

# Methyl and Phenyl Substitution Effects on the Proton Affinities of Hydrides of First and Second Row Elements and Substituent Effects on the Proton Affinities of Ring Carbons in Benzene: A DFT Study

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Theoretical calculations using B3LYP density functional theory (DFT) with the 6-311++G(d,p) basis set have been performed to determine proton affinities (PAs) of a series of H–X compounds and the corresponding methyl- (H<sub>3</sub>C–X) and phenyl- (Ph–X) substituted derivatives with a variety of proton acceptor atoms, such as C, O, N, F, Si, P, S, Cl, etc. Our results illustrate an interesting substituent effect on PAs. The PAs of ring carbon atoms for a series of monosubstituted benzene molecules (Y–C<sub>6</sub>H<sub>5</sub>; Y = F, Cl, CH<sub>3</sub>, OCH<sub>3</sub>, NH<sub>2</sub>, PH<sub>2</sub>, OH, SH, SiH<sub>3</sub>, CN, CF<sub>3</sub>, and NO<sub>2</sub>) have also been estimated. Correlations between proton affinities of H–X, H<sub>3</sub>C–X, and Ph–X and substituent effects on the PAs of the ring carbon atoms for a series of monosubstituted benzene molecules have been studied. It has been observed that substituent effects on the PAs of the ring carbon atoms follow a good Hammett-type correlation.

## 1. Introduction

The proton affinity (PA) of a molecule is an important characteristic, and knowledge of its value is necessary to understand a wide range of processes in chemistry and biology.<sup>1,2</sup> For example, the PA helps to determine the direction of proton- and electron-transfer reactions, to explain acid–base reactions, and to assist in the selection of a reagent gas in analytical mass spectrometry. Knowledge of gas-phase basicity is also crucial for understanding of reactivity of a molecule. There are several experimental methods, such as mass spectrometry,<sup>3</sup> the measurement of gas-phase proton exchange equilibrium constants between two bases, and the ion cyclotron resonance technique,<sup>4</sup> for the determination of PAs. On the basis of these procedures, several thermochemical ladders or basicity scales have been constructed to connect molecules over a wide range of PA values.<sup>5–7</sup> These experimental methods generally provide relative PA values, and absolute values can be obtained only by selecting an anchor, which can adversely affect the accuracy. Recently, Meot-Ner has reviewed the methods used to construct the ladders and also proposed a comprehensive PA scale.<sup>8</sup>

Theoretical calculation of PAs using quantum chemical methods is now a viable alternative to performing tedious experiments. Moreover, the experimental approach will provide PA values related to the most stable protonated species for a molecule that contains multiple potential protonation sites. Thus, determination of site selectivity is not easy from experimental work. Theoretical calculations are free from these constraints, and it is possible, in principle, to calculate the PA values of all

possible protonation sites in a molecule. Several ab initio procedures, such as MP2 and G2(MP2), are known to produce accurate PA values.<sup>9,10</sup> For details, refer to the recent review by Deakyne.<sup>11</sup> From the standpoint of computational time and efficiency, however, density functional methods are probably the most suitable approach for the calculation of PAs, especially for larger systems. The B3LYP method is known to provide very accurate PA values.<sup>12–14</sup>

There has been considerable interest in finding correlations between proton affinity and some molecular properties.<sup>15–18</sup> Taft has shown that, in many cases, substituent effects can be rationalized using the concepts of inductive, resonance, and polarizability effects.<sup>19</sup> Alkyl substituent effects on the PAs of cyanides and isocyanides were also analyzed by Meot-Ner et al. in terms of the polarizability of the substituents.<sup>20</sup> They also observed that PA data for isocyanides complement conventional lone-pair electron donors such as oxygen, nitrogen, and sulfur. These relations are helpful to understand the effects of substituent on PA and also to estimate PAs for substituted compounds from the correlation equation without performing rigorous experiments or calculations for the same.<sup>21–23</sup> A relation between the electronic chemical potential and proton-transfer barriers has also been reported in the works of Tapia et al.<sup>24</sup> While studying the proton affinities of 15 substituted anilines, Lau and Kebarle<sup>25</sup> observed a linear relationship between experimental nitrogen 1s core electron ionization energies and free energies of proton transfer for substituted anilines. Martin and Shirley<sup>26</sup> and David and Rabalais<sup>27</sup> independently proposed a linear relationship between proton affinities and inner-shell ionization energies for oxygen- and nitrogen-containing molecules, and those relations were shown to hold for a considerable number of organic compounds. Later, Karachevtsev and Savkin<sup>28</sup> also reported a good correlation between PA and ionization

