an almost planar structure. The AM1 and other ab initio levels of calculation, including the density functional theory (DFT) calculations, produce out-of-plane angles that are reasonably close to the experimentally observed value.

The inversion barrier of aniline has been studied both experimentally [24–26] and theoretically [6, 7, 27, 28]. It is apparent from Table I that there is considerable scatter in the values of E_{inv} obtained using the different methods. The HF 6-311G** value was closest to the experimental value of 1.50 kcal/mol. Although the B3LYP calculations include electron correlation in approximation, it seemed worthwhile to establish more directly the influence of electron correlation for this property, and we repeated the HF 6-311G** calculation for E_{inv} at the second-order Møller–Plesset (MP2) level using the optimized HF 6-311G** geometry. In agreement with earlier observations [28, 29] the MP2 calculation increased the barrier height by about 0.8 kcal/mol and led to a value (2.29 kcal/mol) somewhat higher than the experimental value.

Also listed in Table I are the Mulliken, electrostatic, and natural charges on the nitrogen atom as calculated at the various levels of theory. The variations of these charges calculated by the different methods are illustrated in Figure 1. Here the semiempirical methods give quite small values for both the Mulliken and natural charges on the nitrogen atom, whereas the ab initio techniques give consistently larger values. (Note that the Mulliken and natural charges are identical at the semiempirical level.) The electrostatic charge is more consistent over the different methods. Considering just the ab initio values, the Mulliken charges still show considerable dependence on the basis set employed, whereas the electrostatic and natural charges are relatively insensitive to changes in the basis set.

SUBSTITUENT EFFECTS

For this analysis all determinations were carried out at the Hartree–Fock 6-311G** level, with the exception of the inversion barrier, which was determined at both the HF 6-311** and MP2 levels. Calculated results for R(C—N) and θ for aniline and 18 of its meta- and para-substituted derivatives are shown in Table II. The variations observed for the bond length R(C—N) upon substitution are seen to be relatively small. Electron-donating substituents tend to slightly increase R(C—N), whereas electron-withdrawing substituents slightly decrease

TABLE I

Properties and charge indices for aniline calculated at different levels of theory.

	R(C—N) (Å)	θ (deg)	E_{inv} (kcal/mol)	Q_M	Q_e	Q_n
AM1	1.400	39.19	1.00	−0.327	−0.956	−0.327
MNDO/d	1.423	48.35	4.22	−0.228	−0.857	−0.228
PM3	1.430	46.40	4.47	0.071	−0.746	0.071
B3LYP 6-31G*	1.400	41.35	1.21	−0.786	−0.822	−0.836
B3LYP 6-31G**	1.398	40.36	1.01	−0.656	−0.797	−0.848
B3LYP 6-311G**	1.396	39.36	0.92	−0.468	−0.763	−0.782
HF 3-21G*	1.376	0.11	0.00	−0.984	−1.094	−0.885
HF 6-31G*	1.397	42.72	1.63	−0.889	−0.944	−0.879
HF 6-31G**	1.394	40.94	1.29	−0.740	−0.922	−0.894
HF 6-311G**	1.396	41.73	1.45	−0.527	−0.851	−0.814
Expt'l	1.402	37°–46°	1.50	n/a	n/a	n/a

