JOTCSA, Volume 3, issue 2, (2016), pp. 89-102. **Research article**

Journal homepage: http://dergipark.ulakbim.gov.tr/jotcsa

e-ISSN: 2149-0120

A USEFUL METHOD FOR THE PREDICTION OF MOLECULAR ELECTROPHILICITY AND NUCLEOPHILICITY

Savaş Kaya[1]*, Cemal Kaya[1], Ilkay Uğurlu[1], and Nazmul Islam[2]

[1]Department of Chemistry, Faculty of Science, Cumhuriyet University, Sivas, 58140, Turkey.
[2]Theoretical and Computational Chemistry Research Laboratory, Department of Basic Science and Humanities/ Chemistry, Techno Global-Balurghat, Balurghat, D. Dinajpur –733103, India.

Abstract: In the present study, a new theoretical model for the calculation of molecular electrophilicity and molecular nucleophilicity based on group electronegativity and molecular hardness equations, derived by us in recent years, is presented. Furthermore, a validity test of the present model is performed with 33 molecules by comparing the computed electrophilicity and nucleophilicity data with the electrophilicity and nucleophilicity data computed using some well-known theoretical methods and their experimental counterparts. The comparative study reveals excellent correlation between theory and experiment. Thus the new theoretical model presented in this work for the calculation of molecular reactivity indices like electrophilicity and nucleophilicity is logical and reliable.

Keywords: Electronegativity, Hardness, Electrophilicity, Nucleophilicity, DFT.
Submitted: February 29, 2016. **Revised:** March 29, 2016. **Accepted:** April 12, 2016.

Cite this: Kaya S, Kaya C, Uğurlu İ, Islam N. A Useful Method for the Prediction of Molecular Electrophilicity and Nucleophilicity. Journal of the Turkish Chemical Society, Section A: Chemistry. 2016 Apr;3(2):89–101.
DOI: 10.18596/jotcsa.04933.

***Correspondence to:** Savaş Kaya. E-mail: savaskaya@cumhuriyet.edu.tr.

INTRODUCTION

It now becomes well established that the molecular reactivity descriptors such as chemical hardness, electronegativity, electrophilicity, and nucleophilicity have greatly taken advantage of the development of Density Functional Theory [1-3]. The DFT has proven to be an important tool in modern quantum chemistry because of its ability to provide the quantitative definitions for chemical concepts like chemical potential (μ) [4] chemical hardness (η) [5-8], and electronegativity (χ) [9,10]. The first and second derivatives of electronic energy (E) with respect to the number of electron (*N*) under the constant external potential, *υ(r)*, are described as chemical potential and chemical hardness, respectively. Softness (σ) [11] is the inverse of chemical hardness. Qualitative expressions related to these chemical concepts are given as follows:

$$\mu = -\chi = (\partial E / \partial N)_{v(r)} \tag{1}$$

$$\eta = (\partial^2 E / \partial N^2)_{v(r)} \tag{2}$$

$$\sigma = 1/\eta \tag{3}$$

Parr and Pearson, with the help of finite differences method, put forwarded the approximate and operational definition of electronegativity and chemical hardness of chemical species as [12, 13]:

$$\chi = -\mu = \frac{I + A}{2} \tag{4}$$

$$\eta = I - A \tag{5}$$

where I is the first vertical ionization energy and A is the electron affinity values of the chemical species.

Ingold [14] introduced the terms of nucleophile and electrophile in the glossary of chemistry. The electrophilicity and nucleophilicity are two very useful theoretical constructs of conceptual chemistry originating from the fruition of the long effort of understanding the mechanism of organic reaction [15]. Electrophilicity is a property of atoms and molecules which signifies the energy lowering process on soaking electrons from donors. Hence, the electrophilicity measures the energy stabilization when the system acquires an additional electronic charge from the environment/donor [15]. The quantitative definition of electrophilicity was put forward by Parr and co-workers [16] following the work of Maynard et al. [17] as a quantitative intrinsic numerical value and suggested the term electrophilicity index, ω, a new global reactivity descriptor of atoms and molecules, as presented below:

$$\omega = \frac{\mu^2}{2\eta} = \frac{\chi^2}{2\eta} = \frac{(I+A)^2}{8(I-A)} \tag{6}$$

Nucleophilicity and electrophilicity are physically multiplicative inverse of each other (*N=1/ω*) [18].