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potentials (IP) for almost 200 molecules. The concept was analyzed and extended further by Maksić and Vianello.<sup>21</sup> Catalán and Yáñez<sup>29</sup> presented a very simple way for evaluating PA of mono- and poly-substituted benzene derivatives from the linear correlation between experimental proton affinities and the calculated 1s orbital energy of the para carbon ( $\epsilon_{1s}$ ) atom. Similar relationships have also been reported for O 1s and N 1s. This relation provides a simple method for estimating proton affinities and also for classifying different centers according to their intrinsic basicity. It has also been demonstrated that the effects of substituents on PA are additive for polysubstituted aromatics, such as benzene and naphthalene.<sup>10,30</sup> Maksić and co-workers carried out calculations for the proton and methyl cation affinities (MCAs) of substituted benzenes.<sup>31</sup> They found a linear correlation between the MCAs and PAs of substituted benzenes calculated at the theoretical MP2/6-31G\*\* level. Deakne has recently reviewed the different models developed to probe the inherent effects of molecular electronic structure on acid–base behavior.<sup>11</sup>

In fact, all of these works reveal interesting links between the proton affinities and different molecular electronic properties. In this context, we set out to study in detail the relationship between the PAs of different methyl- and phenyl-substituted compounds and those of their unsubstituted counterparts. We consider a variety of hydrides of the first and second row elements, namely, C, N, O, Si, P, and S, as the protonation site and observe how the PA values change upon methyl and phenyl substitution at these sites. Although alkyl substituent effects on some of these proton acceptors were studied before individually,<sup>19,20</sup> we are not aware of any study considering a variety of proton acceptors together. We also study the effects of substituents on the PAs of different ring carbon atoms of benzene. One might expect an intrinsic correlation between the electronic effect of substituents at the reaction site and PA values. Our goal is to determine this intrinsic correlation in the PA values for different series of compounds and relate them to structural parameters. We should also mention here that experimental and theoretical PA values are available for many of the molecules studied here. However, we have recalculated the PA values again even for the first and second row hydrides and their corresponding methyl-substituted products to obtain all of the PA values at the same level. This is important for finding any meaningful relationship. Because available experimental and theoretical PA values were estimated using different experimental and theoretical methods, they have different levels of uncertainties associated with them. Experimental values are also available for some of the phenyl systems studied here, but they refer only to the most stable protonated species of the molecules. We have calculated the PA values for all possible protonation sites (including the central atom of the substituent) of the substituted phenyl systems at the same level of theory. This provides a better understanding of how the basicity of different ring carbons changes with substitution at a particular site and helps to identify the most basic site. To the best of our knowledge, there are no detailed calculations of PA values of substituted phenyl systems at the same level of theory. We should point out here that our main aim is to find the intrinsic correlation among the PA data, and therefore, little attention is paid to any individual PA value, and the corresponding literature data are not discussed. We use the B3LYP density functional procedure along with the 6-311++G(d,p) basis set for the calculation of PA values. This DFT method is known to produce quite accurate PA values.<sup>12,13</sup> The suitability of this method is further justified in this work.

**TABLE 1: B3LYP/6-311++G(d,p)-Calculated Proton Affinities (in kJ/mol) of H–X, CH<sub>3</sub>–X, and C<sub>6</sub>H<sub>5</sub>–X at 298 K<sup>a,b</sup>**

X	H–X	CH <sub>3</sub> –X	C <sub>6</sub> H <sub>5</sub> –X
CH <sub>3</sub>	545.9 (543.5)	597.9 (596.3)	–
SiH <sub>3</sub>	642.1 (639.7)	691.2	–
NH <sub>2</sub>	852.7 (853.6)	898.3 (899.0)	877.8
PH <sub>2</sub>	783.7 (785)	851.8 (851.5)	868.8
OH	687.8 (691.0)	753.7 (754.3)	747.1
SH	705.9 (705.0)	772.7 (773.4)	790.1
F	475.2 (484.0)	594.8 (598.9)	618.6
Cl	552.8 (556.9)	640.7 (647.3)	666.1
CF <sub>3</sub>	568.8 (619.5)	651.7	764.1
CN	707.9 (712.9)	785.8 (779.2)	826.7
NO <sub>2</sub>	668.8	738.9 (754.6)	810.0
OCH <sub>3</sub>	753.7 (754.3)	791.0 (792.0)	788.8

<sup>a</sup> Protonation has been considered at the central atom (the first atom in column 1) of X. Quantities within parentheses correspond to the experimental values. <sup>b</sup> Most recommended experimental results, taken from the NIST Webbook.<sup>38</sup>

## 2. Methods of Calculation

All calculations were performed using the Gaussian 03 program package.<sup>32</sup> The geometries of all of the molecules studied here and their corresponding protonated species were fully optimized at the B3LYP level with the 6-311++G(d,p) basis set. Frequency calculations were also performed at the B3LYP/6-311++G(d,p) level to characterize the stationary points and also to estimate the zero-point energy (ZPE) and thermal corrections to the enthalpy. The PA value was calculated at 298 K from the reaction enthalpy of the reaction  $\text{BH}^+ \rightarrow \text{B} + \text{H}^+$

