THE JOURNAL OF PHYSICAL CHEMISTRY A LETTERS

2006, *110,* 3349−3351
Published on Web 02/23/2006

Hydrogen Bonding without Borders: An Atoms-in-Molecules Perspective

R. Parthasarathi,[†] V. Subramanian,*[,†] and N. Sathyamurthy*[,‡]

Chemical Laboratory, Central Leather Research Institute, Adyar, Chennai, India 600 020,
and Department of Chemistry, Indian Institute of Technology, Kanpur, Kanpur, India 208 016

Received: January 26, 2006; In Final Form: February 10, 2006

It is shown that the electron density at the hydrogen bond critical point increases approximately linearly with increasing stabilization energy in going from weak hydrogen bonds to moderate and strong hydrogen bonds, thus serving as an indicator of the nature and gradual change of strength of the hydrogen bond for a large number of test intermolecular complexes.

Introduction

For nearly a century, hydrogen bonding (H-bonding) has been the subject of contemporary research interest due to its prevalence and importance in various branches of sciences.[1−8] Although a great deal of information is available on H-bonding, identification of new types of H-bonds in solid state and supramolecular chemistry and biology has triggered intense research on the nature of H-bonding.[5−8] Various experimental and theoretical methods have been employed to understand the H-bonding interaction in gaseous, liquid and solid states and several criteria based on hydrogen bond strength, geometrical and spectral characteristics have been proposed to classify these interactions[5−7] as strong, moderate and weak.[7,8] The strength of H-bonding interaction ranges from about 1 to 40 kcal/mol, indicating the existence of a continuum of strength. It is important to note that weak H-bonds are hardly distinguishable from van der Waals interaction. The strength of the classical H-bonding varies from 4 to 15 kcal/mol. For strong H-bonds, the strength falls in the range 15−40 kcal/mol. Although electrostatic interaction is taken to be the primary factor responsible for the classical type of H-bonding, pronounced covalent character is found in strong H-bonding and a dominance of dispersive interaction is observed in weak H-bonding. It is worth mentioning that the term H-bond includes a much broader spectrum of interaction than what was recognized earlier. The term “hydrogen bridge” has been used in the literature[1,8] to represent meaningfully different types of H-bond. As the electrostatic character of a weak H-bond increases, there is a transition from weak H-bond to classical or moderate H-bond, while an increase in covalency leads to strong H-bonds.[7,8] However, it is very difficult to quantify the transition from one type of H-bonding to another.[8] Gilli et al. have used an electrostatic-covalent H-bond model (ECHBM) derived from a systematic analysis of structural and spectroscopic data of a large number of O−H···O−H-bonds to quantify the H-bonding interaction.[9] According to this model, weak H-bonds are electrostatic in nature but become increasingly covalent with increasing strength.

Bader’s theory of atoms-in-molecules (AIM) is an elegant theoretical tool used to understand both covalent and non-covalent molecular interactions.[10] The usefulness of this AIM approach in eliciting H-bonding interactions is well-documented.[11−19] The topological properties of electron density at the bond critical points (BCP) have been used to obtain information on the nature of the interaction. Electron density ($\rho(r_c)$) and Laplacian of electron density ($\nabla^2\rho(r_c)$) at the hydrogen bond critical points (HBCPs) have been used as the criteria to quantify the H-bonding interaction. There are several interesting reports in the literature that illustrate that $\rho(r_c)$ at HBCPs and H-bond distance exhibit a linear relationship.[11−18] It has been illustrated that $\rho(r_c)$ and $\nabla^2\rho(r_c)$ display a linear relationship with the H-bond strength.[19] In this study, an attempt has been made to understand the concept of hydrogen bonding without borders using the topological properties of electron density and also to quantify the transition from weak to moderate to strong H-bonding.

