

A New Generalized Concept of Chemical Reactivity and Selectivity

Pratim Kumar Chattaraj* and Utpal Sarkar

Department of Chemistry, Indian Institute of Technology
Kharagpur 721302, India

Received xxx; Preprint published xxx; Accepted xxx ; Published xxx

Internet Electron. J. Mol. Des. 2003, 1, 000–000

Abstract

Basicity of aliphatic amines in gas phase is analyzed in terms of a new generalized index of chemical reactivity and selectivity named philicity which can take care of electrophilic, nucleophilic and radical attacks in a similar fashion.

Keywords. DFT, Reactivity Parameters, Fukui Function, Philicity.

Abbreviations and notations

DFT, Density Functional Theory

FF, Fukui Function

* Correspondence authors E-mail: pkc@chem.iitkgp.ernet.in ; Tel: 91 03222 283304 ; Fax: 91 3222 255303.

1 INTRODUCTION

Global reactivity indices like electronegativity (χ) [1], hardness (η) [2] and electrophilicity ($\omega = \frac{\chi^2}{2\eta}$) [3] and local reactivity indices like Fukui function ($f(\vec{r})$) [4] and local softness ($s(\vec{r})$) [5] have been extensively used in understanding reactivity as well as site selectivity in molecular systems [6]. Within density functional theory (DFT) [7] the electronegativity of an N - electron system characterized by the external potential $v(\vec{r})$ and the total energy E , is defined [8] as the negative of the chemical potential (μ), the first- order energy derivative, $\left(\frac{\partial E}{\partial N}\right)_{v(\vec{r})}$ and the hardness is defined [9] as the corresponding second- order derivative, $\frac{1}{2}\left(\frac{\partial^2 E}{\partial N^2}\right)_{v(\vec{r})}$. On the other hand the local quantities are defined as,

$$f(\vec{r}) = \left(\frac{\partial \rho(\vec{r})}{\partial N}\right)_{v(\vec{r})} = \left(\frac{\partial \mu}{\partial v(\vec{r})}\right)_N \quad (1)$$

and

$$s(\vec{r}) = f(\vec{r})S = \left(\frac{\partial \rho(\vec{r})}{\partial \mu}\right)_{v(\vec{r})} \quad (2)$$

where $\rho(\vec{r})$ and S are the electron density and the global softness respectively.

In order to provide a unified treatment of chemical reactivity and selectivity a new concept of philicity is introduced recently [10] through a resolution of identity. This local philicity index is given as

$$\omega^\alpha(\vec{r}) = \omega f^\alpha(\vec{r}) \quad (3)$$

or its condensed- to- atom variant for the atomic site k in a molecule is defined as

$$\omega_k^\alpha = \omega f_k^\alpha \quad (4)$$

where $\alpha = +, -, 0$ refer to nucleophilic, electrophilic and radical attacks respectively. The ω_k^α is capable of providing other local and global reactivity descriptors.

