match no. 28 pp. 249-259 1992

RATIONALIZATION OF h PARAMETER OF HMO THEORY BY MOLECULAR CONNECTIVITY

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(received: April 1991)

ABSTRACT

The semi-empirical h parameter in the HMO theory is defined in terms of molecular connectivity as $h(\delta)$. The values of h and $h(\delta)$ have been tested for 21 heteroaromatic systems by determining their ionization potential(IP), electron affinity(EA), bond orders and bond lengths. The correlation coefficient between the calculated values and literature values for IP and EA obtained by using h and k parameter and by using $h(\delta)$ and k parameter is almost same.

INTRODUCTION

The quantum mechanical description of any molecule provides information about the electron distribution probabilities and energetics. The Hückel molecular orbital (HMO) method[1] is a primitive quantum mechanical method for pi-electron systems. This method is still the simplest and is as good as other refined methods, particularly for many electron systems.

However, a large amount of very useful physical and chemical information can still be obtained from topological features of the molecule, that is, branching, cyclization, unsaturation and heteroatoms position. Molecular connectivity is a method for developing correlations based on a formal development of molecular topology, using elementary aspects of graph theory[2-5].

Thus the molecular connectivity indices can be used to rationalize the parameters of Hűckel's theory, so that it can be successfully applied in drug research and other fields[6,7]. In this paper we have determined the ionization potential(IP), electron affinity(EA), bond orders and bond lengths of 21 heteroaromatic systems using (i) the semi-empirical values of h and k and (ii) the rationalized values of h by molecular connectivity $h(\delta)$ and semi-empirical values of k.

THEORY

In HMO method, the coulomb integral(α_x) for an atom x, and the resonance integral(β_{cx}) for the bond between carbon and x atom are given by equations (1) and (2)

$$\alpha_x = \alpha + h_x\beta \qquad (1)$$

$$\beta_{cx} = k_{cx}\beta \quad , \qquad (2)$$

where α and β are the standard coulomb and resonance integral for carbon atom and carbon-carbon bond respectively, h_x and k_{cx} are the semi-empirical parameters under discussion. Here h_x is zero for carbon atom and k_{cx} is unity if x is also a carbon atom. The values of h_x and k_{cx} were obtained empirically; therefore their values for various heteroatoms varies in the literature.These parameters can be rationalized by making use of molecular connectivity indices. The semi-empirical value of h_x is based on the assumption that α_x is proportional to the electronegativity[8] and that h_x is proportional to the electronegativity difference[9].

The proportionality constant is taken as unity, therefore

$$h_x = \chi_x - \chi_c \quad , \tag{3}$$

where χ_x and χ_c represents the electronegativities of the heteroatom x and carbon respectively. Based on this concept a uniform method can be found to evaluate h by the use of molecular connectivity index($^1\chi$) and the first order valence molecular connectivity index($^1\chi^v$). Both are calculated from the hydrogen suppressed graph of the molecule and are defined as,

$$^1\chi = \sum(\delta_i\delta_j)^{-1/2} = \sum c_k \tag{4}$$

$$^1\chi^v = \sum(\delta_i^v\delta_j^v)^{-1/2} = \sum c_k \quad , \tag{5}$$

where the sum is over all connections or edges in the hydrogen suppressed graph, and δ_i is the number of atoms adjacent or connected to any atom in the graph, while δ_i^v for any atom i is defined as,

$$\delta_i^v = Z_i^v - h_i \quad , \tag{6}$$

where Z_i^v is the number of valence electrons of the atom i and h_i the number of hydrogens attached to atom i.

Since molecular information encoded in these values is derived from the δ values of the atoms, insight into the significance of molecular connectivity begins with analysis of the δ values, representing essentially a

count of nonhydrogen sigma-bond electrons contributed by any atom i, while δ_i^v is a more inclusive count of all valence electrons(not bonding to hydrogen), thus the relationship is[4]

$$\delta^v = \sigma + p + n - h \qquad (7a)$$

$$\delta = \sigma - h \qquad (7b)$$

$$\delta^v - \delta = p + n \qquad (7c)$$

where p is the number of p-orbital electrons and n the number of lone-pair electrons on the atom i. The δ^v and δ are counts of the electrons in sigma, pi, or lone-pair orbitals and depend on the element represented, its valence(hybrid) state and the number of bonded hydrogen atoms. The number and distribution of electrons certainly influence the electronic characteristics associated with atoms in the valence state. An obvious electronic property of a bonded atom in a molecule is electronegativity. Kier and Hall[4] found Mulliken's electronegativity to be related with $(\delta^v - \delta)$ as,

$$E = 2.05(\delta^v - \delta) + 6.99 \quad , \qquad (8)$$

$$n = 9,\ r = 0.989,\ S = 0.60,\ F = 305$$

where n is the number of data points, r is the correlation coefficient, S is the standard deviation, and F is F-ratio between the variances of calculated and observed values. This correlation is excellent with the standard deviation being less than the estimate of Hinze and Jaffe[10].The intercept is close to the electronegativity of hydrogen(7.17eV) which would have a $(\delta^v - \delta)$ value equal to zero. Since $(\delta^v - \delta) = p + n$, the electrone-

gativity of an atom in its valence state is closely related with the number of electrons in pi and lone-pair orbitals.

