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# Accurate Density-Functional Calculation of Core-Electron Binding Energies of Some Substituted Benzenes

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The core electron binding energies (CEBE's) of benzene, seven monosubstituted benzenes (Ph-X) and one disubstituted benzene ($p$-$NH_2$–$C_6H_4$–$NO_2$) were calculated using density-functional theory (DFT). The unrestricted generalized transition-state (uGTS) model was employed. The DeMon DFT program with a combined functional of Becke's exchange (B88) with Perdew's correlation (P86) was used. The average absolute deviation of the calculated CEBE's of the title compounds was 0.3 eV when the cc-pVDZ basis set was used. The "CEBE shift" of the ring carbon in Ph–X was calculated while taking the CEBE on the ring carbon in Ph–H as a reference. The thus-calculated CEBE shifts agree with experiment within the value of the average absolute deviation, 0.1 eV. The signs and quantitative numerical values of the CEBE shifts are very close to the corresponding Hammett $\sigma$ constants.

X-Ray photoelectron spectroscopy (ESCA) has been widely used in studying the atomic, molecular, and solid state structure. The ESCA spectra are a consequence of the ionization of the core-electrons of atoms that constitute a molecule. Calculating the core-electron binding energy (CEBE) has been a challenge to both theoretical and computational chemists.

Recently, Chong[1—3] proposed a method that enabled one to calculate accurate CEBE's by the density-functional theory (DFT). The method employs an unrestricted generalized transition-state (uGTS) model.[4] Pulfer et al. have confirmed the reliability of the method with a total of seventy-six cases.[5] It is of interest to calculate CEBE's of larger molecules than in most previous cases. Mono- and di-substituted benzenes (Ph–X and X–$C_6H_4$–Y, where Ph represents a phenyl group, $C_6H_5$), are sufficiently large compared to most of the previously investigated molecules. Substituted benzenes play important roles in chemistry and biochemistry. Benzene (Ph–H, **1**) and seven mono-substituted benzenes were studied. They are aniline (Ph–$NH_2$, **2**), nitrobenzene (Ph–$NO_2$, **3**), nitrosobenzene (Ph–NO, **5**), fluorobenzene (Ph–F, **6**), phenol (Ph–OH, **7**), toluene (Ph–$CH_3$, **8**), and benzoic acid (Ph–COOH, **9**). Only one disubstituted benzene, $p$-nitroaniline ($p$-$NH_2$–$C_6H_4$–$NO_2$, **4**), was studied in this work. The substituent effects on the CEBE's can be investigated for these molecules.

## Theory

A transition state (TS) method was first introduced by Slater more than twenty years ago.[6] Consider an electronic process, such as ionization at a fixed molecular geometry. Let us define

$$E(\lambda) = \sum \lambda^k E_k = E_0 + \lambda E_1 + \lambda^2 E_2 + \lambda^3 E_3 + \lambda^4 E_4 \ldots, \quad (1)$$

where $E(0)$ and $E(1)$ correspond to the initial and final states and $\lambda$ is assumed to be a continuous variable in the range $0 \leq \lambda \leq 1$. The change in the energy, $\Delta E$, between the initial ($\lambda = 0$) and final ($\lambda = 1$) states is given by

$$\Delta E = E(1) - E(0) = E_1 + E_2 + E_3 + E_4 + \ldots. \quad (2)$$

In the case of ionization, $\Delta E$ represents the ionization energy ($IE$) of the molecule. Now let us take the derivative of the Eq. 1 with respect to $\lambda$ and call it $F(\lambda)$,

$$F(\lambda) = \partial E/\partial\lambda = E_1 + 2\lambda E_2 + 3\lambda^2 E_3 + 4\lambda^3 E_4 + \ldots. \quad (3)$$

Then, in Slater's original transition-state concept, $\Delta E$ is approximated by

$$F(1/2) = E_1 + E_2 + 3E_3/4 + E_4/2 + 5E_5/16 + \ldots, \quad (4)$$

with an error of

$$\delta_{TS} = -E_3/4 - E_4/2 - 11E_5/16 + \ldots. \quad (5)$$

Williams et al.[4] proposed a generalization of the transition-state technique introduced by Slater. In the generalized transition state (GST) method, $\lambda = 2/3$, rather than 1/2 is considered. The substitution of $\lambda = 2/3$ in Eq. 4 results in

$$F(2/3) = E_1 + 4E_2/3 + 4E_3/3 + 32E_4/27 \ldots. \quad (6)$$

Thus, one can approximate $\Delta E$ by

$$\Delta E \approx [F(0) + 3F(2/3)]/4 \quad (7a)$$

$$= E_1 + E_2 + E_3 + 8E_4/9 + 20E_5/27 + \ldots \quad (7b)$$

with an error of

$$\delta_{GTS} E = -E_4/9 - 7E_5/27 + \ldots. \quad (8)$$

In the GTS method, error starts from the 4th order instead of the 3rd order, which is the case of the TS method. GTS is expected to be a better approximation to $\Delta E$ than the TS method.