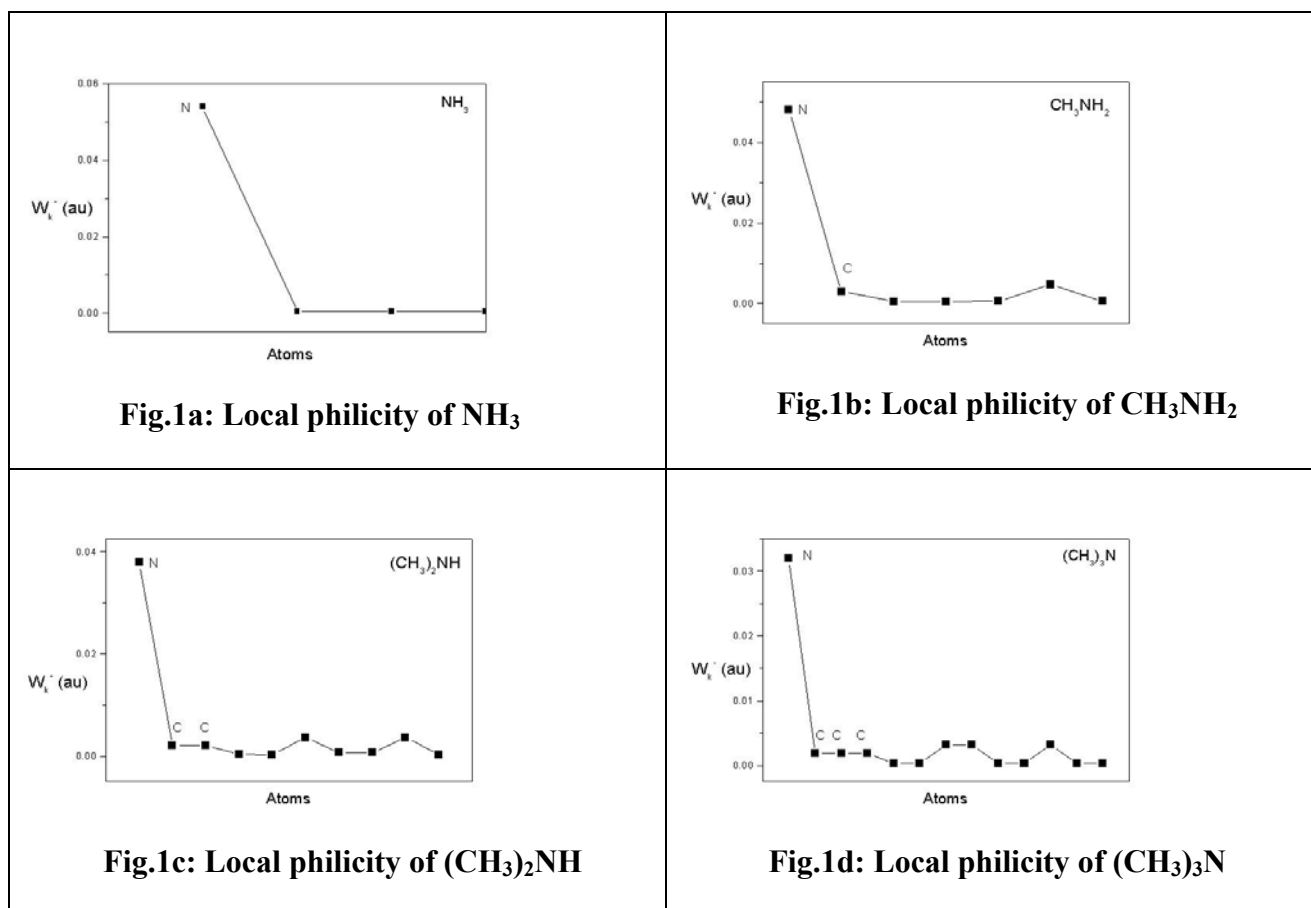
The electrophilic or nucleophilic power is distributed over all atomic sites in a molecule keeping the overall philicity conserved. The atomic site with the highest ω_k^+ will be the most favorable site for nucleophilic attack, the highest ω_k^- for the electrophilic attack and the highest ω_k^0 for the radical attack.

2 COMPUTATIONAL DETAILS

In order to test the efficacy of this new concept, DFT level calculations with B3LYP exchange- correlation functional and 6-31+G* basis set using GAUSSIAN 03 program [11] are performed on several amines. Necessary Fukui functions are calculated using the direct method proposed by Contreras et al [12]. The molecules considered are NH_3 , CH_3NH_2 , $(\text{CH}_3)_2\text{NH}$ and $(\text{CH}_3)_3\text{N}$.

3 RESULTS AND DISCUSSION

For all the molecules ω_k^- is the highest in the N- center indicating that this site would be most favorable for electrophilic attack (say protonation). As shown in Figures 1 the order in which ω_N^- varies is $\text{NH}_3 > \text{CH}_3\text{NH}_2 > (\text{CH}_3)_2\text{NH} > (\text{CH}_3)_3\text{N}$ which corroborates with other theoretical [12-14] and experimental [15] results of the studies on gas phase basicity of aliphatic amines. Unless otherwise specified the atoms are hydrogen in Figures 1.



In table I the numerical data of gas phase basicity, f_N^- and ω_N^- are given. Our f_N^- values are slightly different from that of Contreras et al (*Ref. 12*) because we have used B3LYP/6-31+G* basis set whereas they have used HF/6-311G basis set. An inverse relationship has been observed between gas phase basicity and ω_N^- .

Table I: Basicity, Fukui function and ω_N^-

Amine	Basicity	f_N^-			ω_N^-
		Ref 13	Ref 12	This paper	
NH ₃	-818	-	0.9764	0.9743719	0.053950
CH ₃ NH ₂	-861	0.3173	0.8135	0.8276224	0.048041
(CH ₃) ₂ NH	-890	0.3017	0.7401	0.7341378	0.037861
(CH ₃) ₃ N	-909	0.2902	0.6891	0.6506701	0.031944

On the other hand, ω_k^+ is the highest in the C- centers signifying that the nucleophilic attack will take place in the C- site. The order of preference turn out to be CH₃NH₂ > (CH₃)₂NH > (CH₃)₃N.

We have also checked another homologous series obtained by a methyl substitution on the carbon, viz., CH₃CH₂NH₂, (CH₃)₂CHNH₂ and (CH₃)₃CNH₂ which also provides with the results at par with those from other theoretical [12-14] and experimental [15] studies.

4 CONCLUSIONS

Now we summarize the novel features of this work. The new philicity index is capable of properly delineating the electrophilic/ nucleophilic/ radical attacks on different atomic centers in a molecule. It can provide us with the global reactivity information as well. Gas phase basicity of amines is analyzed as a prototype example. A molecule with high global electrophilicity value would be more reactive towards that with a corresponding low value. For two such molecules the reaction would be through the atomic center having the largest ω_k^- in one molecule with the atomic center having the largest ω_k^+ of the other molecule and vice versa.