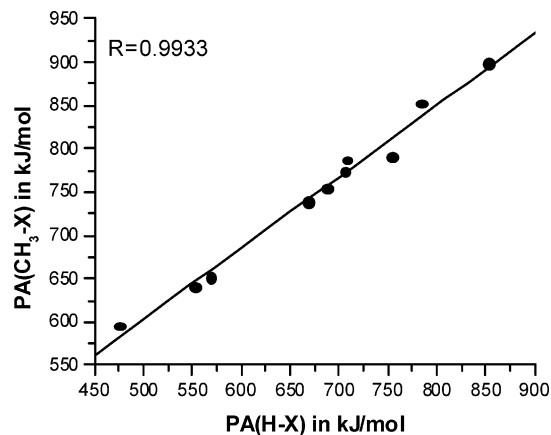
$$\text{PA} = H_f(\text{B}) + H_f(\text{H}^+) - H_f(\text{BH}^+) \quad (1)$$

The enthalpy ( $H_f$ ) of each species at 298 K was estimated from the electronic energy after taking into account the ZPE and other necessary corrections due to translational, rotational, and vibrational motions of the molecule:  $H_f(298 \text{ K}) = E_0 + \text{ZPE} + H_{\text{trans}} + H_{\text{rot}} + H_{\text{vib}} + RT$ .  $H_{\text{trans}}$ ,  $H_{\text{rot}}$ , and  $H_{\text{vib}}$  are the translational, rotational, and vibrational contributions, respectively, to the enthalpy and can be estimated from the standard formulas.<sup>33</sup>

## 3. Results and Discussion

**3.1. Protonation of X–H and X–CH<sub>3</sub>.** We have calculated the PA values for a series of X–H and X–CH<sub>3</sub> compounds with X = H, CH<sub>3</sub>, SiH<sub>3</sub>, OCH<sub>3</sub>, NH<sub>2</sub>, PH<sub>2</sub>, OH, SH, F, Cl, CF<sub>3</sub>, CN, and NO<sub>2</sub> in order to understand the effects of methyl substitution on the PAs of a broad range of first and second row protonated atoms. Table 1 presents the calculated PA values for X–H and X–CH<sub>3</sub> compounds along with the available experimental values. In all of these cases, protonation is considered only at the central atom of X, and it corresponds to the first atom in column 1 (X) of Table 1. Protonated methane and ethane are well-characterized experimentally as well as theoretically.<sup>34</sup> Alkanes, once protonated, rapidly lose a hydrogen molecule. The protonated methane have five reasonable structural forms: two forms are in  $C_s$  symmetry, and one each is in  $C_{3v}$ ,  $C_{4v}$ , and  $D_{3h}$  symmetry.

Our results are in good agreement with the earlier works<sup>35</sup> and also show that one of the  $C_s$ -symmetric structures is the most stable structure. It appears to be a complex between a methyl cation and a hydrogen molecule, rather than between methane and a proton. In this work, the PA of methane is chosen corresponding to this first form with  $C_s$  symmetry. Protonated

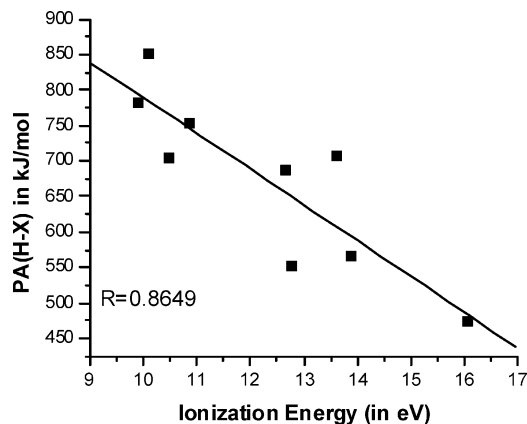


**Figure 1.** Correlation between the proton affinities of H–X and CH<sub>3</sub>–X (X = F, Cl, OH, SH, OCH<sub>3</sub>, NH<sub>2</sub>, PH<sub>2</sub>, CN, CF<sub>3</sub>, and NO<sub>2</sub>).

ethane also can exist in two different forms.<sup>34,36</sup> We recalculated and reoptimized these two forms of protonated ethane. In the most stable structure, there exists a hydrogen-bridging bond between two carbons. The other structure corresponds to H<sub>3</sub>C–CH<sub>4</sub><sup>+</sup>, and protonation takes place at one of the carbon atom. The energy difference between the two forms is about 20 kJ mol<sup>-1</sup>. Our tabulated value corresponds to the most stable structure.