Janak[7] proved that in density-functional theory (DFT)

$$\partial E/\partial n_j = \varepsilon_j(n), \quad (9)$$

where $E$ is the total energy, as constructed in DFT; $n$ is the $j$-th orbital occupation, which can take nonintegral values; and $\varepsilon_j(n)$ is the eigenvalue of the orbital. In the case of an unrestricted treatment, where different spatial orbitals are assigned to alpha and beta electrons, the orbital occupation, $n$, takes a value between zero and one. It can be related to the continuous variable $\lambda$ introduced in Eq. 1 with the relation $n = 1-\lambda$. The substitution of $1-\lambda$ for $n$ in Eq. 9 results a second equality,

$$F(\lambda) = \partial E/\partial\lambda = -\varepsilon_j(1-\lambda), \quad (10)$$

The first equality is Eq. 3. In the case of the GTS method, the ionization energy from the j-th orbital ($IE_j$) is approximated by, combining Eq. 7a and Eq. 10,

$$IE_j = \Delta E \approx -[\varepsilon_j(1) + 3\varepsilon_j(1/3)]/4. \quad (11)$$

Eq. 11 indicates that one has to calculate the eigenvalue of the $j$-th orbital once with its occupation $n = 1$, and once with $n = 1/3$, in order to approximate $IE_j$. This method of calculating the ionization energy with Eq. 11 is called the unrestricted generalized transition state (uGTS) method. For uGTS of $H_2O$, for example, when one calculates $\varepsilon_1(1/3)$ one obtains 1/3 alpha and one beta core electrons. Eq. 11 is our uGTS working formula in the present study. GTS could also be implemented with a restricted treatment, where the same spatial orbital is assigned to the alpha and beta electrons. This method is called restricted GTS (rGTS). For rGTS of $H_2O$, for example, one has 2/3 alpha and 2/3 beta core electrons. A comparison between uGTS and rGTS is given eleswhere.[1] It has been shown that the uGTS model works better than the rGTS model.

For a system with an occupation number of 1/3, the screening of the nuclear charge by the core electron is reduced. The basis functions were scaled in order to account for a reduction of the charge. The screening constants were evaluated according to rules provided by Clementi and Raimondi.[8] For Gaussian-type orbital (GTO) basis sets, the scaling factor is given by

$$\text{Scaling} = \left(\frac{Z-s'}{Z-s}\right)^2, \quad (12)$$

where $Z$ is the nuclear charge of the atom considered; $s$ and $s'$ are the screening constants of the neutral atom and the partial core-ionized cation, respectively. It was found that a scaled-pVTZ basis gives CEBE's that are as accurate as a much larger cc-pV5Z basis.

## Calculations

Calculations of CEBE's were performed at the experimental equilibrium geometry for Ph–$NH_2$,[9] Ph–$NO_2$,[10] *p*-$NH_2$–$C_6H_4$–$NO_2$,[11] Ph–F, PhOH[12] and the calculated geometry found in the literature for Ph–$CH_3$ with ab inicio HF/6–311+$G^{**}$.[13] We calculated the geometry of the other molecules, i.e., the geometry of Ph–NO and Ph–COOH, with ab inicio HF/6-31$G^{**}$. In this study, we used the deMon density functional program[14] with auxiliary fitting functions, denoted by (4,4; 4,4) for C to F and (3,1; 3,1), for H. All calculations were performed with the exchange-correlation potential labeled as B88/P86, made from Becke's 1988 exchange functional[15] and Perdew's 1986 correlation functional.[16] For CEBE calculations of all the molecules, the correlation-consistent polarized double-zeta(cc-pVDZ) basis set from Dunning and co-workers[17,18] were used. For CEBE calculations of benzene, aniline, nitrobenzene and *p*-nitroaniline, a correlation-consistent polarized triple-zeta (cc-pVTZ) basis set was also employed for the sake of a comparison. The screening constants used in the scaling procedure were from the literature.[19] The relativistic corrections were calculated using an empirical equation,[20] and were included in the CEBE's.

## Results and Discussions

Table 1 lists the CEBE's of (**1**) benzene (Ph–H), (**2**) aniline (Ph–$NH_2$), (**3**) nitrobenzene (Ph–$NO_2$) and (**4**) *p*-nitroaniline (*p*-$NH_2$–$C_6H_4$–$NO_2$), calculated using the pVDZ and pVTZ basis sets. The observed CEBE's are also included in the table. The *ipso*(C1), *ortho*(C2), *meta*(C3) and *para*(C4) carbon atoms of the phenyl ring in the substituted benzenes have a different chemical environment. Therefore four different values of the CEBE are expected for the four different types of ring carbons. The calculated as well as observed CEBE's show this fact. The absolute deviations (*AD*) from experiment are given in parentheses immediately after the calculated CEBE's. The agreement between the calculated CEBE's and the experiment is good especially for **1**, **2**, and **3**. The deviations due to the pVTZ basis set is generally smaller than those due to pVDZ. In the case of compound **4**, only one observed CEBE for carbons, 291.1 eV, is reported. This is the average value of the four types of carbon. Apparently, the resolution of the observed spectrum was not sufficient to distinguish the four different CEBE's due to the four types of carbon in the molecule. If one averages over the six CEBE's (one C1, two C2's, two C3's and one C4) calculated using pVTZ for the four chemically different types of carbon, C1↔C6, one finds it to be 291.05 eV, which coincides with the observed value of 291.1 eV. In the case where the pVDZ basis sets are used, the corresponding average value is 290.94 eV, which is also very close to the observed value. This is an indication of the reliability of the calculated CEBE's for the four types of carbon. However, large deviations for the nitrogen atom (1.08 eV) and that of oxygen atom (0.71 eV) in $NO_2$ of **4** were registered when pVDZ sets were used. The corresponding deviations reduce to 0.81 eV and 0.37 eV, re-

