Density Functional Theoretical Studies on the Redox-dependent Hydrogen Bonding

Young Seuk Cho[1] and Sungu Hwang*[2,3]
[1]*Division of Mathematics and Statistics, Pusan National University, Miryang 627-706, Korea*
[2]*Department of Nanomedical Engineering, Pusan National University, Miryang 627-706, Korea*
[3]*BK21 Nano Fusion Technology Team, Pusan National University, Miryang 627-706, Korea*

(Received September 4, 2006; CL-061011; E-mail: sungu@pusan.ac.kr)

Redox-dependent hydrogen bonding has been a subject of extensive attraction since it provides a basis for external control for synthetic supramolecular system such as sensors, molecular electronics, and molecular machines. We performed density functional theoretical calculations on the nitrobenzene/arylurea interactions in order to understand the bonding and its dependence on the reduction/oxidation. We calculated the binding energy in the reduced and oxidized states and correlated the energy differences with the shift in half-wave potential, $\Delta E_{1/2}$, for different *p*-substituted nitrobenzene/diphenylurea pairs.

The switching upon the change of external stimuli such as pressure change, temperature change, electrons, photons, and chemicals constitutes an important area in the supramolecular chemistry. Its utility can be found in the area of sensors, molecular electronics, and molecular machines.[1]

One of the most important interactions in this respect is hydrogen bonding. Recently, Bu et al. reported a redox-switched hydrogen bonding between nitrobenzene derivatives and diphenylurea.[2,3]

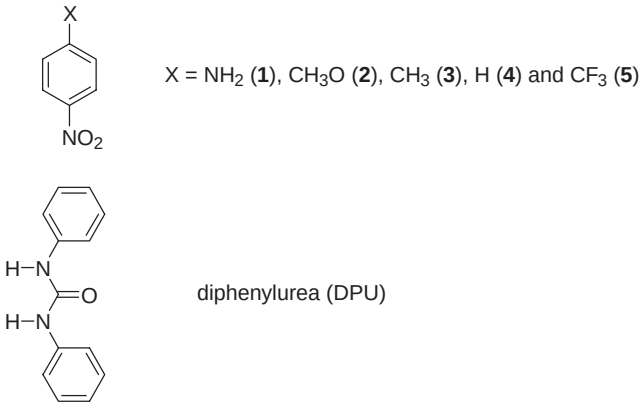
It is well established that nitro group can act as hydrogen acceptors and form both intra- and intermolecular hydrogen bonds in solution and in the solid state. In the context of switching, the dependence of the strength of the bonding upon the change in external stimuli would be of great importance. Experimentally cyclic voltammetry was used in order to estimate the bonding in the solution phase. In order to optimize the interactions, it is highly desirable to understand the hydrogen bonding and its dependence upon the change in the derivatives. We performed density functional theoretical (DFT) calculations on these hydrogen-bonding pairs and correlated the results with the experimental data.

All QM calculations used the Jaguar v5.5 quantum chemistry software.[4] To calculate the geometries and energies of the various molecules, we used the B3LYP flavor of DFT,[5–8] which includes the generalized gradient approximation and a component of the exact Hartree–Fock exchange. Since calculations of vibration frequencies are generally quite time-consuming, the small basis set of 6-31G** basis set was first used to optimize the geometry and calculate the vibration frequencies. The minimized structure was confirmed by the number of imaginary frequency. Single point calculations with 6-311++G** basis set were performed to check the dependence of the results on the inclusion of diffuse function.

Hydrogen bonding was estimated from the binding energy upon complexation without counterpoise correction.

$$\Delta E = E_{\text{complex}} - E_{\text{H-donor}} - E_{\text{H-accepter}} \quad (1)$$

where ΔE, E_{complex}, $E_{\text{H-donor}}$, and $E_{\text{H-accepter}}$ is the binding energy, the energy of complex, the energy of hydrogen-bonding donor, the energy of hydrogen-bonding acceptor, respectively. In Table 1, we summarize the results from B3LYP/6-311++G**//B3LYP/6-31G** calculations.



Scheme 1. Chemical species used in present study.

In Figure 1, we show the correlation between half-wave potential and the electron affinity, which is the change in the total electronic energy upon reduction calculated at B3LYP/6-311++G**//B3LYP/6-31G** level. It gives an excellent correlation coefficient of $R^2 = 0.9158$. Since the correlation results gave very similar trends for B3LYP/6-31G** level, we only tabulated the results from B3LYP/6-311++G**//B3LYP/6-31G** calculations.

Redox-dependent binding is conveniently monitored by looking at the cyclic voltammetry of the redox-active component (receptor) in the presence of and absent of its binding partner (substrate). If the substrate binds more strongly to the oxidized

Table 1. Summary of B3LYP/6-311++G**//B3LYP/6-31G** calculations

	$E_{1/2}$[a] /V	$\Delta E_{1/2}^{0/-}$[b] /mV	EA[c] /kcal·mol^{-1}	$\Delta E_{\text{bind},0}$[d] /kcal·mol^{-1}	$\Delta E_{\text{bind},-}$[e] /kcal·mol^{-1}
1	−1.870	197	−20.44	−9.48	−35.86
2	−1.698	164	−23.60	−8.67	−35.20
3	−1.635	156	−26.16	−8.13	−34.64
4	−1.582	153	−28.11	−7.56	−34.33
5	−1.362	93	−42.31	−7.06	−30.29

[a]Half-wave potential vs FC taken from reference 2. [b]Shift in half-wave potential taken from reference 2. [c]Electron affinity calculated in the present work. [d]Energy difference between neutral complex and (neutral DPU plus neutral NB) calculated in the present work. [e]Energy difference between anionic complex and (neutral DPU plus anionic NB) calculated in the present work.