Table 1 shows that our calculated PA values for X–H and X–CH<sub>3</sub> compounds are quite close to the corresponding experimental values. This very good agreement between our calculated and experimental PA values justifies further our choice of the B3LYP/6-311++G(d,p) method for this study. We must also emphasize here that the calculation of very accurate PA values is not the main purpose of this work; rather, our prime interest is to study the variation of PAs upon substitution. To that end, we believe that the B3LYP procedure adopted here is sufficient to serve our purposes. The proton affinity of phosphine is about 70 kJ mol<sup>-1</sup> lower than that of ammonia. On the other hand, the PA of H<sub>2</sub>S is found to be greater than that of H<sub>2</sub>O. Substitution of a hydrogen atom in water by a CH<sub>3</sub> group (i.e., formation of CH<sub>3</sub>OH) enhances the PA value by nearly 65 kJ mol<sup>-1</sup>. In general, Table 1 shows that methyl substitution in X–H always increases the PA value for the central atom at the X position. Long ago, Munson<sup>37</sup> measured the proton affinities or basicities of some polar hydrocarbon derivatives in the gas phase by mass spectrometry and suggested that replacement of hydrogen by a methyl group increases the base strength of the molecules. Our observation is thus in good agreement with the conclusions of Munson<sup>37</sup> and others<sup>20</sup> on the methyl inductive effect for many compounds containing atoms of the first and second row. In fact, the methyl group is well-known as an electron-donating group, and thus, methyl substitution is expected to increase the electron density at the protonation site X, resulting in an increase in the PA value as well.

The extent of the increase in the PA value due to methyl group substitution (i.e., X–H to X–CH<sub>3</sub>) depends strongly on the nature of central atom (protonation site) in X. More interesting observations can be made from the extent of the effects of methyl substitution on the PA value. Figure 1 shows the correlation between the PA values (given in Table 1) of X–H and X–CH<sub>3</sub>. We should point out here that, in both cases, X is considered to be the protonation site, although that might not be the most preferred protonation site for all of the molecules considered here. The –CH<sub>3</sub> and –SiH<sub>3</sub> groups are not included in the correlation, because in both of these cases, as discussed



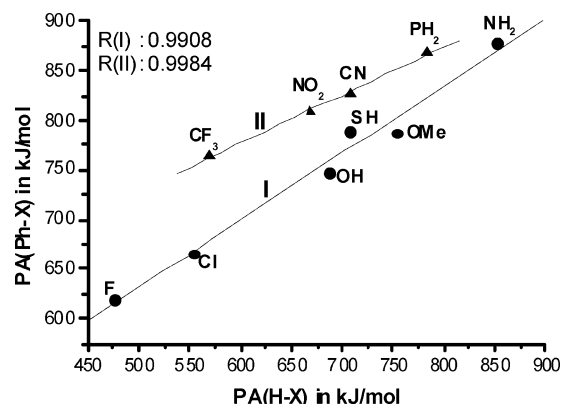
**Figure 2.** Plot of proton affinity (PA) against experimental ionization potential for the X–H molecules listed in Table 1.

before, protonation does not take place directly at the carbon or silicon site and, as a result, they deviate considerably from the correlation line. It is clear from this figure that there exists a good linear relation between the PAs of X–H and X–CH<sub>3</sub>. One can easily observe from the figure that the effect of methyl substitution is not constant; rather, the effect depends on the nature of the central atom in X of the compound H–X. Generally, the effect is greater the higher the electronegativity of the central atom of X. The effect does not differ much when we go from the first row to the second row element of the same group. The correlation equation obtained between the PAs of X–H and X–CH<sub>3</sub> can be expressed as

$$\text{PA}(\text{X}-\text{CH}_3) = 0.8263 \times \text{PA}(\text{X}-\text{H}) + 189.60 \quad (R = 0.9933) \quad (2)$$

In view of the suggested<sup>28</sup> correlation between PA and ionization potential, we tried to observe the same relationship between the PA and IP values of the H–X and CH<sub>3</sub>–X compounds included in Table 1. The experimental IP values were taken from the NIST Webbook.<sup>38</sup> Figure 2 shows the correlation between PA and IP values for H–X compounds. As can be seen, although there is a trend of increasing PA with decreasing IP, the correlation is not impressive ( $R = 0.8649$ ), and there are significant deviations in many cases. Ionization energies estimated by Koopmans' theorem ( $-\epsilon_{\text{HOMO}}$ ) do not provide any better correlation with PA. Similar features were observed for CH<sub>3</sub>–X compounds as well. One needs to identify some other local descriptors to find their correlations with PA values. Local ionization energy might be a good choice in this regard, but further work is needed to define this parameter rigorously and also to study the correlation.