Computational Details

A number of intermolecular complexes of varying strengths, from the van der Waals to the covalent limit have been chosen to study and develop a unified picture of the H-bond. The geometry of all the complexes has been optimized using the second-order Møller−Plesset (MP2) perturbation theory and the augmented correlation consistent polarization plus valence double-ζ (aug-cc-pVDZ) basis set, with the help of the GAUSSIAN 98W suite of programs.[20] The resulting wave functions have been used to compute the topographical features of electron density using the AIM 2000 software package.[21] The stabilization energy (SE) has been calculated using a supermolecule approach:

$$\mathrm{SE} = |E_{\mathrm{complex}} - (E_1 + E_2)| \tag{1}$$

where E_{complex} is the total energy of the H-bonded complex and E_1 and E_2 are the total energies of the monomers. The energies of the monomers were calculated from the respective monomer geometries in the complexes or in other words the energy being

---

* Address correspondence to these authors. Tel: +91 44 24411630. Fax: +91 44 24911589. E-mail: V.S., subuchem@hotmail.com; N.S., nsath@iitk.ac.in.

[†] Central Leather Research Institute.

[‡] Indian Institute of Technology.

10.1021/jp060571z CCC: $33.50

TABLE 1: Electron Density ($\rho(r_c)$) and the Laplacian of Electron Density ($\nabla^2\rho(r_c)$) at the Hydrogen Bond Critical Point and the Stabilization Energy (SE) Values Computed at the MP2/aug-cc-pVDZ Level of Theory for Various Hydrogen-Bonded Complexes

H-bonded complexes	electron density (e/a_o^3)	Laplacian of electron density (e/a_o^5)	SE (kcal/mol)
$CH_4\cdots Ar$	0.0038	0.0037	0.11
$CH_4\cdots SH_2$	0.0045	0.0038	0.23
$CH_4\cdots HF$	0.0047	0.004	0.25
$CH_4\cdots NH_3$	0.0073	0.0055	0.54
$SeH_2\cdots HF$	0.0093	0.005	0.91
$HCl\cdots HCl$	0.0068	0.0053	1.22
$H_2S\cdots PH_3$	0.0091	0.0052	1.37
$SH_2\cdots HF$	0.0093	0.008	1.54
$H_2S\cdots H_2S$	0.0102	0.0062	1.55
$PH_3\cdots H_2O$	0.0119	0.0072	2.17
$PH_3...HCl$	0.0163	0.0082	3.08
$C_2H_4\cdots HF$	0.0183	0.0128	4.16
$H_2O\cdots H_2O$	0.022	0.0232	4.46
$PH_3\cdots HF$	0.0196	0.0129	4.48
$HCN\cdots HCl$	0.0211	0.0188	4.68
$CHOH\cdots H_2O$	0.0234	0.0196	4.81
$NH_2COH\cdots H_2O$	0.0193	0.0198	4.85
$HCl\cdots H_2O$	0.0258	0.0254	5.09
$CH_3OH\cdots H_2O$	0.0198	0.0202	5.16
$CH_3OH\cdots CH_3OH$	0.0264	0.026	5.22
$C_6H_5OH\cdots H_2O$	0.0262	0.0285	6.28
$HCN\cdots HF$	0.0266	0.0314	6.88
$NH_3\cdots HCl$	0.0497	0.029	9.33
$NH_3\cdots HF$	0.0482	0.0376	12.4
$NH_4^+\cdots H_2O$	0.0453	0.0428	19.8
$NH_3\cdots NH_4^+$	0.0667	0.0288	28.6
$OH^-\cdots H_2O$	0.0883	0.035	31.7
$H_3O^+\cdots H_2O$	0.1517	−0.057	49.7

the result of complexation was taken into account. The calculated SEs have been corrected for basis set superposition error using the counterpoise method suggested by Boys and Bernardi.[22]

