THE JOURNAL OF
PHYSICAL
CHEMISTRY A

VOLUME 107, NUMBER 19, MAY 15, 2003

LETTERS

New Quantum Chemical Parameter for the Substituent Effect in Benzene Based on Charge Flux

Jin Yong Lee,*,† Byung Jin Mhin,*,‡ and Kwang S. Kim*,§

*Nano Technology Research Center, Department of Chemistry, Chonnam National University,
300 Yongbong-Dong, Bugku, Gwangju 500-757, Korea, Department of Chemistry, PaiChai University,
493-6 Domadong, Seoku, Taejun 302-735, Korea, and National Creative Research Initiative Center for
Superfunctional Materials and Department of Chemistry, Division of Molecular and Life Sciences,
Pohang University of Science and Technology, San 31, Hyojadong, Namgu, Pohang 790-784, Korea*

Received: November 11, 2002; In Final Form: February 26, 2003

Charge distributions determining the electrostatic potential in monosubstituted benzenes are investigated. As a result, a new quantum chemical parameter for substituent effect, which would be useful in information coding (in terms of molecular electrostatic potential), is introduced. The curvature of charge distribution over the benzene clearly shows a good linear relationship with known experimental substituent constants, while the amount of charge transferred does not fully reflect the substituent effect. Because the curvature is a new and good quantum chemical parameter to describe the substituent effect, our results would be used as a strategy for design of new functional molecules such as molecular scale electronics using the electrostatic potential distributions.

Molecular scale electronics has emerged as a very interesting field because of the rapid miniaturization of conventional microscale electronic devices.[1] Resonant tunneling diode (RTD) is based on π-conjugated molecular wire with a quantum well.[2,3] One basic explanation of the diode property is believed that the electron transfer through the lowest unoccupied molecular orbital (LUMO) of the molecule with the given substituent favors one direction over the other. Recently, the variation of electrostatic potential was suggested for information coding.[4] This indicates that the electrostatic potential or charge redistribution, which would be responsible for the electron transfer, plays a critical role in molecular devices. Thus, here, we investigate charge distributions determining the electrostatic potential in monosubstituted benzenes. As a result, a new quantum chemical parameter for substituent effect, which would be useful in information coding (in terms of molecular electrostatic potential), is introduced.

As a prototype of π-conjugated systems, there have been many studies on changes of structures and donor/acceptor strengths due to substituents of benzene.[5] The substituent constant, first introduced by Hammett, is widely used as one of the most useful parameters for the substituent effect in aromatic systems because the empirical Hammett equation has been successful in treating thousands of reactions.[6] In general, it quantifies the capability of a substituent to perturb the electron distribution in the molecule. Therefore, many attempts have been made to find a theoretical basis for the concepts of substituent constants from the quantum chemical properties, such as total energy, atomic charges, electrostatic potentials, electrostatic field, and local ionization potential.[7] However, detailed under-

---

* To whom correspondence should be addressed. E-mail for Jin Yong Lee: jinyong@chonnam.ac.kr. E-mail for Byung Jin Mhin: mhin@mail.paichai.ac.kr. E-mail for Kwang S. Kim: kim@postech.ac.kr. Fax for Kwang S. Kim: +82-54-279-8137.

† Chonnam National University.

‡ PaiChai University.

§ Pohang University of Science and Technology.