**3.2. PA Values of C<sub>6</sub>H<sub>5</sub>–X.** The PA values for a series of Ph–X compounds with X = H, CH<sub>3</sub>, SiH<sub>3</sub>, OCH<sub>3</sub>, NH<sub>2</sub>, PH<sub>2</sub>, OH, SH, F, Cl, CF<sub>3</sub>, CN, and NO<sub>2</sub> were calculated to evaluate the effects of phenyl substitution on the PAs of a broad range of proton-acceptor central atoms in X. Of course, as discussed in the next section, the central atom of X is not always the most preferred protonation site for Ph–X compounds. However, it is always considered here as the protonation site, because our intention is to study the phenyl substitution effect on PAs. Table 1 presents the calculated PA values for these Ph–X compounds. Toluene (Ph–CH<sub>3</sub>) and phenylsilane (Ph–SiH<sub>3</sub>) are not included here because, in both of these cases, our attempt to protonate at the CH<sub>3</sub> and SiH<sub>3</sub> sites failed; the proton always moved to the ipso position. As observed for methyl substitution, phenyl substitution (going from H–X to Ph–X) also increases the PA



**Figure 3.** Correlation between the proton affinities of H-X and Ph-X. The central atom in X is always considered as the protonation site. Systems are divided into two sets: ring carbon is the most preferred protonation site (I) and X is the most preferred protonation site (II).

value in comparison to that of the parent H-X molecule. Figure 3 displays the relation between the PA values of H-X and Ph-X molecules. Although the linear relationship is not as good as that observed for methyl substitution when all of the molecules are taken together, the PA values of H-X and Ph-X tend to exhibit a linear correlation. In most of the cases, phenyl substitution increases the PA value more than methyl substitution. Interestingly, the effect is very mild when X is an electron-donating group, such as OCH<sub>3</sub> and NH<sub>2</sub>. On the other hand, a dramatic increase of PA values can be observed for electron-withdrawing groups, such as CF<sub>3</sub>, CN, and NO<sub>2</sub>. In fact, as discussed later, protonation at the central atom of these three groups is much more preferred than protonation at the ring carbons. Obviously, phenyl substitution does not change the basicity at the X site significantly when X is an electron-donating group, because such groups tend to push electrons in the opposite direction. At the same time, an electron-withdrawing group tries to drag ring electrons toward itself, and as a result, increases its basicity. The correlation equation between the PAs of Ph-X and H-X for 10 proton acceptors included in Table 1 (excluding CH<sub>3</sub>-X and SiH<sub>3</sub>-X) can be expressed as

$$\text{PA}(\text{X}-\text{Ph}) = 0.6516 \times \text{PA}(\text{X}-\text{H}) + 335.47 \quad (R = 0.9068) \quad (3)$$

It appears from the figure that a better correlation can be obtained if the points are divided into two groups: (i) systems that prefer protonation at the ring carbon and (ii) those that prefer protonation at X (such as CF<sub>3</sub>, NO<sub>2</sub>, CN, and PH<sub>2</sub>). As shown in Figure 3, this gives rise to the following two correlation equations depending on whether protonation at ring the carbon is preferred (eq 4 and plot I in Figure 3) or protonation at substituent X is preferred (eq 5 and plot II in Figure 3)

$$\text{PA}(\text{X}-\text{Ph}) = 0.6766 \times \text{PA}(\text{X}-\text{H}) + 293.73 \quad (R = 0.9908) \quad (4)$$

$$\text{PA}(\text{X}-\text{Ph}) = 0.4833 \times \text{PA}(\text{X}-\text{H}) + 487.66 \quad (R = 0.9984) \quad (5)$$

The problem now is to know a priori which will be the most preferred protonation site and decide accordingly what correlation equation should be used. It appears from our study that, at least for electron-withdrawing groups, protonation at X is preferred. Table 1 shows that, for strong electron-donating groups (such as OCH<sub>3</sub> and NH<sub>2</sub>), a methyl group enhances the

**TABLE 2: B3LYP/6-311++G(d,p)-Calculated Proton Affinities (in kJ/mol) of Different Ring Carbons of Substituted Benzenes (X-C<sub>6</sub>H<sub>5</sub>) at 298 K<sup>a</sup>**

X	C <sub>1</sub> (ipso)	C <sub>2</sub> (ortho)	C <sub>3</sub> (meta)	C <sub>4</sub> (para) <sup>b</sup>
CH <sub>3</sub>	762.3	796.9	781.3	802.8 (800.0)
SiH <sub>3</sub>	827.6	774.5	770.5	773.8
NH <sub>2</sub>	721.0	868.3	789.7	886.5 (849.8)
PH <sub>2</sub>	795.0	790.6	766.5	801.0
OH	706.5	814.5	761.4	824.9 (810.8)
SH	737.7	804.3	759.8	819.1
F	687.4	757.2	733.8	766.4 (761.5)
Cl	704.5	761.8	739.0	769.1
CF <sub>3</sub>	706.6	719.0	720.5	715.3
CN	672.1	712.6	703.8	711.4 (642.2)
NO <sub>2</sub>	672.9	691.6	697.3	689.8 (618.4)
OCH <sub>3</sub>	719.3	837.0	775.2	846.1

<sup>a</sup> Calculated PA value of benzene is 766.0 kJ/mol. <sup>b</sup> Quantities within parentheses are PA values estimated from empirical eq 6 and taken from ref 29.