Based on the valence electron theory of Lewis, Ingold [14] proposed an electrophilicity scale to describe electron-deficient (electrophile) and electron-rich (nucleophile) species as follows:

$$k_\sigma = C\omega N \tag{7}$$

where *C* is the proportionality constant. k_σ is the hydrogen bond stretching force constant. Further, it is important to note that nucleophilicity (*N*) is proportional to (1/electrophilicity) as noted above.

One of the remarkable developments regarding electronegativity concept has been provided by Sanderson by introducing a new electronic structure principle famous as "Electronegativity equalization principle [19-21]." According to this principle "when two or more different atoms combine to form a molecule, their electronegativities change to a common intermediate value and become equalized." In recent times, we presented a new equation to calculate the electronegativities of molecules and functional groups from ionization energies and electron affinities of pre-bonded atoms considering Sanderson's electronegativity equalization principle and Iczkowski-Margrave's electronegativity study [22]. The equation [23] derived by us is presented below:

$$\chi_M = \frac{\sum_{i=1}^{N}\left(\frac{I_i + A_i}{I_i - A_i}\right) + 2q_M}{\sum_{i=1}^{N}\left(\frac{2}{I_i - A_i}\right)} \tag{8}$$

where, χ_M and q_M are electronegativity and charge of molecule or functional group, respectively. *N* is number of atoms in the molecule and I_i and A_i are the ionization energy and electron affinity of *i*-th atom.

Chemical hardness is a measure of the resistance of a chemical species towards the deformation of electric charge cloud under small perturbation and this quantity is an indicator of chemical reactivity [24, 25]. The concept introduced by Pearson has important applications in chemistry.

Hard and Soft Acid-Base (HSAB) [26, 27] Principle and Maximum Hardness Principle (MHP) [28] based on chemical hardness concept make the structure-reactivity relationship more understandable. Recently we presented a new equation shown below [29] to calculate the chemical hardnesses of molecules and functional groups:

$$\eta_M = \frac{\left(2\sum_{i=1}^{N}\frac{b_i}{a_i}\right)+q_M}{\sum_{i=1}^{N}\frac{1}{a_i}} \qquad \textbf{(9)}$$

In this equation, η_M and q_M are chemical hardness and charge of molecule, respectively. N is the total number of atoms in the molecule. a_i and b_i parameters in Eq. 9 are defined as: $a_i=(I+A)/2$ and $b_i=(I-A)/2$. These parameters for some selected atoms are presented in Table 1.

The aim of this article is to calculate the nucleophilicity and electrophilicity data of molecules with the help of new theoretical model mentioned above.

RESULTS AND DISCUSSION

In the present study, we calculated the nucleophilicity and electrophilicity of some selected molecules considering Eq. 10 for charged molecules and Eq. 11 for neutral molecules. Then, we compared the results obtained by us with other theoretical methodologies and experimental data. Table 2 reports the electrophilicity and nucleophilicity values calculated via various methods for some selected molecules. Considering the calculated values, we can say that the obtained results using Eq.10 and Eq. 11 are exceptionally compatible with the results of geometric mean equation of Chattaraj. Chattaraj has proposed the geometric mean equation for calculations regarding the electrophilicity values of molecules assuming that electrophilicity gets equalized like chemical hardness and electronegativity during molecule formation process. The electrophilicity equalization principle of Chattaraj, Giri and Duley [30] has been criticized by Szentpaly [31]. Considering large molecules such as fullerene, Szentpaly suggested that there is not an acceptable evidence regarding equalization of electrophilicity. After the publication of Szentpaly, Chattaraj [32] tried to justify and to urge the electrophilicity equalization principle. Indeed, this situation is suggestive that the equalization of electrophilicity becomes difficult depending on number of atoms of the molecule. We believe that electrophilicity equalization principle of Chattaraj is useful for the calculating of electrophilicities of small molecules and this electronic structure principle cannot be ignored entirely. The agreement between the results of geometric mean of Chattaraj and the results of present study in Table 2 will provide as a support to Electrophilicity equalization principle because the electrophilicity and nucleophilicity values obtained by us is very close to Chattaraj's results.