Acknowledgment

We thank CSIR, New Delhi for financial assistance and Professors M. Galvan, P. Fuentealba and R. Contreras and Drs. S. Roy, A. P. Felipe and V. Subramanian for their help in various ways.

5 References

- [1] K.D. Sen and C.K. Jorgensen, *Electronegativity, Structure and Bonding*, Springer- Verlag, Berlin, 1987, vol. **66**.
- [2] R.G. Pearson, *Chemical Hardness: Application from Molecules to Solid*, Wiley- VCH: Weinheim, Germany, 1997.
- [3] R G. Parr, L. v. Szentpaly and S. Liu, Electrophilicity Index *J. Am. Chem. Soc.* 1999, **121**, 1922.
- [4] R.G. Parr and W. Yang, Density Functional Approach to the Frontier-Electron Theory of Chemical Reactivity *J. Am. Chem. Soc.* 1984, **106**,4049.

- [5] R.G. Parr and W. Yang, Hardness, Softness and the Fukui Function in the Electronic Theory of Metals and Catalysis *Proc. Natl. Acad. Sci.* 1985, **82**,6723.
- [6] P. Geerlings, F. De Proft and W. Langenaeker, Conceptual Density Functional Theory *Chem. Rev.* 2003, **103**, 1793.
- [7] R.G. Parr and W. Yang, *Density Functional Theory of Atoms and Molecules*; Oxford University Press: Oxford, UK, 1989.
- [8] R.G. Parr, R.A. Donnelly, M. Levy and W.E. Palke, Electronegativity: The density functional viewpoint *J. Chem. Phys.* 1978, **68**, 3801.
- [9] R.G. Parr and R.G. Pearson, Absolute Hardness: Companion Parameter to Absolute Electronegativity *J. Am. Chem. Soc.* 1983, **105**, 7512.
- [10] P. K. Chattaraj, B. Maiti and U. Sarkar, Philicity: A Unified Treatment of Chemical Reactivity and Selectivity *J. Phys. Chem. A*, 2003, **107**, 4973.
- [11] M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, J.A. Montgomery, Jr., T. Vreven, K.N. Kudin, J.C. Burant, J.M. Millam, S.S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J.E. Knox, H.P. Hratchian, J.B. Cross, C. Adamo, J. Jaramillo, R. Gomperts, R.E. Stratmann, O. Yazyev, A.J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P.Y. Ayala, K. Morokuma, G.A. Voth, P. Salvador, J.J. Dannenberg, V.G. Zakrzewski, S. Dapprich, A.D. Daniels, M.C. Strain, O. Farkas, D.K. Malick, A.D. Rabuck, K. Raghavachari, J.B. Foresman, J.V. Ortiz, Q. Cui, A.G. Baboul, S. Clifford, J. Cioslowski, B.B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R.L. Martin, D.J. Fox, T. Keith, M.A. Al-Laham, C.Y. Peng, A. Nanayakkara, M. Challacombe, P.M. W. Gill, B. Johnson, W. Chen, M.W. Wong, C. Gonzalez, and J.A. Pople, Gaussian, Inc., Pittsburgh PA, 2003.
- [12] R.R. Contreras, P. Fuentealba, M. Galvan, and P. Perez, A direct evaluation of regional Fukui functions in molecules *Chem. Phys. Lett.* 1999, **304**, 405.
- [13] W. Yang and W.J. Mortier, The Use of Global and Local Molecular Parameters for the Analysis of the Gas-Phase Basicity of Amines *J. Am. Chem. Soc.* 1986, **108**, 5708.
- [14] B. Safi, K. Choho, F. De Proft and P. Geerlings, Theoretical study of the basicity of alkyl amines in vacuo and in different solvents: a density functional theory approach *Chem. Phys. Lett.* 1999, **300**, 85.
- [15] S.G. Lias, J.F. Liebman and R.D. Levin, Evaluated gas phase basicities and proton affinities of molecules; heats of formation of protonated molecules *J. Phys. Chem. Ref. Data* 1984, **13**, 695.

Biographies

P. K. Chattaraj obtained his Ph.D. degree from Indian Institute of Technology, Bombay. Subsequently he did his postdoctoral research in the University of North Carolina at Chapel Hill. He is currently a Professor of chemistry in Indian Institute of Technology, Kharagpur. Professor Chattaraj's research interests include density functional theory, nonlinear dynamics, ab initio calculations and the theory of chemical reactivity. He was a visiting faculty at several universities throughout the globe. Professor Chattaraj is a Fellow of the Indian Academy of Sciences, Bangalore. He is a recipient of several Awards and Medals.

U. Sarkar received his B.Sc. (Physics Honours) from the University of Burdwan and M.Sc. (Physics) from the Visva-Bharati University, Santiniketan. Then he joined the research group of Professor P. K. Chattaraj for his Ph.D. degree in the Chemistry Department, Indian Institute of Technology, Kharagpur as a CSIR (Government of India) Fellow.