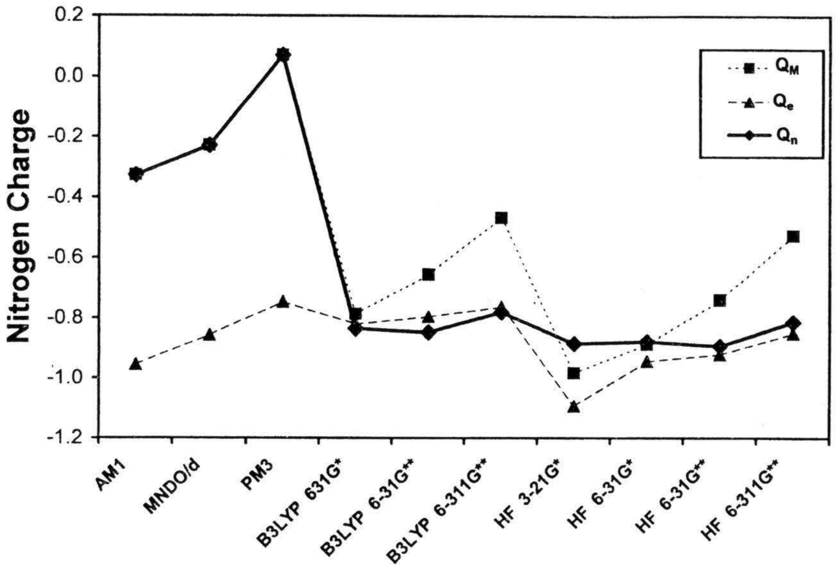


FIGURE 1. Variations in the Mulliken charge Q_M, the electrostatic charge Q_e, and the natural charge Q_n values when calculated at different levels of theory.

this bond length. As expected, meta substituents exert a smaller influence than do para substituents, although, with the exception of the *p*-amino, *p*-cyano, and *p*-nitro groups, even the para substituents have generally little effect on the C—N bond length. A fair correlation between R(C—N) and the Hammett σ values of the substituents is found:

$$R(\text{C—N}) = -0.0177(\pm 0.0022)\sigma + 1.396(\pm 0.001)$$

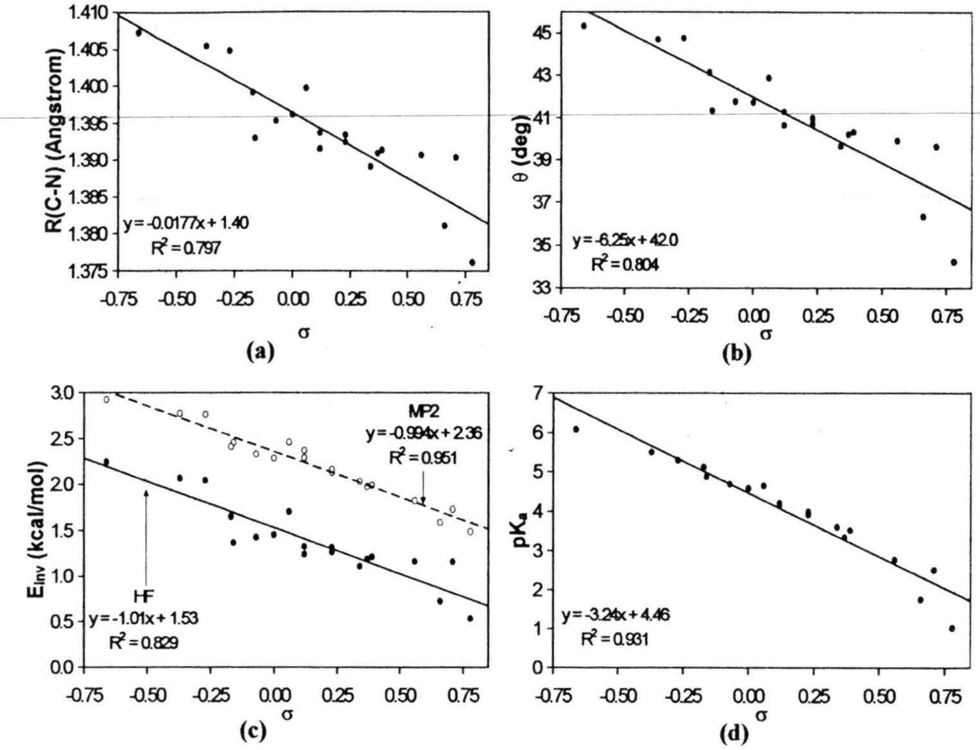
$$n = 19, \quad r^2 = 0.797, \quad s = 0.0034, \quad F = 67.$$

(Here n = the number of compounds, r = the correlation coefficient, s = the standard deviation, and

TABLE II

Calculated property and charge values for aniline derivatives, with experimental pK_a's.