10.1021/jp027426f CCC: $25.00

TABLE 1: Structural Parameters of the Monosubstituted Benzene Derivatives

X	r_a	r_b	r_c	θ_x	θ_a	θ_b	θ_c
S^-	1.4240	1.3949	1.4032	115.3	122.3	121.1	117.9
O^-	1.4486	1.3919	1.4071	113.9	122.6	121.7	117.5
NMe_2	1.4163	1.3945	1.3974	117.4	120.9	121.2	118.4
NH_2	1.4083	1.3945	1.3986	118.5	120.5	120.9	118.7
OMe[a]	1.4025	1.3966	1.3980	119.9	119.7	120.8	119.1
OH[a]	1.3994	1.3964	1.3984	120.2	119.6	120.6	119.3
Cl	1.3956	1.3977	1.3977	121.4	119.0	120.5	119.7
NC	1.4017	1.3948	1.3984	120.8	119.3	120.4	119.9
CN	1.4063	1.3942	1.3986	120.1	119.7	120.2	120.1
COH[a]	1.4039	1.3943	1.3999	119.8	120.1	119.8	120.3
BH_2	1.4150	1.3945	1.3999	117.5	121.5	119.7	120.3
BF_2	1.4092	1.3951	1.3990	118.5	120.8	119.8	120.2
BCl_2	1.4132	1.3940	1.3987	117.7	121.2	119.9	120.0
NO_2	1.3954	1.3950	1.3991	122.3	118.5	120.2	120.3
N_2^+	1.4115	1.3877	1.4038	124.1	117.0	120.2	121.4
H	1.3985	1.3985	1.3985	120.0	120.0	120.0	120.0

[a] r_b, r_c, θ_a, and θ_b are the averaged values of the two different values for C_s symmetry. Refer to Figure 1 for the notation.

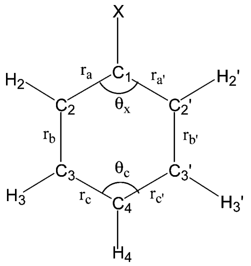

Figure 1. Structural parameters and atomic indexing.

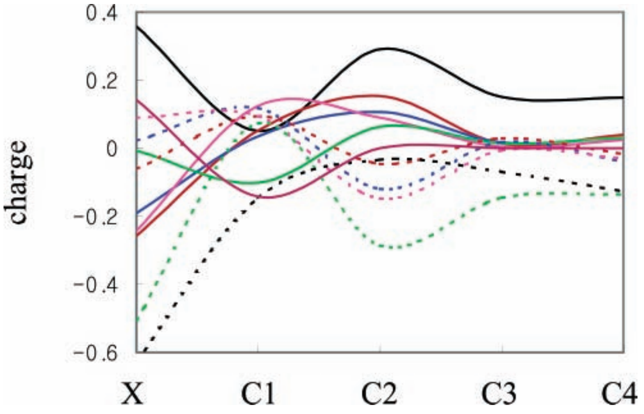

Figure 2. The charge distributions (Q) along the one-dimensional projected sites of monosubstituted benzenes: solid lines for N_2^+ (black), NO_2 (red), CN (blue), NC (pink), BCl_2 (green), and H (violet) and dotted lines for S^- (black), OH (red), NH_2 (blue), NMe_2 (pink), and O^- (green). We obtained the same charge distribution pattern when we used the π-electron charges of each carbon atom in benzene because the π-charges of hydrogen atoms are negligible. Only 10 monosubstituted benzenes and pure benzene are shown for clarity to avoid somewhat overlapped images. In the case of highly polarizable and soft sulfur atom, the charge distribution is almost same with that of the benzene.

standing for the substituent effect at the molecular level still lacks. Therefore, it is desirable to find a new quantum chemical parameter that shows good linear relationships with the known experimental substituent constants.

In this regard, we have carried out ab initio calculations of various monosubstituted benzene systems. All of the calculations have been carried out with the density functional theory employing Becke's three parameters with Lee−Yang−Parr correlation functional (B3LYP) with 6-31+G* basis sets using a suite of Gaussian programs.[8] The substituent causes the intramolecular charge transfer (ICT) in the benzene ring, geometrical distortion, and charge redistribution.[9] On the basis of the valence bond structures in monosubstituted benzene, the aromatic ring changes toward the quinoid structure, and thus the C−C bond lengths r_a and r_c lengthen, whereas r_b shortens as noted in Table 1 (see Figure 1 for notation). The bond angle, in particular at the para position ($\Delta\theta_c$), shows a good correlation with the donor−acceptor strength, as already noted in previous works.[10]