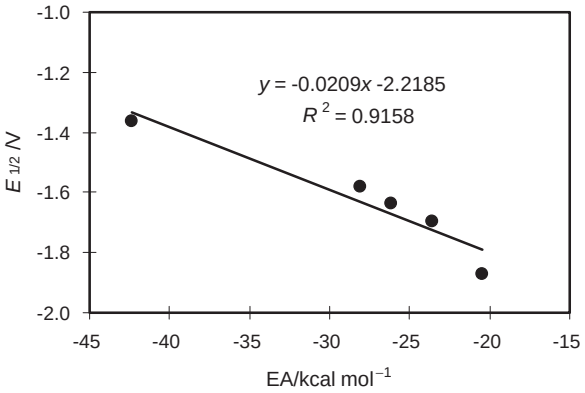


Figure 1. Correlation between half-wave potential and electron affinity.

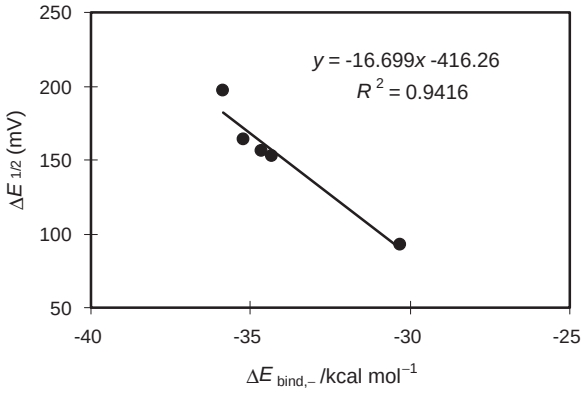


Figure 2. Correlation between the shift in the half-wave potential and the energy of hydrogen bonding in the reduced forms.

form of the receptor, it makes it more difficult to reduce the receptor, which results in the negative shift of the half-wave potential, $E_{1/2}$, of the receptor in the presence of the substrate. On the other hand, if the substrate binds more strongly to the reduced form of the receptor, it will be easier to reduce the receptor in the presence of the substrate, and the $E_{1/2}$ shifts positively.[2] The correlation for the nitrobenzene/diphenylurea is shown in Figure 2. The strength of the hydrogen bonding in the complex anions (reduced forms) are well correlated with the shift in half-wave potential ($R^2 = 0.9416$).

In Figure 3, we depict the structures of the hydrogen-bonding pair (X = H, **4**) before and after reduction. As expected, the hydrogen-bond distance is decreased by 0.28 Å upon reduction, which is also reflected by the increase in the binding energy from -7.56 to -34.33 kcal·mol^{-1}.

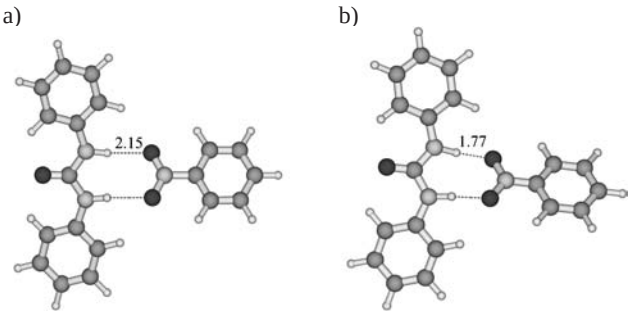


Figure 3. Optimized structures of nitrobenzene/diphenylurea complex: a) neutral state and b) anionic state.

In summary, we performed DFT calculations on the nitrobenzene/arylurea system. There is very weak interaction between these species in the oxidized state, i.e. in the neutral form. However, reduction of nitrobenzene derivatives to their radical anions creates very strong hydrogen-bonding interaction with arylureas. The dependence of the interaction upon the change of the derivative on the benzene ring suggests a method for the fine tuning of the switching.

This work was supported by a grant from Korea Research Foundation (KRF-2004-015-C00221).

References

1 J. W. Steed, J. L. Atwood, *Supramolecular Chemistry*, John Wiley & Sons, Chichester, **2000**.
2 J. Bu, N. D. Lilienthal, J. E. Woods, C. E. Nohrden, K. T. Hoang, D. Truong, D. K. Smith, *J. Am. Chem. Soc.* **2005**, *127*, 6423.
3 C. Chan-Leonor, S. L. Martin, D. K. Smith, *J. Org. Chem.* **2005**, *70*, 10817.
4 *Jaguar: v5.5*, Schrodinger, Portland, OR, **1991–2003**.
5 J. C. Slater, *The Self-Consistent Field for Molecules and Solids*, McGraw-Hill, New York, **1974**.
6 S. H. Vosko, L. Wilk, M. Nusair, *Can. J. Phys.* **1980**, *58*, 1200.
7 A. D. Becke, *Phys. Rev. A* **1988**, *38*, 3098.
8 C. Lee, W. Yang, R. G. Parr, *Phys. Rev. B* **1988**, *37*, 785.

Published on the web (Advance View) November 4, 2006; doi:10.1246/cl.2006.1362