Results and Discussion

The calculated SE values for all the complexes are presented in Table 1 along with the values of electron density and Laplacian of electron density at the HBCPs. They show clearly that there is a linear relationship (red line) between SE and $\rho(r_c)$, as illustrated in Figure 1a. The correlation coefficient is 0.97. The value of $\rho(r_c)$ increases in going from a van der Waals interaction (in $CH_4\cdots Ar$) to a classical H-bonding interaction (in $H_2O\cdots H_2O$) and a strong H-bonded interaction (in $H_3O^+\cdots H_2O$). For convenience, different regimes of hydrogen bonding (weak, moderate, strong, etc.) are marked in the same figure. The smooth change in the values of $\rho(r_c)$ from 0.004 to 0.15 e/a_o^3 reflects the smooth transition from weak (van der Waals) hydrogen bond to moderate (classical) and strong hydrogen bond. Thus, it becomes clear that it is possible to describe the strength of the different types of H-bond with the help of a single parameter, i.e., $\rho(r_c)$ at the HBCPs.

The plot of the Laplacian of the electron density at the HBCP against SE in Figure 1b reveals a good linear relationship (correlation coefficient 0.90) between the two, once the three strongest hydrogen bonds are left out. The Laplacian is positive and it increases almost linearly with an increase in SE for all species except $H_3O^+\cdots H_2O$, for which the Laplacian becomes negative. The change from positive to negative is dramatic and is illustrative of the change from a strong hydrogen bond to a covalent bond. Here it is important to point out that the result for $H_3O^+\cdots H_2O$ corresponds to a Zundel ion[23] in which the proton is held symmetrically between the two water molecules

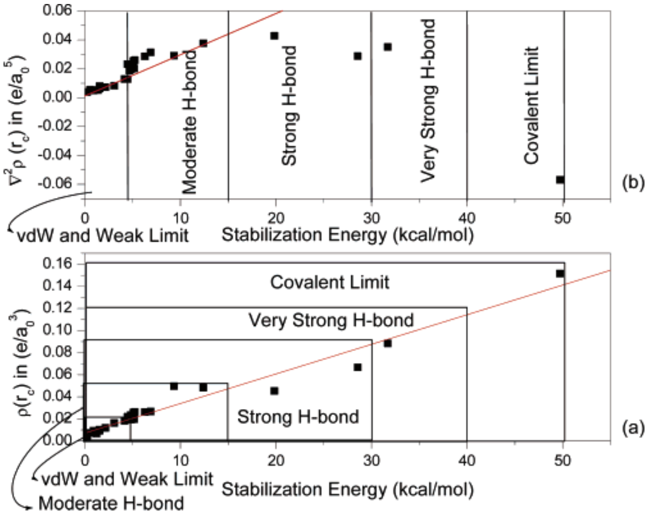

Figure 1. Diagram showing the relationship between (a) the electron density ($\rho(r_c)$) and (b) the Laplacian of electron density ($\nabla^2\rho(r_c)$) at the hydrogen bond critical point and the stabilization energy for different hydrogen-bonded complexes.

and the potential energy curve has a single minimum that is characteristic of a covalent bond. For an Eigen ion,[24] the proton would be covalently bonded to one water molecule and hydrogen bonded to the other. Interestingly, the interaction between $NH_4^+\cdots NH_3$ and $OH^-\cdots H_2O$ remains a strong hydrogen bond.

In the classical view, H-bonds are mainly electrostatic in nature with some covalent character. The original concept of H-bonds has been modified in recent years to include weak interactions that have their origin in dispersive forces and thus merge into van der Waals interaction. As a result, we observe a range of H-bonding interaction without borders, with the values of $\rho(r_c)$ and $\nabla^2\rho(r_c)$ reflecting the strength of the hydrogen bond.

Concluding Remarks

It has been shown that there is a linear relationship between the electron density and the Laplacian of the electron density values at the HBCP and the strength of H-bond and that there is a smooth change in the nature of interaction from van der Waals to classical H-bonding to strong H-bonding.

Acknowledgment. This study has been supported by a grant from the Council of Scientific and Industrial Research, New Delhi.

References and Notes

(1) Latimer, W. H.; Rodebush, W. H. *J. Am. Chem. Soc.* **1920**, *42*, 1419

(2) Pauling, L. *The Nature of the Chemical Bond*; Cornell University Press: Ithaca, NY, 1960.