Equation(8) is applicable only for second row atoms. The general expression relating Mulliken electronegativities to the δ value for 19 atoms of the first, second, and third rows which are prominent in forming covalent bonds, takes the form of,

$$E = 7.99\frac{(\delta^{v}-\delta)}{N^{2}} + 7.07, \qquad (9)$$

$$n = 19, \quad r = 0.988, \quad S = 0.48, \quad F = 660$$

where N is the principal quantum number. Now based on these discussions and using Equations(3) and (9) we can define Hückel parameter h_x as

$$h_x = 7.99\left[\left(\frac{\delta^{v}-\delta}{N^{2}}\right)_x - \left(\frac{\delta^{v}-\delta}{N^{2}}\right)_c\right] , \qquad (10)$$

Equation(10) can be utilised to evaluate h to be used in HMO calculation, let us denote this value of h based on molecular connectivity consideration as $h(\delta)$.

CALCULATIONS

In Hückel theory the energy of any molecular orbital is given as

$$E = \alpha + n\beta , \qquad (11)$$

where n are the coefficients derived from the roots of the secular equation. By Koopmans's theorem;

$$IP = \alpha + n(E_{HOMO})\beta \qquad (12)$$

$$EA = \alpha + n(E_{LUMO})\beta \ . \qquad (13)$$

Now the value of α and β for both equations (12) and (13) can be separately evaluated by using some known values of ionization potential and electron affinity. With the use of IP of benzene and naphthalene as 9.38eV and 8.26eV respectively[11], and electron affinities as -0.54eV and 0.15eV respectively[12], we get

$$IP = 6.448 + 2.932n(E_{HOMO}) \qquad (14)$$

$$EA = 1.266 + 1.806n(E_{LUMO}) \ . \qquad (15)$$

From either approach, the HMO theory gives $n(E_{HOMO})$ of benzene 1.000, $n(E_{HOMO})$ of naphthalene 0.618, $n(E_{LUMO})$ of benzene -1.000, and $n(E_{LUMO})$ of napthalene -0.618. Using $h(\delta)$ and k as well as the semi-empirical values of h and k for various heteroatoms[Ref.11 page135], we have calculated the IP and EA from equations (14) and (15) respectively. These values are given in Table 1 alongwith the literature values.

We have also calculated the bond order (P) of all the systems by both the approaches and used the following relation for determining the value of the bond length (r)

$$r = A - B.P \ . \qquad (16)$$

Dewar and Gleicher's[14] values of A and B for different type of bonds were taken. The bond orders calculated by both the methods and the corresponding values of bond length and their literature value for a few systems are given in Table 2.

TABLE 1

CALCULATED ELECTRON AFFINITIES & IONIZATION POTENTIALS OF SOME HETERO-AROMATIC SYSTEMS*

Sl. No.	Molecule	E_{LUMO}		Electron Affinity (eV)			E_{HOMO}		Ionization Potential (eV)		
		a	b	Obsd	Calc[a]	Calc[b]	a	b	Obsd	Calc[a]	Calc[b]
1.	Aniline	-0.129	0.216		1.03	1.66	0.745	0.626	7.69[15]	8.63	8.28
2.	Phenol	0.265	0.139	1.53[13]	1.74	1.52	0.826	0.959	8.50[16]	8.87	9.26
3.	Pyridine	0.039	-0.138	1.10[13]	1.34	1.02	0.998	1.001	9.28[17]	9.37	9.38
4.	p-Quinone	0.255	0.401	1.83[20]	1.73	1.99	0.817	0.765	8.63[20]	8.84	8.69
5.	o-Diamino-benzene	-0.181	0.024	1.12[13]	0.94	1.31	0.604	0.470	7.61[19]	8.22	7.83
6.	m-Diamino-benzene	-0.105	0.071		1.08	1.39	0.682	0.572	7.35[15]	8.45	8.12
7.	p-Diamino-benzene	-0.058	0.133		1.16	1.51	0.576	0.455	7.25[19]	8.14	7.78
8.	Catechol	0.057	0.052	1.51[13]	1.37	1.36	0.953	0.752		9.24	8.65
9.	Resorcinol	0.013	0.067	1.36[13]	1.29	1.39	1.103	0.719	8.13[19]	9.68	8.56
10.	Hydro-quinone	0.004	0.117	1.31[13]	1.27	1.48	0.862	0.673	8.32[13]	8.98	8.42
11.	p-Amino-phenol.	0.213	0.316		1.65	1.84	0.621	0.731	8.51[19]	8.27	8.59
12.	3,4-Diami-nophenol	0.159	0.241	1.74[13]	1.55	1.70	0.713	0.632	8.35[19]	8.54	8.30
13.	Pyridazine	-0.089	0.096	1.54[13]	1.10	1.44	1.106	0.764	8.91[18]	9.69	8.69
14.	Pyrimidine	-0.101	0.105	1.36[13]	1.08	1.46	1.077	1.340	9.47[17]	9.60	10.38
15.	Pyrazine	-0.128	0.132	1.12[13]	1.04	1.50	0.998	1.002	9.36[18]	9.37	9.38