		R(C—N) (Å)	θ (deg)	E_{inv}(HF) (kcal/mol)	E_{inv}(MP2) (kcal/mol)	pK_a	σ	Q_M	Q_e	Q_n
1	H	1.3961	41.73	1.454	2.285	4.58	0.00	−0.5264	−0.8499	−0.8143
2	*m*-amino	1.3929	41.34	1.364	2.458	4.88	−0.16	−0.5276	−0.8209	−0.8136
3	*m*-bromo	1.3913	40.33	1.210	1.990	3.51	0.39	−0.5249	−0.8431	−0.8114
4	*m*-chloro	1.3906	40.20	1.188	1.977	3.34	0.37	−0.5249	−0.8302	−0.8113
5	*m*-cyano	1.3906	39.91	1.163	1.823	2.76	0.56	−0.5319	−0.8438	−0.8109
6	*m*-fluoro	1.3890	39.65	1.112	2.030	3.59	0.34	−0.5247	−0.8523	−0.8118
7	*m*-hydroxy	1.3914	40.66	1.239	2.288	4.17	0.12	−0.5260	−0.8548	−0.8128
8	*m*-methoxy	1.3936	41.27	1.326	2.374	4.20	0.12	−0.5257	−0.8416	−0.8135
9	*m*-methyl	1.3952	41.77	1.424	2.332	4.69	−0.07	−0.5299	−0.8605	−0.8144
10	*m*-nitro	1.3902	39.64	1.159	1.731	2.50	0.71	−0.5257	−0.8442	−0.8109
11	*p*-amino	1.4073	45.32	2.247	2.925	6.08	−0.66	−0.5297	−0.8965	−0.8157
12	*p*-bromo	1.3923	40.70	1.260	2.130	3.91	0.23	−0.5267	−0.8491	−0.8121
13	*p*-chloro	1.3933	41.00	1.316	2.164	3.98	0.23	−0.5266	−0.8388	−0.8124
14	*p*-cyano	1.3810	36.32	0.723	1.589	1.74	0.66	−0.5292	−0.8414	−0.8085
15	*p*-fluoro	1.3995	42.88	1.703	2.461	4.65	0.06	−0.5259	−0.8357	−0.8141
16	*p*-hydroxy	1.4055	44.70	2.067	2.772	5.50	−0.37	−0.5261	−0.8028	−0.8151
17	*p*-methoxy	1.4048	44.77	2.044	2.762	5.29	−0.27	−0.5281	−0.8370	−0.8152
18	*p*-methyl	1.3991	43.13	1.651	2.413	5.12	−0.17	−0.5297	−0.8438	−0.8147
19	*p*-nitro	1.3762	34.22	0.537	1.488	1.02	0.78	−0.5258	−0.8475	−0.8067



(a) (b) (c) (d)

FIGURE 2. Correlations of the properties examined with the Hammett σ constants of the substituents: (a) The amino group C—N bond distance vs. σ, (b) the out-of-plane angle θ vs. σ, (c) the inversion barriers $E(\mathrm{HF})_{\mathrm{inv}}$ and $E(\mathrm{MP2})_{\mathrm{inv}}$ vs. σ, and (d) the amino group pK_a vs. σ.

F = the F statistic for the regression.) This is illustrated in Figure 2.

The para substituents show a much better correlation with R(C—N) ($r^2 = 0.941$) than do the meta substituents ($r^2 = 0.554$). Unfortunately, very little reliable gas-phase experimental data is available for the geometries of substituted anilines [30], and X-ray structures are unreliable for the present purpose because of the influence of crystal packing forces.

As shown in Table II, substituents have a greater effect on the OOP angle θ than on the C—N bond length. Although meta substitution has little influence on θ, para substitution causes a significant change, with electron-donating substituents increasing θ and electron-withdrawing substituents decreasing this angle. This variation is exemplified by the correlation of our calculated values for θ with the Hammett σ constants of the substituents:

$$\theta = -6.25(\pm 0.75)\sigma + 42.0(\pm 0.3)$$
$$n = 19, \qquad r^2 = 0.804, \qquad s = 1.18, \qquad F = 70.$$

This dependence is illustrated in Figure 2. When just the para substituents are examined, the correlation improves to $r^2 = 0.921$, whereas for the meta-substituted compounds $r^2 = 0.800$.