To study the change of ICT for different substituents, we investigated the total and π-electron charges at atomic sites. The total atomic charges were obtained from the dipole moment derivatives, which are known to give very reliable values for planar molecules; that is, the charge of atom A (q_A) is $\partial\mu_z/\partial z_A$ when the molecule is on the $x-y$ plane.[11] Let the amount of charge separation between benzene and substituent be Δq. In the case of benzene (X = H), Δq is −0.142. If a substituent (X) is a more electron-donating group than H, Δq has been considered to be smaller than −0.142. However, some functional groups considered as electron-donating groups (such as NMe_2, NH_2, OMe, and OH) have Δq larger than −0.142. Therefore, the amount of charge transferred is not a good parameter to assign a substituent as an electron donor or acceptor. We thus have investigated the charge distributions at carbon atoms over the benzene (Figure 2). Q(C1) represents the sum of charges on C1 and H1; similarly, Q(C4) represents that on C4 and H4. Q(C2) and Q(C3) represent the sum of charges on C2, C2′, H2, and H2′ and C3, C3′, H3, and H3′, respectively. The figure clearly discriminates the electron-donating and -accepting substituents. For donors, the charge distribution shows a concave shape from the C1 through the C3, while for acceptors, it shows a convex shape. On the basis of this pattern, S^-, O^-, NMe_2, NH_2, OMe, OH, and Cl are donors and N_2^+, NO_2, BCl_2, BF_2, BH_2, CHO, CN, and NC are acceptors, which are in excellent agreement with the traditional classification of common donors and acceptors. In all of the substituents, the maximum perturbation takes place at the meta position, and shows charge alternation behavior.[12] In explaination of the electrophilic aromatic substitution reaction from the resonance structure, the ortho−para or meta preference was successfully understood by the resonance stability of the intermediate. This should not be confused with the maximum charge perturbation at the meta position of monosubstituted benzene derivatives themselves in this study. Several basis sets ranging from STO-3G[13] to 6-31G*[14] have been employed to describe the electrostatic potential, and these Mulliken population analyses show practically the same results for quantum chemical parameters. Thus, the parameters would not significantly depend on basis sets or the methods to determine the atomic charges.

It should be addressed that the characteristics of electron donors and acceptors do not depend on the amount of charge transferred from or to benzene but depend on the curvature of charge flux representing the charge alternation and distribution on the benzene along the one-dimensional direction. Considering the charge distribution of aniline (X = NH_2), which has a strong electron-donating amino group, the Δq of aniline is larger than that of benzene. The sum of charges of NH_2 in aniline is more than that of H in benzene. In terms of the amount of charge transferred, the amino group is predicted to be a weaker donor than the hydrogen, which is wrong. Similar cases are also found in the electron-donating groups of NMe_2, OMe, and OH. However, the pattern of charge distribution over the benzene clears such contradictions.

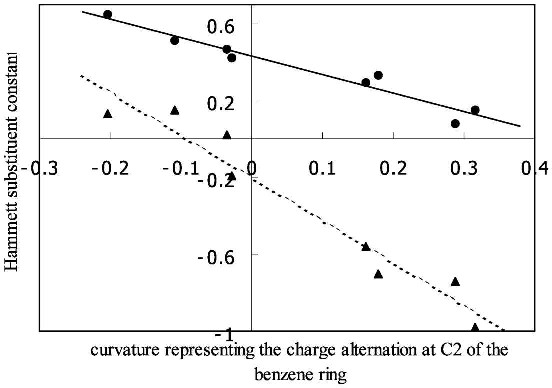

Figure 3. Correlation between calculated curvature and experimental substituent constants: (solid line with ●) σ_I (field effect); (dotted line with ▲) σ_R (resonance effect). The data sets correspond to NO_2, CN, NC, Cl, OMe, OH, NH_2, and NMe_2 from the left. Experimental data were obtained from Table 1 in ref 5d, as well as ref 5f.