TABLE 1 (Contd.)

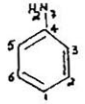
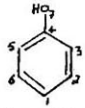
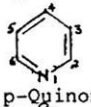
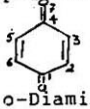
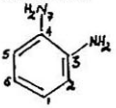
Sl. No.	Molecule	E_{LUMO}		Electron Affinity (eV)			E_{HOMO}		Ionization Potential (eV)		
		a	b	Obsd	Calc[a]	Calc[b]	a	b	Obsd	Calc[a]	Calc[b]
16.	2-Amino-pyridine	0.126	0.157		1.49	1.55	0.812	0.792	8.51[19]	8.83	8.77
17.	2-Hydroxy-pyridine	0.136	0.218		1.51	1.66	0.672	0.716	8.54[19]	8.42	8.55
18.	Fluoro-quinone	0.241	0.490	1.92[20]	1.70	2.15	1.021	0.962		9.44	9.27
19.	Chloro-quinone	0.250	0.569	2.05[20]	1.72	2.29	1.031	0.897	9.21[13]	9.47	9.08
20.	Bromo-quinone	0.247	0.230	2.01[20]	1.71	1.68	0.981	0.991		9.32	9.35
21.	Iodo-quinone	0.152	0.113	2.00[20]	1.54	1.47	0.965	0.882		9.28	9.03

a - Using empirical h from Huckel molecular orbital theory.

b - Using h(δ) from molecular connectivity.

* - Figures in parenthesis indicate the reference number.

TABLE 2
CALCULATED AND OBSERVED BOND LENGTHS AND BOND ORDERS OF SOME HETERO-AROMATIC SYSTEMS

Compound	Bond	Bond Order		Bond Length		
		a	b	Obsd[14,21]	Calc[a]	Calc[b]
Aniline	1-2	0.663	0.662	1.382	1.397	1.397
	2-3	0.673	0.674	1.391	1.396	1.395
	3-4	0.637	0.634	1.397	1.402	1.402
	4-7	0.291	0.311	1.340	1.394	1.390
Phenol	1-2	0.664	0.666	1.367	1.397	1.397
	2-3	0.671	0.667	1.392	1.396	1.397
	3-4	0.645	0.662	1.401	1.400	1.397
	4-7	0.248	0.118	1.348	1.354	1.376
Pyridine	1-2	0.654	0.275	1.340	1.331	1.397
	2-3	0.670	0.759	1.400	1.396	1.380
	3-4	0.665	0.602	1.390	1.397	1.408
p-Quinone	1-2	0.661	0.355	1.369	1.398	1.452
	2-3	0.661	0.537	1.371	1.398	1.419
	4-7	0.263	0.328	1.338	1.352	1.341
o-Diamino-benzene	1-2	0.663	0.662	1.390	1.397	1.397
	2-3	0.649	0.647	1.382	1.400	1.400
	3-4	0.612	0.605	1.400	1.406	1.408
	1-6	0.664	0.662	1.390	1.397	1.397
	4-7	0.277	0.296	1.385	1.396	1.393

[a] Hückels molecular orbital theory

[b] Molecular connectivity.

In Table 3 the values of correlation coefficient between our calculated values and available literature values is given.

Table 3: Correlation coefficient between calculated values and literature values for IP and EA

Property	correlation coefficient using h and k	correlation coefficient using $h(\delta)$ and k
IP	.838	.878
EA	.827	.815

We find that for IP the values obtained with the use of $h(\delta)$ and k are in better agreement with literature values than those obtained with the use of empirical h and k. In the case of EA the trend is reverse. But correlation coefficient by either of the method is very close to each other for both the properties.

By further refinement in $h(\delta)$ and finding an expression for $k(\delta)$ also the investigation can be made for finding the extent to which molecular connectivity can be utilised to simplify the HMO method. Because calculation of $h(\delta)$ and $k(\delta)$ is much easier than calculation of semi-empirical h and k.

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