The Hammett σ constants yield a fairly good correlation with the inversion barriers calculated at the Hartree–Fock 6-311G** level:

$$E_{\mathrm{inv}}(\mathrm{HF}) = -1.01(\pm 0.11)\sigma + 1.53(\pm 0.04)$$
$$n = 19, \qquad r^2 = 0.829, \qquad s = 0.18, \qquad F = 82.$$

Again, the para-substituted compounds are a much better fit ($r^2 = 0.958$) than the meta-substituted derivatives ($r^2 = 0.701$). Addition of correlation at the MP2 level significantly improves the overall fit to

$$E_{\mathrm{inv}}(\mathrm{MP2}) = -0.994(\pm 0.055)\sigma + 2.36(\pm 0.02)$$
$$n = 19, \qquad r^2 = 0.951, \qquad s = 0.087, \qquad F = 329.$$

In this case the para compounds ($r^2 = 0.957$) and the meta compounds ($r^2 = 0.942$) are nearly equally well accounted for, indicating that the major improvement in the correlation has occurred for the meta derivatives.

It is evident from Table II that electron-donating substituents on the phenyl ring increase the pK_a of aniline's amino group, and electron-withdrawing substituents decrease the pK_a. Hammett σ constants were initially developed to describe the electronic influences of substituents on chemical reactions and equilibria. Accordingly, it is reasonable to expect that they might also provide a reliable measure of the substituents' effects on the pK_a of the amino moiety, and this is indeed the case:

$$\mathrm{p}K_a = -3.24(\pm 0.21)\sigma + 4.46(\pm 0.09)$$

$$n = 19, \quad r^2 = 0.931, \quad s = 0.34, \quad F = 231.$$

(This equation differs from an earlier equation, p$K_a = -2.90\Sigma\sigma + 4.58$, for substituted anilines suggested by Perrin [31], who used a different set of σ values.) In this instance the meta derivatives are better fit ($r^2 = 0.989$) than the para derivatives ($r^2 = 0.938$).

ATOMIC CHARGE PARAMETERS

It was of interest to see if any correlations existed between the variations in the formal charge on the nitrogen atom, as measured by different methods, and the properties examined. The two structural properties, the C—N bond distance R(C—N) and the OOP angle θ, showed no significant correlation with either the Mulliken or the electrostatic charges ($r^2 < 0.04$ in both instances). However, both of these structural properties exhibited good correlations with the natural charge Q_n. For R(C—N) the correlation was

$$\mathrm{R(C{-}N)} = -3.08(\pm 0.26)Q_n - 1.11(\pm 0.22)$$

$$n = 19, \quad r^2 = 0.889, \quad s = 0.003, \quad F = 136.$$

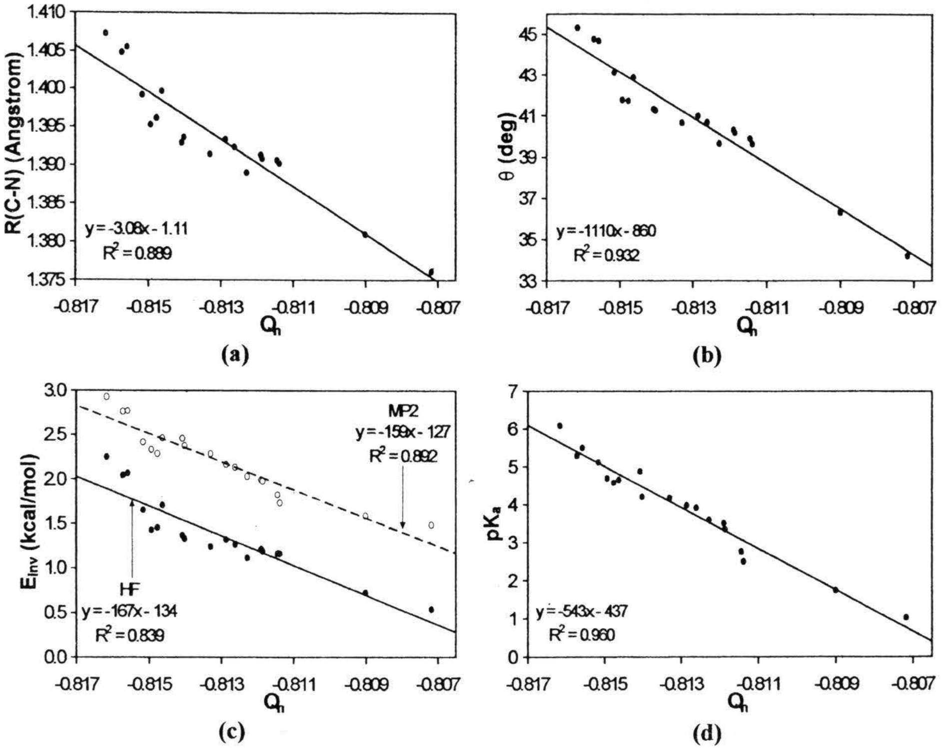
Here the para derivatives were better fit ($r^2 = 0.958$) than the meta derivatives ($r^2 = 0.792$). For the out-of-plane angle,