Table 1. Calculated Core-Electron Binding Energies (in eV) for (**1**) Benzene (Ph–H), (**2**) Aniline (Ph–$NH_2$), (**3**) Nitro Benzene (Ph–$NO_2$) and (**4**) *p*-Nitroaniline (*p*-$NH_2$–$C_6H_4$–$NO_2$) Using pVDZ and pVTZ Basis Sets with the uGTS Method in Density Functional Theory

| Molecule | Hole, 1s | pVDZ[a)] | pVTZ[a)] | Obsd[b) 20,21] |
|---|---|---|---|---|
| (**1**) Ph–H | C | 290.28(0.13) | 290.35(0.06) | 290.41 |
| (**2**) Ph–$NH_2$ | C1 | 291.23(0.06) | 291.35(0.06) | 291.29 |
| | C2 | 289.83(0.12) | 289.92(0.03) | 289.95 |
| | C3 | 290.02(0.23) | 290.11(0.14) | 290.25 |
| | C4 | 289.65(0.22) | 289.74(0.11) | 289.85 |
| | N | 405.28(0.10) | 405.38(0.00) | 405.38 |
| (**3**) Ph–$NO_2$ | C1 | 291.92(0.17) | 292.06(0.03) | 292.09 |
| | C2 | 291.18(0.12) | 291.26(0.04) | 291.3 |
| | C3 | 291.06(0.06) | 291.14(0.14) | 291.0 |
| | C4 | 291.07(0.03) | 291.14(0.04) | 291.1 |
| | N | 411.11(0.53) | 411.37(0.27) | 411.64 |
| | O | 538.05(0.40) | 538.38(0.07) | 538.45 |
| (**4**)*p*-$NH_2$–$C_6H_4$–$NO_2$ | C1(–$NH_2$) | 292.08 | 292.21 | |
| | C2 | 290.47 | 290.58 | |
| | C3 | 290.75 | 290.86 | |
| | C4(–$NO_2$) | 291.09 | 291.22 | |
| | C(average) | 290.94(0.16) | 291.05(0.05) | 291.1 |
| | N(in $NO_2$) | 410.12(1.08) | 410.39(0.81) | 411.2 |
| | N(in $NH_2$) | 406.05(0.05) | 406.15(0.15) | 406.0 |
| | O(in $NO_2$) | 537.19(0.71) | 537.53(0.37) | 537.9 |
| *AAD* | | (0.26) | (0.15) | (0) |

a) Absolute deviations (AD) from experiment are given in parenthesis immediately after calculated CEBE's. b) CEBE's for carbons of *p*-$NH_2$–$C_6H_4$–$NO_2$ are averaged over four types of carbon.[23]

spectively (see Table 1) when pVTZ was employed. Still, these deviations are considered to be relatively large.

The average absolute deviation (*AAD*) from experiments, calculated using all of the atoms in Table 1, was 0.26 eV when the pVDZ basis set was employed, whereas *AAD* was 0.15 eV when the pVTZ basis set was used. A previous investigation[5] of over 60 cases showed that *AAD* from experiments was 0.2 eV when pVTZ was used. Our present calculation reconfirmed the previous conclusion about the accuracy of calculated CEBE's. If one uses the pVDZ basis set to calculate the CEBE's, AAD increases by about 0.1 eV compared to the case where the pVTZ basis set is employed. A pVDZ basis set consists of 14 contracted Gaussian-type functions (CGTFs), whereas pVTZ consists of 30 CGTFs. The size of pVTZ is more than twice as large as that of pVDZ. When pVTZ was used for all atoms of *p*-nitroaniline (**4**), the total number of basis sets exceeded the size of the array dimensions. The pVTZ basis was adapted only for the heavy atoms in **4**. We used the pVDZ basis set for all of the hydrogen atoms in **4**. The computing time and requirement for the computing facilities increase substantially when going from pVDZ to pVTZ for the size of molecules that we are studying. We decided to use the pVDZ basis set to calculate the CEBE's of the remaining substituted benzenes. Since AAD is expected to be only 0.1 eV greater when pVDZ is used in comparison to the case where a much more time-consuming pVTZ is used.