Table 1. Experimental Parameters for Some Atoms (eV)

Atom	*I*	*A*	*a*	*b*
H	13.598	0.754	7.176	6.422
Li	5.392	0.618	3.005	2.387
Be	9.323	0.295	4.809	4.514
B	8.298	0.280	4.289	4.009
C	11.260	1.262	6.261	4.999
N	14.534	0.070	7.302	7.232
O	13.618	1.461	7.539	6.078
F	17.423	3.401	10.412	7.011
Na	5.139	0.548	2.843	2.295
Mg	7.646	0.541	4.093	3.552
Al	5.986	0.433	3.209	2.776
Si	8.152	1.390	4.771	3.381
P	10.487	0.747	5.617	4.870
S	10.360	2.077	6.218	4.141
Cl	12.968	3.613	8.290	4.677
K	4.341	0.501	2.421	1.920
Ca	6.113	0.024	3.068	3.044
Sc	6.561	0.188	3.374	3.186
Cr	6.767	0.666	3.716	3.050
Mn	7.434	-0.498	3.468	3.960
Fe	7.902	0.151	4.026	3.875
Ni	7.640	1.156	4.398	3.242
Cu	7.726	1.235	4.480	3.245
Zn	9.390	-0.490	4.450	4.940
As	9.789	0.814	5.301	4.487
Se	9.752	2.020	5.886	3.866
Cs	3.894	0.471	2.180	1.710
Br	11.814	3.363	7.588	4.225
I	10.451	3.059	6.755	3.696

Although geometric mean equation and Equation 13 presented by Islam and Ghosh does not contain any statement that gives the relation with the charge of nucleophilicity and electrophilicity, electrophilicity and nucleophilicity values of charged molecules can be determined with the help of Equation 10. In Table 3, the calculated chemical hardness, electronegativity, electrophilicity and nucleophilicity values for the some functional groups are provided. Electrophilicity is a measure of interest that exhibits to electrons of chemical species and it is anticipated that electrophilicity increases as positive charge increases. On the other hand, it is predicted that the nucleophilicity that is a measure of tendency of electron giving of chemical species decreases as the charge increases. In our past publications, we showed that the chemical hardness and electronegativity of any functional group increases as linear as its charge increases. However, it is understood from Figure 1 that denotes the change with the charge of nucleophilicities and electrophilicities of some functional groups, there is a parabolic correlation between charge with electrophilicity and nucleophilicity.

The electrophilicity of any functional groups increases as parabolic with the increasing of its charge. On the contrary, the nucleophilicity of any functional group decreases as parabolic with the decreasing of its charge.

Table 2. Comparison of nucleophilicity and electrophilicity values that was calculated via various methods.