$$\theta = -1110(\pm 70)Q_n - 860(\pm 59)$$

$$n = 19, \quad r^2 = 0.932, \quad s = 0.70, \quad F = 234.$$

The correlation between θ and Q_n for the para-substituted compounds was somewhat better ($r^2 = 0.974$) than that for the meta-substituted compounds ($r = 0.910$). The overall correspondences are shown in Figure 3.

There was also no significant correlation between the inversion barrier E_{inv} and the Mulliken and electrostatic charges on the nitrogen atom. However, E_{inv} as determined at the Hartree–Fock level had a



(a) (b) (c) (d)

FIGURE 3. Correlations of the properties examined with the amino nitrogen atom natural charge Q_n: (a) The amino group C—N bond distance vs. Q_n, (b) the out-of-plane angle θ vs. Q_n, (c) the inversion barriers $E(\mathrm{HP})_{\mathrm{inv}}$ and $E(\mathrm{MP2})_{\mathrm{inv}}$ vs. Q_n, and (d) the amino group pK_a vs. Q_n.

TABLE III

Correlation coefficients among the properties and parameters studied.

	R(C—N)	θ	E_{inv}(HF)	E_{inv}(MP2)	pK_a	σ	Q_M	Q_e	Q_n
R(C—N)	1	0.993	0.992	0.935	0.934	−0.893	−0.198	−0.041	−0.943
θ	0.993	1	0.975	0.941	0.956	−0.897	−0.186	−0.027	−0.966
E_{inv}(HF)	0.992	0.975	1	0.944	0.922	−0.910	−0.212	−0.065	−0.916
E_{inv}(MP2)	0.935	0.941	0.944	1	0.974	−0.975	−0.146	−0.050	−0.944
pK_a	0.934	0.956	0.922	0.974	1	−0.965	−0.160	−0.071	−0.980
σ	−0.893	−0.897	−0.910	−0.975	−0.965	1	0.242	0.126	0.918
Q_M	−0.198	−0.186	−0.212	−0.146	−0.160	0.242	1	0.301	0.182
Q_e	−0.041	−0.027	−0.065	−0.050	−0.071	0.126	0.301	1	0.059
Q_n	−0.943	−0.966	−0.916	−0.944	−0.980	0.918	0.182	0.059	1

fair correlation with the natural charge

$$E_{\text{inv}}(\text{HF}) = -167(\pm 18)Q_n - 134(\pm 14)$$
$$n = 19, \quad r^2 = 0.839, \quad s = 0.17, \quad F = 88.$$

For this, the para derivatives were better fit ($r^2 = 0.908$) than the meta derivatives ($r^2 = 0.870$). As was the case for the Hammett constants, the overall fit of E_{inv} with Q_n improved when the energy calculations were performed at the MP2 level:

$$E_{\text{inv}}(\text{MP2}) = -159(\pm 13)Q_n - 127(\pm 11)$$
$$n = 19, \quad r^2 = 0.892, \quad s = 0.13, \quad F = 140.$$

Here the para compounds were a better fit ($r^2 = 0.917$) than the meta compounds ($r^2 = 0.829$).