Table 2 lists the CEBE's of the remaining five mono-substituted benzenes calculated using only the pVDZ basis set. The observed CEBE's are available for compounds **6**, **7**, and **8** and a part of **5**. AAD of the CEBE's, calculated using only those listed in Table 2, from experiment is 0.29 eV. When more than two observed CEBE's are available for the same atom, their average value was used to calculate AAD. There are a total of 32 observed CEBE's of individual atoms in Tables 1 and 2 put together. We used all of the observed data set to calculate AAD of the CEBE's computed with the pVDZ that comprises Tables 1 and 2. The thus-calculated AAD value is 0.29 eV. We reconfirmed the fact that the AAD expected with pVDZ is 0.3 eV using a large data set.

From the point of view of chemical interest, *CEBE shifts* that can be calculated from the CEBE's are more interesting than the absolute numerical values of the CEBE's, themselves. Table 3 lists the "CEBE shifts" that were calculated, taking the CEBE of the benzene molecule (Ph–H) as a reference. The thus-calculated CEBE shifts should closely reflect the substitution effects of substituent X on the four types of carbon (C1, C2, C3 and C4) in the substituted benzenes (Ph–X). The CEBE shifts calculated using pVDZ in molecules **2**, **3**, and **4** agree very well with those calculated using pVTZ. As far as the CEBE shift in substituted benzenes is concerned, both pVDZ and pVTZ give the same degree of accuracy. If the observed CEBE shifts are compared with the calculated ones, one can find good agreement between

Table 2. Calculated Core-Electron Binding Energies (in eV) for the Remaining Five Substituted Benzenes (Ph–X, X = NO, F, OH, $CH_3$, COOH) Using pVDZ Basis Sets with the uGTS Method in Density Functional Theory

| Molecule | Hole, 1s | pVDZ | Obsd[21-24] |
|---|---|---|---|
| (**5**) Ph–NO | C1 | 291.08 | |
| | C2 | 290.78 | |
| | C3 | 290.81 | |
| | C4 | 290.83 | |
| | N | 407.28 | 407.8 |
| | O | 538.10 | 538.7 |
| (**6**) Ph–F | C1 | 292.55 | 292.5/292.9/292.7/292.85 |
| | C2 | 290.54 | 290.54/290.7 |
| | C3 | 290.61 | 290.87/290.9 |
| | C4 | 290.41 | 290.4/290.54 |
| (**7**) Ph–OH | C1 | 291.88 | 292.0 |
| | C2 | 290.24 | 290.2 |
| | C3 | 290.31 | 290.6 |
| | C4 | 290.00 | 290.2 |
| | O | 539.12 | 538.9 |
| (**8**) Ph–$CH_3$ | C1 | 290.33 | 290.9 |
| | C2 | 290.03 | 290.2 |
| | C3 | 290.14 | 290.4 |
| | C4 | 290.06 | 290.1 |
| | C(in $CH_3$) | 290.75 | 290.1/290.31 |
| (**9**) Ph–COOH | C1 | 290.73 | |
| | C2 | 290.48 | |
| | C3 | 290.49 | |
| | C4 | 290.51 | |
| | C(COOH) | 294.18 | |
| | O(C=O) | 537.35 | |
| | O(OH) | 539.68 | |
| *AAD* | | (0.29) | (0.0) |

theory and experiment for most cases. A large deviation, 0.44 eV, of the calculated CEBE shift from experiment was found at the C1 atom of Ph–$CH_3$. This is rather an exception. AAD of the CEBE shifts calculated with pVDZ is 0.1 eV.

The sign of the CEBE shift in Table 3 is either negative or positive. The negative CEBE shift is due to the destabilization of the 1s electron of the carbon atom. The destabilization of the 1s electron of the atom occurs when the electron density in the surroundings increases. The opposite is the case when a positive CEBE shift is registered. A positive CEBE shift is due to the stabilization of the 1s electron in the atom. The stabilization is caused by a decrease in the electron density in the surroundings. Negative CEBE shifts at the C2, C4 (and C3) atoms of substituted benzenes can be observed in Ph–$NH_2$ (**2**), Ph–$CH_3$ (**8**) and Ph–OH (**7**) (Table 3). The substituents $NH_2$, $CH_3$ and OH cause an increase in the electron density in the phenyl ring. They are well known as electron-donating substituents. In the case of Ph–$NH_2$, the C4 atom has the largest negative CEBE shift, the C2 atom has the second largest negative CEBE shift, and the C3 atom has the least negative CEBE shift. This implies that an increase in the electron density at (or in the neighborhood of) the carbon atoms of the phenyl ring in molecule **2** is in the order C4 > C2 > C3. The established order agrees both in theory and experiment. The increase of electron density at (or in the neighborhood of) C4 and C2 can be explained qualitatively by the resonance effect. According to the resonance-effect theory, the electronic charge increases at the C4 and C2 carbons in Ph–X if X is electron donating, such as $NH_2$. No increase in the electronic charge is expected at the C3 carbon according to resonance theory. However, some accumulation of electronic charge at not only the C4 and C2 carbons, but also at the C3 carbon, is expected due to the negative CEBE shifts at these positions. In the case of molecules Ph–$CH_3$ (**8**) and Ph–OH (**7**), a similar situation as the case of Ph–$NH_2$ prevails. However, the magnitude of the CEBE shifts towards the negative region in **8** and **7** is not as great as that in **2**. The electron-donating capacity of the $NH_2$ is greater than those of the $CH_3$ and OH. The electron-donating capacity of $CH_3$ is slightly greater than that of OH. The CEBE shift at C3 in Ph–OH is positive both in experiment and theory, while that in Ph–$NH_2$ and Ph–$CH_3$ are negative. The CEBE shift at the C1 atom is always positive, even with the substituent is electron-donating, as can be seen for molecules **2**, **7**, and **8**. The heavy atom in X of Ph-X withdraws a substantial amount of electron density from the C1 atom of the phenyl ring, which causes a large positive CEBE shift.