	Electrophilicities (eV)			Nucleophilicities (eV)		
Molecule	**Parr**	**Chattaraj**	**Present work**	**Parr**	**Chattaraj**	**Present work**
I_2	2.60	3.088	3.104	0.385	0.323	0.322
BrI	2.629	3.245	3.240	0.381	0.308	0.308
S_2	1.98	2.334	2.336	0.505	0.428	0.428
Br_2	2.68	3.409	3.406	0.373	0.293	0.294
Cl_2	3.31	3.677	3.681	0.302	0.271	0.272
P_2	1.56	1.619	1.619	0.641	0.617	0.617
SO	1.78	2.336	2.315	0.562	0.428	0.432
CH	1.83	1.984	1.974	0.546	0.504	0.506
O_2	1.88	2.338	2.338	0.532	0.427	0.427
OH	2.481	2.165	2.172	0.403	0.462	0.460
NH	1.786	1.909	1.921	0.559	0.524	0.521
F_2	3.493	3.864	3.864	0.286	0.258	0.258
CS_2	1.64	2.203	2.195	0.609	0.454	0.456
COS	1.58	2.204	1.984	0.632	0.454	0.504
SO_2	2.01	2.337	2.278	0.497	0.428	0.439
O_3	2.419	2.338	2.338	0.413	0.428	0.428
NH_2	1.71	1.940	1.948	0.585	0.515	0.514
N_2O	1.70	1.977	2.003	0.588	0.505	0.499
$POCl_3$	2.048	2.851	2.910	0.488	0.350	0.344
SO_3	2.168	2.337	2.289	0.461	0.428	0.437
C_2H_2	1.62	1.984	1.961	0.617	0.504	0.509
CH_3	1.26	1.994	1.972	0.793	0.502	0.507
HNO_3	1.72	2.156	2.163	0.581	0.464	0.463
$C_6H_4O_2$	2.147	2.035	2.015	0.466	0.491	0.496
LiF	2.41	2.014	3.12	0.414	0.496	0.321
LiCl	2.08	1.905	2.75	0.480	0.525	0.364
LiBr	1.77	1.878	2.51	0.564	0.532	0.398
NaF	2.26	2.014	3.12	0.442	0.496	0.321
NaCl	2.78	1.905	2.75	0.359	0.525	0.360
NaBr	1.95	1.850	2.51	0.513	0.541	0.398
KF	2.06	1.850	3.19	0.485	0.541	0.314
KCl	2.28	1.769	2.82	0.438	0.565	0.355
KBr	2.00	1.714	2.58	0.500	0.584	0.386

Table 3. The nucleophilicity and electrophilicity (eV) values calculated for charged molecules.

Molecule	Charge	Chemical Hardness	Electronegativity	Electrophilicity	Nucleophilicity
CH_3	-1	10.33	3.91	0.740	1.352
	0	12.07	6.90	1.973	0.507
	+1	13.80	9.91	3.558	0.281
NH_2	-1	10.97	2.77	0.349	2.865
	0	13.38	7.21	1.942	0.515
	+1	15.78	11.66	4.307	0.232
NO_2	-1	10.45	3.19	0.486	2.057
	0	12.94	7.47	2.156	0.464
	+1	15.42	11.75	4.476	0.224
NO_3	-1	10.88	4.32	0.857	1.167
	0	12.75	7.49	2.200	0.455
	+1	14.62	10.65	3.879	0.258
OH	-1	8.84	1.12	0.071	14.08
	0	12.50	7.37	2.173	0.460
	+1	16.20	13.62	5.725	0.175
CN	-1	8.69	0.78	0.035	28.57
	0	12.06	6.69	1.856	0.538
	+1	15.43	12.61	5.153	0.194
SCN	-1	8.54	3.04	0.541	1.848
	0	10.73	6.49	1.963	0.509
	+1	12.91	9.94	3.827	0.262
COOH	-1	9.94	4.16	0.870	1.149
	0	11.71	7.08	2.140	0.467
	+1	13.48	10.00	3.709	0.269
SO_3H	-1	9.97	4.87	1.189	0.841
	0	11.40	7.12	2.223	0.449
	+1	12.84	9.36	3.411	0.293
SO_2Cl	-1	8.57	4.79	1.339	0.746
	0	10.39	7.33	2.586	0.387
	+1	12.23	9.89	3.999	0.250

Although geometric mean equation and Equation 13 presented by Islam and Ghosh does not contain any statement that gives the relation with the charge of nucleophilicity and electrophilicity, electrophilicity and nucleophilicity values of charged molecules can be determined with the help of Equation 10. In Table 3, the calculated chemical hardness, electronegativity, electrophilicity and nucleophilicity values for the some functional groups are provided. Electrophilicity is a measure of interest that exhibits to electrons of chemical species and it is anticipated that electrophilicity increases as positive charge increases.

On the other hand, it is predicted that the nucleophilicity that is a measure of tendency of electron giving of chemical species decreases as the charge increases. In our past publications, we showed that the chemical hardness and electronegativity of any functional group increases as linear as its charge increases. However, it is understood from Figure 1 that denotes the change with the charge of nucleophilicities and electrophilicities of some functional groups, there is a parabolic correlation between charge with electrophilicity and nucleophilicity. The electrophilicity of any functional groups increases as parabolic with the increasing of its charge. On the contrary, the nucleophilicity of any functional group decreases as parabolic with the decreasing of its charge.