A very good correlation was found between Q_n and the measured pK_a of the amino group for this set of compounds:

$$\text{p}K_a = -543(\pm 27)Q_n - 437(\pm 22)$$
$$n = 19, \quad r^2 = 0.960, \quad s = 0.26, \quad F = 404.$$

This correspondence is illustrated in Figure 3. For the subset of the para-substituted anilines the correlation was exceptionally good ($r^2 = 0.982$), while this correlation was still fairly good ($r^2 = 0.876$) for the meta-substituted subset of compounds.

The different properties and indices also were highly intercorrelated. A summary of the correlation coefficients found between the variables investigated is given in Table III.

Discussion

It is apparent from the information in Table III that the variations caused by substitution in the four properties examined are closely tied together. As one would anticipate from general principles, electron-withdrawing substituents enhance planarity of the aniline framework, thereby shortening R(C—N), decreasing θ, and lowering the inversion barrier E_{inv}. The accompanying loss of electron density from the amino nitrogen atom decreases the pK_a of the amino group. Conversely, electron-donating substituents favor pyramidal sp^3 hybridization at the amino nitrogen, leading to a longer C—N bond length, greater out-of-plane angle θ, and a larger value of E_{inv}. Also, the pK_a of the amino nitrogen is increased by electron-donating substituents. The sizes of the effects on the properties can be associated with the electron-withdrawing and -donating strengths of the substituents.

The HF 6-311G** level of theory appears to yield reasonably accurate values for the structural properties examined here. The C—N bond lengths are, within the accuracy of the available data, close to the few values reported. For aniline the C—N bond length from X-ray diffraction is 1.402 Å [2], close to the calculated value of 1.396 Å. For para-nitroaniline the amino C—N bond length is reported to be 1.371 Å from X-ray diffraction [32], again close to the calculated value of 1.376 Å. The experimental value for para-diaminobenzene is uncertain, likely falling in the range 1.412–1.427 Å [33], which is somewhat higher than our calculated value of 1.407 Å. The calculated values for the out-of-plane angle θ also fall within the experimental limits for the few cases available. For para-fluoroaniline θ has been estimated to be about 46° [34], reasonably close to the calculated value of 43°, and in para-aminoaniline θ is reported to be 43 ± 4° [33], compared to our calculated value of 45°.

It is interesting, but certainly coincidental, that the values calculated for E_{inv} at the HF 6-311G** level are virtually identical to the (few) known experimental values, whereas those determined when account is taken of electron correlation at the MP2 level are higher. The HF 6-311G** E_{inv} values for both aniline and para-fluoroaniline fall within the experimental uncertainites: aniline 1.50 kcal/mol (exp.) [24–26] vs. 1.45 kcal/mol (calc.); and para-fluoroaniline 1.71 kcal/mol (exp.) [25] vs. 1.70 kcal/mol (calc.). The result that MP2 calculations overestimate the inversion barrier was also observed in an earlier study [28].

The traditional Hammett σ constants are seen to give a fair account of the variations caused by substitution in aniline. While the correlations of σ with R(C—N) and θ are only modest, σ yields rather good correlations for both E_{inv}(MP2) and the amino group pK_a. From the improvement of fit in going from E_{inv}(HF) to E_{inv}(MP2), one can infer that the Hammett constants, based as they are upon experimental observations, take some natural account of the electron correlation energy.

As for the use of atomic charges as indicators for structural and other property variations, the shortcomings of the Mulliken charges are well known [13, 17], and they are quite apparent in this study. Although simple to calculate, Mulliken charges (1) sometimes yield unphysical negative values, (2) can vary considerably with the basis set employed, and (3) often show unrealistic values in ionic compounds [17].

Electrostatic charges, which are fit to the electrostatic potential about the molecule, might be expected to perform better, but they too did not yield significant correlations with any of the properties examined. In contrast, the natural charge Q_n [17] on the amino nitrogen atom proved to be a very useful regression descriptor for all four of the properties studied in this report. In fact, for three of the properties—R(C—N), θ, and pK_a—the natural charge Q_n was superior to the classical Hammett σ constants as a regression parameter, and it performed comparably for the fourth property (E_{inv}). These results support suggestions made by others [13, 17] that Q_M and Q_e should no longer be used and suggest that, at least on the basis of the results found for the present compounds and properties, the natural charge Q_n would appear to be a suitable replacement.

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