The CEBE shifts in the ring carbons in the Ph–X are all positive for X = $NO_2$ (in molecule **3**), NO (**5**), F (**6**) and COOH (**9**), which are well known as electron-withdrawing groups. The potency of a substituent X to withdraw electrons from a ring in Ph–X is directly related to the magnitude of the CEBE shifts. The greater is the potency, the greater is the CEBE shift. If the values of the CEBE shift at C2 in the four molecules are compared, one finds the following descending order: **3** > **5** > **6** > **9**. The same order prevails for the CEBE shift at position C3 of the molecules. The order changes to **3** > **5** > **9** > **6** in the case of position C4. We conclude that the descending order of the potency of a substituent X to withdraw an electron from the ring in Ph–X is $NO_2$ > NO > F > COOH. The magnitude of the calculated CEBE shifts at positions C3 and C4 are close to each other in molecule **3**. The same situation prevails in **5** and **9**. In molecule **6**, the value of the CEBE shift varies depending upon the positions.

Lindberg et al[25] showed that CEBE shifts correlate linearly to the Hammett substituent constants ($\sigma$)[26] in substituted benzene derivatives. Some of the Hammett $\sigma$ constants of substituted benzenes are included in Table 3 for the sake of a comparison. It is very interesting to observe that the signs and quantitative numerical values of the Hammett constants are very close to the corresponding CEBE shifts. For instance, the Hammett constants of C3 and C4 in Ph–$NH_2$ are −0.160 and −0.660, respectively, whereas the observed CEBE shifts of the corresponding atoms are −0.16 and −0.56. The corresponding calculated CEBE shifts with pVDZ are −0.26 and

Table 3. Observed and Calculated CEBE Shifts (in eV) of Carbon Atoms in Benzene Ring of Substituted Benzenes (Ph–X). The CEBE Shifts in the Table Have Been Calculated as the Difference Between CEBE of Carbon Atom in the Substituted Benzene and CEBE of the Carbon Atom in Benzene. Hammett $\sigma$ constants and NMR shifts are also included

| Molecule | Hole, 1s | Obsd | pVDZ | pVTZ | Hammett $\sigma$ | NMR shift[28] |
|---|---|---|---|---|---|---|
| Ph–H (**1**) | C | 0.00 | 0.00 | 0.00 | 0.000 | 0.0 |
| Ph–$NH_2$ (**2**) | C1 | +0.88 | +0.95 | +1.00 | | +18.0 |
| | C2 | −0.46 | −0.45 | −0.43 | | −13.3 |
| | C3 | −0.16 | −0.26 | −0.24 | −0.161 | +0.9 |
| | C4 | −0.56 | −0.63 | −0.61 | −0.660 | −9.8 |
| Ph–$NO_2$ (**3**) | C1 | +1.68 | +1.64 | +1.71 | | +20.2 |
| | C2 | +0.89 | +0.90 | +0.91 | | −4.8 |
| | C3 | +0.59 | +0.78 | +0.79 | +0.710 | +0.9 |
| | C4 | +0.69 | +0.79 | +0.79 | +0.778 | +5.8 |
| *p*-$NH_2$–$C_6H_4NO_2$ (**4**) | C1 | | +1.80 | +1.86 | | +16.0 |
| | C2 | | +0.19 | +0.23 | | +3.2 |
| | C3 | | +0.47 | +0.51 | | −2.9 |
| | C4 | | +0.89 | +0.87 | | −12.0 |
| Ph–F (**6**) | C1 | +2.33 | +2.27 | | | +34.8 |
| | C2 | +0.21 | +0.26 | | | −12.9 |
| | C3 | +0.48 | +0.33 | | +0.337 | +1.4 |
| | C4 | +0.06 | +0.13 | | +0.062 | −4.5 |
| Ph–OH (**7**) | C1 | +1.59 | +1.60 | | | +26.9 |
| | C2 | −0.21 | −0.04 | | | −12.7 |
| | C3 | +0.19 | +0.03 | | +0.121 | +1.4 |
| | C4 | −0.21 | −0.28 | | −0.370 | −7.3 |
| Ph–$CH_3$ (**8**) | C1 | +0.49 | +0.05 | | | +8.9 |
| | C2 | −0.21 | −0.25 | | | +0.7 |
| | C3 | −0.01 | −0.14 | | −0.069 | −0.1 |
| | C4 | −0.31 | −0.22 | | −0.170 | −2.9 |
| Ph–NO (**5**) | C1 | | +0.80 | | | +37.4 |
| | C2 | | +0.50 | | | −7.7 |
| | C3 | | +0.53 | | | +0.8 |
| | C4 | | +0.55 | | | +7.0 |
| Ph–COOH (**9**) | C1 | | +0.45 | | | +2.1 |
| | C2 | | +0.20 | | | +1.5 |
| | C3 | | +0.21 | | | 0 |
| | C4 | | +0.23 | | | +5.1 |