PA value at the X position slightly more than a phenyl group. On the contrary, a phenyl group enhances the PA value much more than a methyl group for electron-withdrawing groups, such as CF<sub>3</sub>, CN, and NO<sub>2</sub>.

**3.3. Substituent Effects on the PAs of Ring Carbons.** We determined the PA values for different ring carbon atoms to evaluate the effects of substituents on intrinsic basicity for a series of monosubstituted benzenes, X-C<sub>6</sub>H<sub>5</sub> with X = CH<sub>3</sub>, SiH<sub>3</sub>, OCH<sub>3</sub>, NH<sub>2</sub>, PH<sub>2</sub>, OH, SH, F, Cl, CF<sub>3</sub>, CN, and NO<sub>2</sub>. Long ago, Catalán and Yáñez<sup>16,29</sup> demonstrated a correlation between the PAs of ring carbons and C 1s binding energies and predicted the PA values of different ring carbon atoms using this correlation. The C 1s orbital energies were first determined by ab initio STO-3G calculations, and then the PAs were estimated from the equation:

$$\text{PA} = 1035.75\epsilon_{\text{C } 1s} + 11607.97 \quad (6)$$

where the PAs were in kcal/mol and the C 1s orbital energy ( $\epsilon_{\text{C } 1s}$ ) was in atomic units.

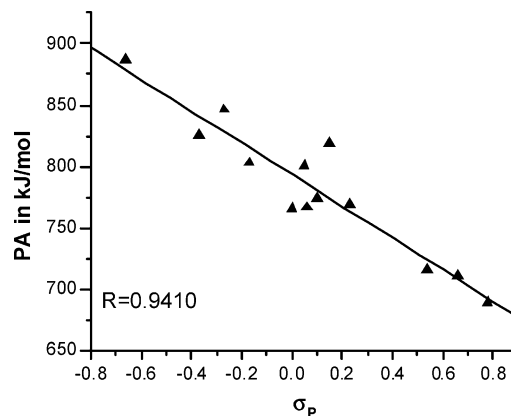
Recently, Maksić et al.<sup>31</sup> calculated the PA values (at 0 K) for the ortho, meta, and para carbon atoms for benzenes substituted with -CH<sub>3</sub>, -F, -OH, -CHO, and -CN at the MP2(fc)/6-31G\*\*//HF/6-31G\* theoretical level. Their calculated values for these five systems can be compared to our B3LYP-calculated values. The inclusion of strong electron-donating and -withdrawing groups as substituents in our study enhances the scope of our analysis. Moreover, the PA values at the ipso position of benzene for all of these substituents have never before been calculated.

Our calculated PA values at 298 K for different ring carbon atoms of monosubstituted benzenes are reported in Table 2. The PA values at 0 K for -CH<sub>3</sub>, -F, -OH, and -CN substituted benzenes were found to follow the same trend as given by Maksić et al.<sup>31</sup> For fluorobenzene and phenol, the difference between our calculated PA values and those reported by Maksić et al.<sup>31</sup> is less than 4 kJ mol<sup>-1</sup>, whereas for toluene and cyanobenzene, the PA values differ by about 10 kJ mol<sup>-1</sup>. The calculated PA value for benzene (761.3 kJ/mol) is in reasonably good agreement with the experimental value of 752.7 kJ/mol.<sup>30</sup> However, our calculated PA values differ widely from those predicted by Catalán and Yáñez<sup>29</sup> from the empirical eq 6. The difference is especially significant for strong electron-donating (NH<sub>2</sub>) and -withdrawing (CN, NO<sub>2</sub>) groups. For example, our calculated PA values at the para positions of aniline and nitrobenzene are 38 and 75 kJ/mol higher than their predicted values, respectively. This clearly indicates that the empirical

eq 6 does not hold well for strong electron-donating and -withdrawing groups. Most remarkably, using that empirical correlation (eq 6), the meta carbon was predicted to be the most basic site for cyanobenzene, whereas our calculated results, as well as those of Maksić et al.,<sup>31</sup> show that the basicities of the ortho and para carbon atoms are almost the same as and higher than that for meta carbon atom. Of course, this difference in the PA values obtained from eq 6 and our calculated results can be attributed to the fact that eq 6 is based on the properties of neutral molecules. It does not directly include the effects of geometrical and electronic relaxation on protonation. These effects on PAs are partially included through the parameters in the correlation equation. Therefore, eq 6 can provide consistent results only when geometrical and electronic relaxation effects on PAs vary systematically throughout the series. Moreover, the poor quality of the STO-3G basis set used for calculating the C 1s orbital energies can affect the accuracy of PA values obtained using eq 6. In fact, we observed a better correlation ( $R = 0.97$ ) between our B3LYP-calculated C 1s orbital energies and the PA values for para carbon atoms in Ph-X compounds.