Among functional groups investigated, we find that BCl_2, BF_2, and BH_2 are very interesting acceptor groups. The BF_2 and BH_2 give 0.100 and 0.057 electrons to benzene, and BCl_2 withdraws a very small amount of charge (0.007) from benzene. This is because the electronegativity of boron is very small, even smaller than that of the H atom. The X atoms of BX_2 have partial negative charges, and the boron has partial positive charge, and the net charge of BX_2 is more positive than that of the H atom of benzene. However, the boron has an empty p_z orbital to hold some π-electrons from benzene. This is responsible for novel interactions such as BH_2-NH_3 dimer[15] (H−H interactions) and SiH_4-BX_3[16] and benzene$-BX_3$[17] complexes ($\pi-p_z$ interactions).

Figure 3 shows a good linear relationship between the curvature of the charge distribution and the known experimental substituent constants. The curvature at a given position is obtained by the second derivative of the fitted graphs as shown in Figure 2, and its physical meaning is the change of charge flux. Electron acceptors have a positive curvature at C2 and C2′, while electron donors have a negative one. Thus, the curvature of a graph showing one-dimensional charge distribution from the substituents to the benzene would be a good quantum chemical parameter to understand the substituent effect on benzene. The curvature could give some physical insights into how a substituent disturbs the electrons in aromatic molecules. From the fitting of calculated curvature vs Hammett constant [σ_I and σ_R] for the monosubstituted benzene systems, which were observed experimentally, it could be possible to estimate the Hammett constants for unobserved systems. The predicted values of [σ_I and σ_R] (for which the experimental data are not available) for S^-, O^-, BH_2, BF_2, BCl_2, and N_2^+ are [0.34, −0.21], [0.06, −0.68], [0.55, 0.13], [0.57, 0.16], [0.54, 0.11], and [0.64, 0.27], respectively. It should be noted that these parameters are different from the charge of X with which a substituent cannot be properly classified as an electron donor or acceptor.

In summary, we have studied the effects of a substituent on the structural distortion and the charge distribution of benzene for monosubstituted benzenes with various electron-donating and -accepting groups. The electron-donating and -accepting groups disturb the ipso-angle oppositely. The curvature of charge distribution over the benzene clearly shows a good linear relationship with known experimental substituent constants, while the amount of charge transferred does not fully reflect the substituent effect. The curvature is a new and good quantum chemical parameter to describe the substituent effect. Our results could be used as a strategy for design of new functional molecules such as molecular scale electronics using the electrostatic potential distributions.

Acknowledgment. This work was supported by KISTEP (CRI) and KORDIC (4th Supercomputing Application Support Program).

References and Notes

(1) (a) Ellenbogen, J. C.; Love, J. C. *Proc. IEEE* **2000**, *88*, 386. (b) Pappenfus, T. M.; Chesterfield, R. J.; Frisbie, C. D.; Mann, K. R.; Casado, J.; Raff, J. D.; Miller, L. L. *J. Am. Chem. Soc.* **2002**, *124*, 4184. (c) Schon, J. H.; Meng, H.; Bao, Z. *Science* **2001**, *294*, 2138. (d) Chen, J.; Reed, M. A.; Rawlett, A. M.; Tour, J. M. *Science* **1999**, *286*, 1550.

(2) (a) Metzger, R. M.; Chen, B.; Hopfner, U.; Lakshmikantham, M. V.; Vuillaume, D.; Kawai, T.; Wu, X.; Tachibana, H.; Hughes, T. V.; Sakurai, H.; Baldwin, J. W.; Hosch, C.; Cava, M. P.; Brehmer, L.; Ashwell, G. J. *J. Am. Chem. Soc.* **1997**, *119*, 10455. (b) Seminario, J. M.; Zacharias, A. G.; Tour, J. M. *J. Am. Chem. Soc.* **1999**, *121*, 411.