−0.63, respectively. In the Ph–OH molecule, the Hammett constant at position C3 shows a positive value of +0.121; the CEBE shifts of the corresponding atom also have positive values of +0.19 (obsd) and +0.03(pVDT). The Hammett constant of position C4 has a negative value of −0.370; the CEBE shifts of the corresponding atom also have negative values of −0.21 (obsd) and −0.28(pVDZ). The average absolute deviation between the Hammett constants and the calculated CEBE shifts with pVDZ is 0.05, while the average absolute deviation between the Hammett constants and the observed CEBE is 0.09. If one plots the Hammett $\sigma$ constants at the C4 position (para carbon) of each of the five monosubstituted benzens in Table 3 against the calculated CEBE shifts (pVDZ), a linear relationship is found between them (Fig. 1A). This is a confirmation of what was found by Linderberg et al.[25] A good correlation[27] of the CEBE shifts with the electronic substituent parameters of Taft and Topson,[28] of Charrton,[29] were also found. The electronegaitivity[30] and gas-phase basicity[31] are known to correlate well with the CEBE shifts.

The last column of Table 3 lists the observed relative NMR shifts of the substituted benzenes. The reference molecule is benzene. The NMR shift depends on the electron density near to the nucleus. The CEBE shift also depends on the electron density near to the nucleus. We can, therefore, expect some correlation between the CEBE shift and the NMR shift. In molecule Ph–$NH_2$, for instance, the signs of the CEBE shift at C1, C2, C3 and C4 are +, −, −, − respectively, whereas the signs of the NMR shifts at the corresponding atoms are +, −, +, −. The signs of the shifts of CEBE and NMR agree at

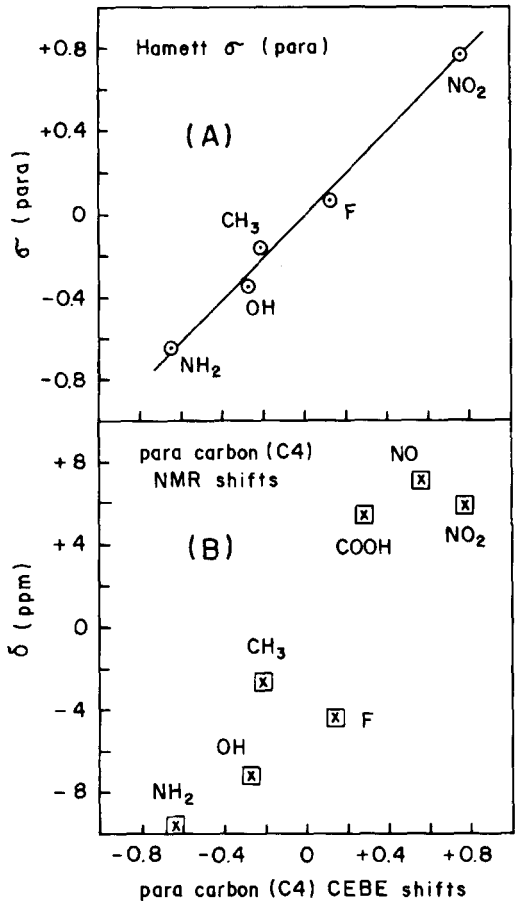


Fig. 1. Correlation between; (A) calculated CEBE shifts (pVDZ) and Hammett $\sigma$ constants; (B) the calculated CEBE shifts and NMR shifts at para carbon (C4) of mono substituted benzenes.