Table 2 shows that the PA values at the ipso (C<sub>1</sub>) position of monosubstituted benzenes are lower than those for the ortho, meta, and para positions except for the -SiH<sub>3</sub> group. For phenylsilane, the ipso position is found to be the most basic site. The ipso carbon atom is also found to be more basic than the ortho and meta carbon atoms of phenylphosphine. In fact, except for -SiH<sub>3</sub> and -PH<sub>2</sub> groups, both electron-donating and -withdrawing groups reduce the PA at the ipso position in comparison to that of benzene. Of course, this reduction is much greater for electron-withdrawing groups. Interestingly, even methyl substitution reduces the PA of the ipso carbon in toluene from that observed for benzene. In contrast, methyl substitution always enhances the PA for hydrides of first or second row elements. For electron-donating groups, such as CH<sub>3</sub>, OCH<sub>3</sub>, and NH<sub>2</sub>, as substituents, the PA value for the para carbon atom is the highest, and that for the ortho carbon atom is 5–18 kJ mol<sup>-1</sup> lower than the PA value at the para position. Similar trends can be observed for PH<sub>2</sub>-, OH-, SH-, F-, and Cl-substituted benzenes. For all of these substituents, the basicity of the meta carbon atom is substantially lower than those of the ortho and para carbon atoms. These groups can thus be termed as para- (or ortho-) orienting groups for electrophilic addition reactions. On the other hand, the PA value at the meta position is found to be highest for trifluoromethylbenzene and nitrobenzene. Although the difference in PA values between the meta and para positions is not very high for these two compounds, these two electron-withdrawing substituents can be termed as mild meta-orienting groups. The difference in PA values between the ipso and para (or ortho) positions is quite large for electron-donating substituents, whereas for electron-withdrawing substituents, this difference is found to be rather small. For example, this PA difference amounts to 166 and only 17 kJ mol<sup>-1</sup> in aniline and nitrobenzene, respectively. Electron-donating substituents, therefore, make ring carbon atoms more dissimilar than do electron-withdrawing groups. In view of the observed<sup>26,27,29</sup> relation between PAs and inner-shell ionization energies, it can be stated that substituents affect the  $\sigma$ -electron framework of the aromatic ring.

In the preceding section, we analyzed the effects of phenyl substitution on the proton affinities of a variety of proton-acceptor atoms in X while going from H-X to Ph-X. Although phenyl substitution increases the proton affinity, as shown in Figure 3, the relation between the PA values of H-X and Ph-X is not strictly linear when all of the points are taken together. It

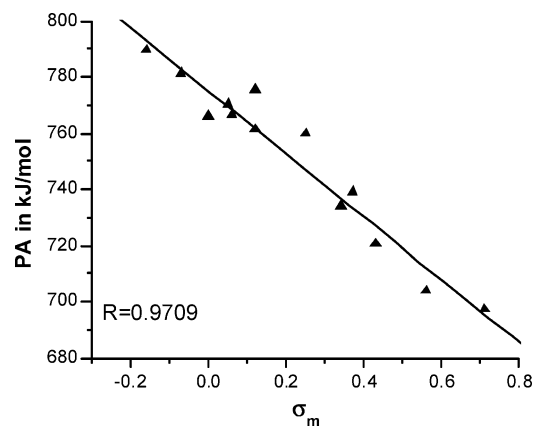


**Figure 4.** Plot of proton affinities (PAs given in Table 2) for the para carbon (C<sub>4</sub>) of monosubstituted benzenes (X-C<sub>6</sub>H<sub>5</sub>) against Hammett's parameters ( $\sigma_p$ ).

is clear from the PA values in Tables 1 and 2 that, in many cases, especially when X is an electron-donating group, the PA of a ring carbon (mostly C<sub>4</sub>) is more than that of the central atom of group X. On the other hand, for electron-withdrawing groups (such as CF<sub>3</sub>, CN, and NO<sub>2</sub>), protonation is preferred at the X position rather than at the ring carbon. We wanted to observe the relation between the PA values for H-X and the maximum PA values for Ph-X compounds. Interestingly, we observed a far better correlation ( $R = 0.9684$ ) between these values than we observed before for the PA values corresponding to the central atom of the substituent X in Ph-X ( $R = 0.9068$ ; Figure 3 and eq 3). The correlation equation obtained between the PA values of H-X and Ph-X (maximum value among all sites) can be expressed as

$$\text{PA}(\text{Ph-X}) = 0.3462 \times \text{PA}(\text{H-X}) + 583.38 \quad (R = 0.9684) \quad (7)$$