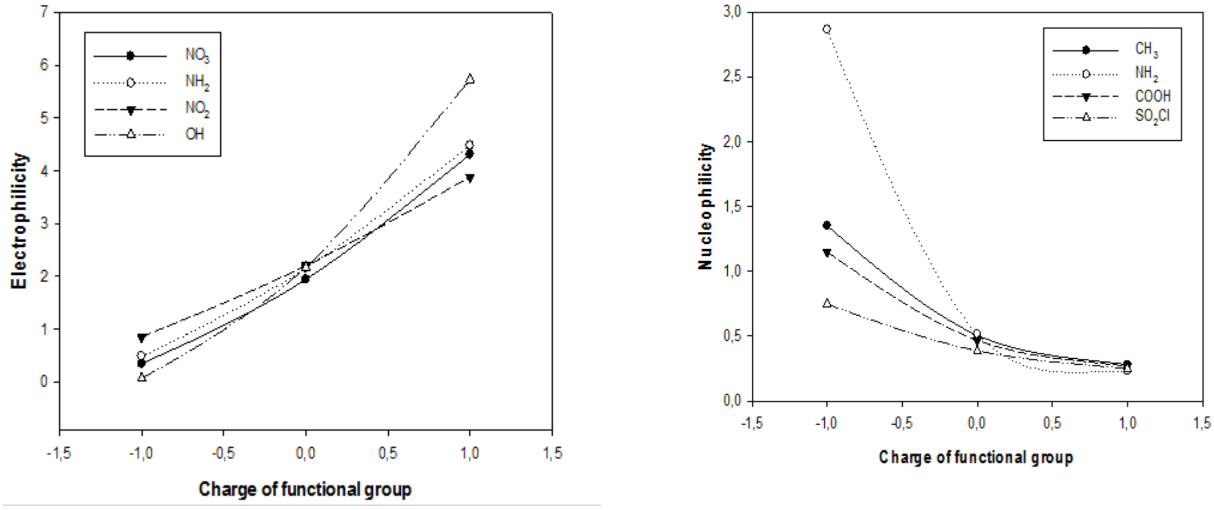

Figure 1. The change with the charge of electrophilicity and nucleophilicity for some selected functional groups.

Consequently, it can be said that nucleophilicity and electrophilicity values of both neutral molecules or functional groups and charged molecules or functional groups can be calculated considering the ionization energy and electron affinity values of constituent atoms. In addition to this, the results of present method are compatible with geometric mean method of Chattaraj. We proposed that Chattaraj's equalization principle and geometric mean equation related to electrophilicity concept are convenient for the studies regarding small molecules. Lastly, it is required to mention from the limitation of proposed methodology. It should be noted that the proposed new useful method is more reliable for small molecules such as in Table 2. In the calculation regarding big molecules, the method proposed can give incorrect results.

Theoretical Model

As mentioned above, the electrophilic power of a chemical species is associated with electronegativity and chemical hardness of that species. It is important to note that chemical hardness and electronegativity values for all molecules considered in this study have been calculated via Eq. 9 and Eq. 8, respectively. To determine the electrophilicity values of molecules and functional groups, Parr's formula (Equation 6) has been considered.

To calculate the electrophilicity of any molecule, with the help of Parr's electrophilicity index and equations derived by us, we proposed the following equation:

$$\omega_M = \frac{{\chi_M}^2}{2\eta_M} = \frac{\left[\sum_{i=1}^{N}\left(\frac{I_i + A_i}{I_i - A_i}\right) + 2q_M \Big/ \sum_{i=1}^{N}\left(\frac{2}{I_i - A_i}\right)\right]^2}{2\left[\left(2\sum_{i=1}^{N}\frac{I_i - A_i}{I_i + A_i}\right) + q_M \Big/ \sum_{i=1}^{N}\frac{1}{I_i - A_i}\right]} \qquad \textbf{(10)}$$