C1, C2, and C4, but disagree at C3. In molecule Ph–OH, the signs of the CEBE shift at C1, C2, C3 and C4 are +, −, +, − respectively; the signs of the NMR shifts at the corresponding atoms are also +, −, +, −. The signs of the shifts of CEBE and NMR agree at all of the four carbons. For the majority of cases treated, there are partial agreements of the signs between the CEBE shifts and the NMR shifts. However, no clear quantitative agreements between the shifts in CEBE and NMR are observed. If one plots the NMR shift at the C4 position of each of the seven monosubstituted benzens in Table 3 against the calculated CEBE shift (Fig. 1B), some qualitative correlation is found between the CEBE shifts and the NMR shifts, though there is no good linear relationship between them. No clear linear relationship was observed between the NMR shifts and the Hammett σ constants.[32]

*p*-Nitroaniline (*p*-NA, **4**) is the only disubstituted benzene whose CEBE's were calculated in the present work. We want to know what would be the effect of the disubstitution, in comparison to monosubstitution, on the CEBE's of the ring carbons. Figure 2 shows a schematic relation among the molecules aniline (**2**), nitrobenzene (**3**), and *p*NA (**4**). *p*NA-(**4**) is considered to be a result of the substitution of H with $NO_2$ at the *para* position of aniline (**2**). The CEBE shifts of the ring carbons in *p*NA must be influenced by the two

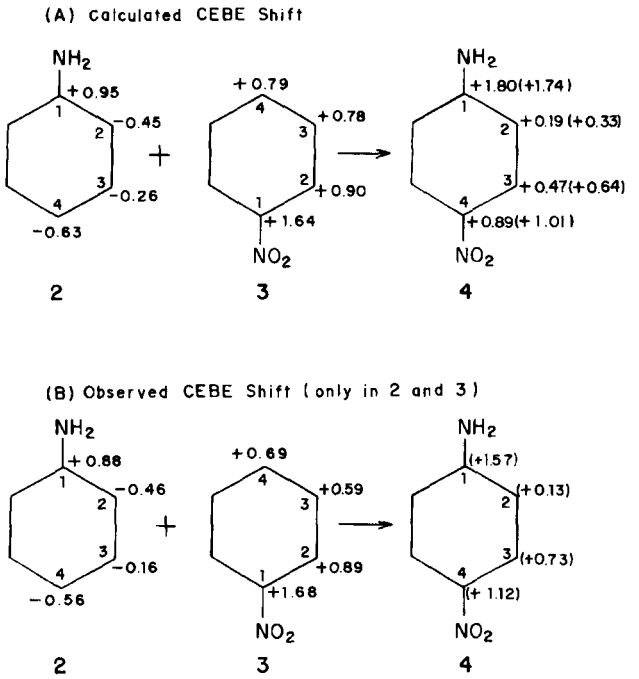


Fig. 2. Relationship between CEBE shifts of ring carbons in mono- and disubstituted benzenes. The values in parentheses are those calculated with Eq. 13 in the text. The calculated CEBE shifts in (A) are those obtained with cc-pVDZ basis set.

substituents, $NH_2$ and $NO_2$, simultaneously. The question is: what would be the relation between the CEBE shifts of the ring carbons of the two monosubstituted benzenes (**2** and **3**) and the disubstituted benzene (**4**) ? Are the CEBE shifts of the ring carbons in the $NH_2$–$C_6H_4$–$NO_2$ related to those of the mono substitutes, $NH_2$–Ph and Ph–$NO_2$ ? Is the following equation valid ?

(CEBE shifts in **2**) + (CEBE shifts in **3**) = (CEBE shifts in **4**) (13)

Figure 2 (A) shows the mutual relationship between the CEBE shifts of **2**, **3** and **4** corresponding to Eq. 13. The values in parenthesis in **4** are the CEBE shifts that were calculated using Eq. 13. There are fair agreements between the CEBE shifts of **4** calculated with Eq. 13 and the authentic ones. The CEBE shift of the benzene ring carbons in *p*-$NH_2$–$C_6H_4$–$NO_2$ is as if it is determined by the cumulative effect of the individual substituents, $NH_2$ and $NO_2$. The CEBE shift of the ring carbons in **4** calculated with Eq. 13 using observed values of **2** and **3**, are given in Fig. 2(B). No observed CEBE shift of **4**, itself, is available for a comparison. If someone can observe the CEBE shift of the ring carbon in molecule **4**, they may not be far from those given in Fig. 2(B). The theoretical and experimental CEBE shifts of **4**, calculated according to Eq. 13, agree reasonably well. The average absolute difference between the real computed CEBE shifts and those from Eq. 13 is 0.12 eV for the cc-pVDZ basis and 0.14 eV for the cc-pVTZ basis (both within the range of accuracy of our method).

We next consider the effect of the phenyl (Ph) ring on

CEBE of an atom in the substituent X in Ph–X. Table 4 lists the CEBE's of the atom in substituent X or H–X together with the corresponding atom in Ph–X. In the case of Ph–$NH_2$, for example, the observed and calculated CEBE's of the N atom in Ph–$NH_2$ and H–$NH_2$ are listed together. The observed CEBE of N in Ph–$NH_2$ is 405.38 eV, while the observed CEBE of N in H–$NH_2$ is 405.57. The difference in the two CEBE's, 405.38 − 405.57 = −0.19 (eV), give the effect of substitution from H to Ph in H–$NH_2$. This value can be called the "CEBE shift", which is given in Table 4 with the symbol "$\Delta$". The corresponding theoretical values are −0.14 eV if the pVDZ basis set is used, and −0.31 eV when the pVTZ is used. The CEBE shift is negative, which means that the electron in the 1s orbital in the N atom is destabilized due to an increase in the electron density on the N atom. The phenyl ring donates electrons to the substituent –$NH_2$ in Ph–$NH_2$.