It is always interesting to analyze the substituent effect on molecular properties and determine a correlation equation relating them. The proton affinities of substituted phenoxide (Ph-O<sup>-</sup>) and thiophenoxide (Ph-S<sup>-</sup>) ions were found to be well-correlated with Hammett's parameters.<sup>39</sup> Generally, Hammett's parameters are used to describe the remote substituent effect on a functional group. These parameters include both the field (F) and resonance (R) effects of a substituent. We feel that it is worthwhile to observe whether Hammett's reactivity parameters can also be used to describe the effects of substituents on the reactivity of ring carbon atoms. Hammett's parameters are not available for ipso and ortho positions. Moreover, steric interactions might have an important role in these two positions, and it is difficult to include the extent of that interaction within a substituent reactivity parameter. We have, therefore, analyzed the substituent effect on the basicity (PA) of meta and para ring carbon atoms in terms of Hammett's parameters.<sup>40</sup> Figure 4 displays the correlation between the PA values (given in Table 2) for para ring carbon atoms and Hammett's parameters ( $\sigma_p$ ). A similar relation between the PA values for meta ring carbon and  $\sigma_m$  is shown in Figure 5. These figures show that good linear correlations exist between the PA values and Hammett's parameters, and thus, substituent effects even on ring carbon atoms can be estimated using Hammett's parameters. The -SH group is found to deviate from both of these (especially for para) correlation curves and, as a result, worsens the overall correlation. For para substituents, the correlation coefficient ( $R$ ) becomes 0.9704 when the -SH group is excluded from the analysis. It should also be pointed out here



**Figure 5.** Plot of proton affinities (PAs given in Table 2) for the meta carbon ( $C_3$ ) of monosubstituted benzenes ( $X-C_6H_5$ ) against Hammett's parameters ( $\sigma_m$ ).

that a set of modified Hammett's parameters ( $\sigma_p^+$ ), proposed by Brown and Okamoto,<sup>41</sup> are often used to take into account the possible conjugation effect between the substituent and reactive center. However, we observed that the unmodified Hammett's parameters ( $\sigma_p$ ) provide a slightly better correlation than can be obtained with the  $\sigma_p^+$  constants.

The correlation equations obtained for the para (eq 8) and meta (eq 9) positions from linear fittings are

$$\text{PA (kJ/mol)} = 793.39 - 128.94\sigma_p \quad (R = 0.9410) \quad (8)$$

$$\text{PA (kJ/mol)} = 775.11 - 112.11\sigma_m \quad (R = 0.9709) \quad (9)$$

These empirical correlation equations can be used to determine easily the PA values of ring carbon atoms of substituted benzenes from the Hammett's constants of the substituents.

## Summary

Methyl substitution in  $X-H$  always increases the PA value for the central atom at the  $X$  position. Thus, replacement of hydrogen by a methyl group increases the base strength of molecules. The extent of the increase in the PA value due to methyl group substitution (i.e.,  $X-H$  to  $X-CH_3$ ) depends strongly on the nature of the central atom in  $X$ . There exists a good linear relation between the PAs of  $X-H$  and  $X-CH_3$ . The higher the electronegativity of the protonated atom in  $X$ , the greater the change in PA due to methyl substitution. The effect does not differ much between the first row and second row elements of the same group. Generally, phenyl substitution is also found to increase the PA of the central atom in  $X$ . However, when  $X$  is an electron-donating group, protonation at the ring carbon is seen to be preferred over that at  $X$ . The opposite is true when  $X$  is an electron-withdrawing group. For trifluoromethyl-, cyano-, and nitrobenzenes, protonation at the  $-CF_3$ ,  $-CN$ , and  $-NO_2$  groups is found to be preferred over that at the ring carbons.

Generally, the PA values for the ipso ( $C_1$ ) position of monosubstituted benzenes are lower than those for ortho, meta, and para positions, except for the  $-SiH_3$  group. For phenylsilane, the ipso position is found to be the most basic site. The ipso carbon atom is also found to be more basic than the ortho and meta carbon atoms of phenylphosphine. Both electron-donating and -withdrawing groups reduce the PA at the ipso position in comparison to that for benzene. Electron-donating substituents, such as  $CH_3$ ,  $OCH_3$ , and  $NH_2$ , increase the PA values substantially for both ortho and para carbon atoms. The

para carbon is found to be the most basic site for these substituents. A rather similar trend can be observed for  $PH_2$ -,  $OH$ -,  $SH$ -,  $F$ -, and  $Cl$ -substituted benzenes. These groups can be termed as para- (or ortho-) orienting groups for electrophilic addition reactions. On the other hand, for trifluoromethylbenzene and nitrobenzene, the PA value at the meta position is found to be highest. These two electron-withdrawing substituents can be termed as mild meta-orienting groups. For electron-donating substituents, the difference in PA values between the ipso and para (or ortho) positions is quite large, whereas for electron-withdrawing substituents, this difference is rather small. Good linear correlations were observed between the PA values for ring carbon atoms and Hammett's parameters. These correlation equations can be used for measuring the basicity of ring carbons of substituted benzenes for which experimental or rigorous theoretical results are not available.

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