It should be noted that the charge effect on electrophilicity and nucleophilicity can be analyzed through Eq. 10. As for neutral species q_M=0, the Equation 10 can be simplified for the calculation of electrophilicities of neutral molecules as the following:

$$\omega_M = \frac{1}{8}\frac{\sum_{i=1}^{N}(I_i + A_i)^2}{\sum_{i=1}^{N}(I_i - A_i)} \qquad \textbf{(11)}$$

The Equation 11 above looks similar to Equation 6. But Eq. 6 provides the calculation of molecular electrophilicities from ionization energy and electron affinities of molecules. On the other hand, the Eq. 11 provides the computation of molecular electrophilicity using the ionization energy and electron affinities of constituent atoms forming the molecule. So the scope of application of Equation 11 is wider than equation 6. In addition, the inverse of Eq. 11 can be used to calculate the nucleophilicities of neutral molecules because electrophilicity and nucleophilicity are physically multiplicative inverse of each other.

In the literature, for calculation of electrophilicities of molecules, a few methods different from Parr's electrophilicity index are available. One of them was proposed by Chattaraj and co-workers. According to Chattaraj, the electrophilicity of a molecule may be expressed as geometric mean of electrophilicities of constituent atoms in the molecule and can be calculated via following equation [30]:

$$\omega_{\mathrm{M}} = \left(\prod_{i=1}^{\mathrm{N}}\omega_i\right)^{1/\mathrm{N}} \qquad \textbf{(12)}$$

In the Equation 12, ω_i (i= 1, 2, 3… N) refers to isolated atom electrophilicity value and N is number of atoms in the molecule.

Another method for determination of electrophilicities of molecules was proposed by N. Islam and D. C. Ghosh [15]. According to their study, electrophilicity index (ωM) in electron volts unit of molecules can be calculated via following equation:

$$\omega_M = \frac{K.7{,}2(n+1)}{\sum_i r_i} \qquad \textbf{(12)}$$

In this equation, n stands for number of atoms connected to central atom in molecule, ri is atomic radius in angstrom (Å) unit and standardized value of K is 0.382516 for diatomic molecules and is 0.712 for polyatomic molecules. In this stage, we want to state that all methods mentioned in the study can be used for the calculation for both electrophilicities and nucleophilicities of molecules.

CONCLUSION

In the present study, a new method based on molecular hardness and molecular electronegativity to calculate the nucleophilicities and electrophilicities of molecules is presented. The results obtained in the study support the electrophilicity equalization principle. Thus the new theoretical model presented in this work for the calculation of molecular reactivity indices like electrophilicity and nucleophilicity is logical and reliable.

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MOLEKÜLER ELEKTROFİLLİK VE NÜKLEOFİLLİĞİN TAHMİN EDİLMESİ İÇİN FAYDALI BİR YÖNTEM

Öz: Bu çalışmada, tarafımızdan son yıllarda türetilen grup elektronegativite ve moleküler sertlik eşitliklerine dayalı moleküler elektrofillik ve moleküler nükleofillik değerlerinin hesaplanması için yeni bir teorik model sunulmuştur. Bunun dışında, mevcut modelin geçerlilik testi 33 molekül ile yapılmış, bazı iyi bilinen teorik yöntemler ve onların deneysel kısımları kullanılarak bulunan elektrofillik ve nükleofillik verileri bizim çalışmamızda üretilenlerle karşılaştırılmıştır. Karşılaştırmalı çalışma teori ve deney arasında mükemmel bir uyum göstermektedir. Bu sebeple, bu çalışmada gösterilen yeni teorik model, elektrofillik ve nükleofillik gibi moleküler reaktivite indislerinin hesaplanması için mantıksal ve güvenilir sonuçlar vermektedir.

Anahtar kelimeler: Elektronegatiflik, Sertlik, Elektrofillik, Nükleofillik, DFT.

Gönderilme tarihi: 29 Şubat 2016, **Düzenleme tarihi:** 29 Mart 2016, **Kabul tarihi:** 12 Nisan 2016.