(3) Seminario, J. M.; Zacharias, A. G.; Tour, J. M. *J. Am. Chem. Soc.* **2000**, *122*, 3015.

(4) Tour, J. M.; Kozaki, M.; Seminario, J. M. *J. Am. Chem. Soc.* **1998**, *120*, 8486.

(5) (a) Swain, C. G.; Lupton, E. C., Jr. *J. Am. Chem. Soc.* **1968**, *90*, 4328. (b) Charton, M. *Prog. Phys. Org. Chem.* **1981**, *13*, 119. (c) Topsom, R. D. *Prog. Phys. Org. Chem.* **1987**, *16*, 125. (d) Hansch, C.; Leo, A.; Taft, R. W. *Chem. Rev.* **1991**, *91*, 165. (e) Suresh, C. H.; Gadre, S. R. *J. Am. Chem. Soc.* **1998**, *120*, 7049. (f) Hansch, C.; Leo, A. *Substituents Constants for Correlation Analysis in Chemistry and Biology*; Wiley-Interscience: New York, 1979.

(6) Hammett, L. P. *Chem. Rev.* **1935**, *17*, 125.

(7) (a) Kim, K. H.; Martin, Y. C. *J. Org. Chem.* **1991**, *56*, 2723. (b) Haeberlein, M.; Murray, J. S.; Brinck, T.; Politzer, P. *Can. J. Chem.* **1992**, *70*, 2209. (c) Karaman, R.; Huang, J.-T. L.; Fry, J. L. *J. Comput. Chem.* **1990**, *11*, 1009.

(8) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B. G.; Chen, W.; Wong, M. W.; Andres, J. L.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98*; Gaussian, Inc.: Pittsburgh, PA, 1998.

(9) Reynolds, W. F.; Dais, P.; MacIntyre, D. W.; Topsom, R. D.; Marriott, S.; Nagy-Felsobuki, E. V.; Taft R. W. *J. Am. Chem. Soc.* **1983**, *105*, 378.

(10) (a) Domenicano, A.; Murray-Rust, P. *Tetrahedron Lett.* **1979**, *24*, 2283. (b) Domenicano, A.; Vaciago, A. *Acta Crystallogr.* **1979**, *B35*, 1382. (c) Domenicano, A.; Mazzeo, P.; Vaciago, A. *Tetrahedron Lett.* **1976**, *13*, 1029. (d) Domenicano, A.; Vaciago, A.; Coulson, C. A. *Acta Crystallogr.* **1975**, *B31*, 221; *B31*, 1630.

(11) (a) Dinur, U. *Chem. Phys. Lett.* **1990**, *166*, 211. (b) Dinur, U. *J. Phys. Chem.* **1991**, *95*, 6201. (c) Lee, J. Y.; Kim, K. S.; Mhin, B. J. *J. Chem. Phys.* **2001**, *115*, 9484.

(12) Hart, D. J.; Ford, W. T. *J. Org. Chem.* **1974**, *39*, 363.

(13) Janesko, B. G.; Gallek, C. J.; Yaron, D. *J. Phys. Chem. A* **2003**, *107*, 1655.

(14) Zou, J.-W.; Zhao, W.-N.; Shang, Z.-C.; Huang, M.-L.; Guo, M.; Yu, Q.-S. *J. Phys. Chem. A* **2002**, *106*, 11550.

(15) Klooster, W. T.; Koetzle, T. F.; Siegbahn, P. E. M.; Richardson, T. B.; Crabtree, R. H. *J. Am. Chem. Soc.* **1999**, *121*, 6337.

(16) Hu, S.; Kim, J.; Tarakeshwar, P.; Kim, K. S. *J. Phys Chem. A* **2002**, *106*, 6817.

(17) Tarakeshwar, P.; Lee, S. J.; Lee, J. Y.; Kim, K. S. *J. Phys. Chem. B* **1999**, *103*, 184.