Table 4. The Effect of Phenyl (Ph) Ring on CEBE (in eV) of the Atom in the Substituent X in the Substituted Benzene (Ph-X) is Given as the Difference ($\Delta$) between CEBE of Ph–X and that of X. The CEBE Value Corresponds to the Atom in Bold Face.

| Molecule | Obsd[21-24] | pVDZ | pVTZ |
|---|---|---|---|
| Ph–**N**$H_2$ | 405.38 | 405.28 | 405.38 |
| H–**N**$H_2$ | 405.57 | 405.42 | 405.69 |
| $\Delta$ | −0.19 | −0.14 | −0.31 |
| Ph–**N**$O_2$ | 411.64 | 411.11 | 411.37 |
| **N**$O_2$ | 412.6 | 412.58 | 413.01 |
| $\Delta$ | −0.96 | −1.47 | −1.64 |
| Ph–**N**$O_2$ | 538.45 | 538.05 | 538.38 |
| **N**$O_2$ | 541.3 | 541.49 | 541.90 |
| $\Delta$ | −2.85 | −3.44 | −3.52 |
| Ph–**N**O | 407.8 | 407.28 | |
| H–**N**O | — | 409.22 | |
| $\Delta$ | | −1.94 | |
| Ph–**N**O | 538.7 | 538.10 | |
| H–**N**O | — | 541.37 | |
| $\Delta$ | | −3.27 | |
| Ph–**F** | 693.3 | 692.48 | |
| H–**F** | 694.18 | 693.45 | |
| $\Delta$ | −0.88 | −0.97 | |
| Ph–**O**H | 538.9 | 539.12 | |
| H–**O**H | 539.86 | 539.33 | |
| $\Delta$ | −0.96 | −0.21 | |
| Ph–**C**$H_3$ | 290.1/290.31 | 290.86 | |
| H–**C**$H_3$ | 290.86 | 290.82 | |
| $\Delta$ | −0.76/−0.55 | −0.07 | |
| Ph–**C**OOH | — | 537.35 | |
| H–**C**OOH | 538.97 | 538.53 | |
| $\Delta$ | | −1.18 | |
| Ph–**C**OOH | — | 539.68 | |
| H–**C**OOH | 540.63 | 540.51 | |
| $\Delta$ | | −0.83 | |
| Ph–**C**OOH | | 294.18 | |
| H–**C**OOH | | 295.25 | |
| $\Delta$ | | −1.07 | |

In organic chemistry, the phenyl ring, –$C_6H_5$, is known to be moderately of the electron-donating type. The CEBE shifts calculated with pVDZ closely parallel to those calculated with pVTZ. The agreements between the observed CEBE shifts and the theoretical ones are reasonable for most of the cases listed in the table. The average absolute deviation of the calculated CEBE shift from the experiment is 0.45 eV, which is much larger than 0.10 eV, which is the AAD of the CEBE shift of the four types of carbon in the phenyl ring.

## Conclusion

It was shown that the AAD of the calculated CEBE's of the ring carbons in benzene, seven mono (Ph–X) and one disubstituted (X–$C_6H_4$–Y) benzenes from experiment, was 0.3 eV when pVDZ basis sets were employed. When the pVTZ basis set was employed in benzene, two mono and one disubstituted benzenes, the AAD of the calculated CEBE's of ring carbons from experiment was 0.2 eV, which reconfirmed the previous conclusion about the accuracy of the calculated CEBE's using pVTZ. The "CEBE shift" of the ring carbon in Ph–X was calculated taking the CEBE on the ring carbon in Ph–H as a reference. The thus calculated CEBE shifts agree with the experiment within an AAD value of 0.1 eV. As far as the CEBE shift in substituted benzenes are concerned, both pVDZ and pVTZ give the same degree of accuracy. With the magnitude and sign of the CEBE shift, it was possible to classify substituent X in Ph–X as being either electron-donating or electron-withdrawing. The result of this classification completely agrees with what is described in a textbook on organic chemistry. A linear relationship between the CEBE shifts of the mono substituted benzenes and the Hammett $\sigma$ constants was observed. The signs and quantitative numerical values of the CEBE shifts are very close to the corresponding Hammett constants. The CEBE shift may provide a convenient method for obtaining the Hammett σ constants when they are unavailable or uncertain (possible disagreement between different determinations). This could thus be helpful to physical organic chemistry. In this respect, the computed CEBE's become valuable when the experimental values have not been reported.

The following points were demonstrated: (1) not only do we get excellent CEBE shifts, but we can also obtain accurate absolute values for the CEBE's, even for something as large as *p*-nitroaniline; (2) we can give individual CEBE's, even when the experiment could only give an average (eg *p*-NA); (3) we have predicted the CEBE's for $C_6H_5NO$, $C_6H_5COOH$, (not yet reported).

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