(3) Jeffrey, G. A.; Saenger, W. *Hydrogen Bonding in Biology and Chemistry*; Springer-Verlag: Berlin, 1991.

(4) Buckingham, A. D.; Legon, A. C.; Roberts, S. M. *Principles of Molecular Recognition*; Blackie Academic & Professional: London, 1993.

(5) Jeffrey, G. A. *An Introduction to Hydrogen Bonding*; Oxford University Press: New York, 1997.

(6) Scheiner, S. *Hydrogen Bonding. A Theoretical Perspective*; Oxford University Press: Oxford, U.K., 1997. Steiner, T. *Angew. Chem., Int. Ed.* **2002**, *41*, 48.

(7) Desiraju, G. R.; Steiner, T. *The Weak Hydrogen Bond in Structural Chemistry and Biology*; Oxford University Press: Oxford, U.K., 1999.

(8) Desiraju, G. R. *Acc. Chem. Res.* **2002**, *35*, 565.

(9) Gilli, G.; Gilli, P. *J. Mol. Struct.* **2000**, *552*, 1.

(10) Bader, R. F. W. *Atoms in Molecules: A Quantum theory*; Clarendon Press: Oxford, U.K., 1990.

(11) Popelier, P. L. A. *J. Phys. Chem. A* **1998**, *102*, 1873.

(12) Cubero, E.; Orozco, M.; Hobza, P.; Luque, F. J. *J. Phys. Chem. A* **1999**, *103*, 6394.

(13) Grabowski, S. J. *J. Phys. Chem. A* **2001**, *105*, 10739.

(14) Scheiner, S.; Grabowski, S. J.; Kar, T. *J. Phys. Chem. A* **2001**, *105*, 10607.

(15) Wojtulewski, S.; Grabowski, S. J. *Chem. Phys.* **2005**, *309*, 183.

(16) Zierkiewicz, W.; Jurecka, P.; Hobza, P. *Chem. Phys. Chem*. **2005**, *6*, 609.

(17) Wojtulewski, S.; Grabowski, S. J. *J. Mol. Struct. (THEOCHEM)* **2003**, *645*, 287.

(18) Gora, R. W.; Grabowski, S. J.; Leszczynski, J. *J. Phys. Chem. A* **2005**, *109*, 6397.

(19) Parthasarathi, R.; Subramanian, V.; Sathyamurthy, N. *J. Phys. Chem. A* **2005**, *109*, 843. Parthasarathi, R.; Amutha, R.; Subramanian, V.; Nair, B. U.; Ramasami, T. *J. Phys. Chem. A* **2004**, *108*, 3817. Parthasarathi, R.; Subramanian, V. *Struct. Chem.* **2005**, *16*, 243.

(20) 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*, revision A.7; Gaussian, Inc.: Pittsburgh, PA, 1998.

(21) Biegler-Konig, F.; Schonbohm, J.; Derdau, R.; Bayles, D.; Bader, R. F. W. *AIM 2000*, version 1; Bielefeld, Germany, 2000.

(22) Boys, S. F.; Bernardi, F. *Mol. Phys.* **1970**, *19*, 553.

(23) Schuster, P., Zundel, G., Sandorfy, C., Eds. *The Hydrogen Bond. Recent Developments in Theory and Experiments*; North-Holland: Amsterdam, 1976. Also see: Zundel, G. *Adv. Chem. Phys.* **2000**, *111*, 1.

(24) Eigen, M. *Angew. Chem., Int. Ed. Engl.* **1964**, *3*, 1. Eigen, M. *Angew. Chem.* **1963**, *75*, 489. Eigen, M.; Maeyer, L. D. *Proc. R. Soc. A* **1958**, *247*, 505. Xie, Y.; Remington, R. B.; Schaefer, H. F., III. *J. Chem. Phys.* **1994**, *101*, 4878.