International Journal of Chemical Science
Online ISSN: 2523-2843, Print ISSN: 2523-6075; Impact Factor: RJIF 5.22
Received: 25-05-2019; Accepted: 27-06-2019
www.chemicaljournals.com
Volume 3; Issue 4; July 2019; Page No. 97-100

Study of Reactivity Descriptors of Cinnoline, Quinoxaline and Quinazoline with the help of density functional theory

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Abstract
DFT has been used as an important quantum mechanical tool for calculating ground state properties of interaction of many electron system. Fukui function, density distribution function and softness parameters of atom for the compounds Cinnoline, Quinoxaline and Quinazoline are calculated with the help of DFT which provided a valuable information about the activity of the compounds.

Keywords: DFT, Fukui function, softness parameter

Introduction

A significant attempt for the calculation of the softness values of a number of acid and base ions was made by Klopman. His calculations were based upon the perturbtion theory of charge and frontier controlled reactions [1]. The charge controlled reactions were used to explain the ionic interactions and frontier controlled reactions to explain the covalent interactions. Klopman equation was modified by Singh et.al. And its applications was widely explored by them [2, 3]. Parr *et al*. published a paper on the application of density functional theory to chemical systems which gave an advance treatment to the concept of reactivity [4]. DFT is a quantum mechanical method which focuses on the one-electron density function Ψ instead of on wave functions [5]. Misono *et al*. proposed the following equation for determining the values of hardness and softness [6].

$$y = 10(I_n/I_{n+1})(r_i/\sqrt{n}) \quad (1)$$

$$(10x)^{\frac{1}{2}} = X_i = X_m^0 + (\Sigma I_n)^{\frac{1}{2}} \quad (2)$$

Where r_i = ionic radius of metal ion and n is the formal charge. The dual parameter scale based on x and y is as follows – x is closely related to hardness or electronegativity and y to softness. With these parameter the log of stability constants of metal ion complexes is expressed well for hard-hard complexes and to a lesser extent for soft-soft complexes by the eqation:

$$\log k = \alpha X + \beta Y + Y \quad (3)$$

Where α and β are the basicity parameters. To identify difficult problems recent studies have introduced data modelability [7-9].

Methodology

DFT has been emerged as an important method for calculating the ground state properties of interacting many electron systems such as atoms molecules or solids [10-12]. Parr introduced a quantity μ, known as electronic chemical potential, for every chemical system [13]. A chemical system is an atom, molecule ion or radical or several such units in a state of interaction. According to Parr μ must be constant every where in such a system. μ is given by the relationship- $\mu = -\left(\frac{\delta E}{\delta N}\right)_v = \left(\frac{I+A}{2}\right) = \chi_M$. It is important that χ_M or just χ is entirely different from Pauling's original meaning of electronegativity, which was a property of an atom in a molecule.

In DFT the ground state energy of an atom or a molecule is written in terms of electron density $\rho_{(r)}$, and the external potential $V_{(r)}$ in the form [14]

$$E(\rho) = F(\rho) + \int dr\, \rho_{(r)}\, V_{(r)} \quad (4)$$

Where $F(\rho) = T(\rho) + Vee(\rho), T(\rho)$ is the electronic energy function. The operational definition of global hardness and global softness are obtained by the finite difference approximation of equation [15].

$$\eta = \frac{1}{2}(I - E) \quad (5)$$

$$S = \frac{1}{(I-E)} \quad (6)$$

The values of ionization potential (IP) electron affinity (EA), charge (q) and fukui function (f) at the two ring

nitrogs, N_1 and N_2 have been calculated with the help of DFT and presented in table 1 and 2.

Table 1: Various parameters at N_1

Parameter	Cinnoline	Quinoxaline	Quinazoline
Ionisation potential	14.7374	14.84155	16.22372
Electron Affinity	-6.090637	-4.358453	-5.698025
Charge	-0.01485	-0.022437	-0.122032
Atom electron density	1.6381	1.6038	162662
Electronegativity	4.32338	5.24155	5.26285
Radius of atom	0.74	0.74	0.74
Fukui function	0.2340143	0.2291143	0.2323743
Density distribution fn	11.27687	11.04074	11.19784
Softness of atom $E_m^{\dagger}$	3.146653	5.263387	5.202122

Table 2: Various parameters at N_2

Parameter	Cinnoline	Quinoxaline	Quinazoline
Ionisation potential	14.39768	14.84087	15.798401
Electron Affinity	-5.750915	-4.357766	-5.268315
Charge	-0.009977	-022386	-.121632
Atom electron density	1.63343	1.60385	1.61562
Electronegativity	4.32338	5.24155	5.26285
Radius of atom	0.74	0.74	0.74
Fukui function	0.2333472	0.2291214	0.2308029
Density distribution fn	11.24472	11.04109	11.12211
Softness of atom $E_m^{\dagger}$	3.173428	5.361873	5.200671

The internal angle between the orbitals containing electron pairs in the valency shell of the central atom in a molecule is known as bond angle. It gives an information about the distribution of the different orbitals in three dimensional space around the central atom. The bond angles among various atoms of Cinnoline, Quinoxaline and Quinazoline are given in table 3 and 4.

Table 3: Bond angles among various atoms of benzodiazine i.e. Cinnoline, Quinoxaline and Quinazoline

Type of Bond	Cinnoline	Quinoxaline	Quinazoline
C_1=C_2-C_3	120.727728	120.999570	120.62824
C_2-C_3=C_4	120.830333	121.003416	120.941828
C_3=C_4-C_5	119.060396	119.098484	119.131617
C_4-C_5=C_6	120.325402	119.899650	120.016285
C_5-C_6=C_7	117.553250	119.921742 C_5=C_6-N_7	117.49278
C_6-C_7=C_8	118.201713	118.778926 C_6-N_7=C_8	120.967273 C_6-C_7=N_8
C_7=C_8-N_9	121.154079	121.297803 N_7-C_8-C_9	119.4301 C_7=N_8-C_9
C_8-N_9-N_{10}	122.017438	121.339720 C_8-C_9=N_{10}	123.155831 N_8-C_9-N_{10}
C_2=C_1-H_{11}	121.126616	121.138743	121.143596
C_1=C_2-H_{12}	120.19336	120.068603	120.276866
C_2-C_3-H_{13}	119.013131	118.909175	118.977691
C_3=C_4-H_{14}	121.100319	121.128368	121.093601
C_6-C_7-H_{15}	119.796556	121.454626 C_8-C_9-H_{17}	121.655187 C_6-C_7-H_{18}
C_7=C_8-H_{16}	124.147814	117.195858 N_7=C_8-H_{16}	117.650718 N_8-C_9-H_{17}
C_5-N_{10}-N_9	118.432721	121.227512 C_5-N_{10}-C_9	119.382421 C_5-N_{10}-C_9

Table 4: Sequence of Bond angle in the three isomeric benzodiazines

Compound	Sequence of Bond angles			
Cinnoline	C_7=C_8-H_{16}	> C_8-N_9-N_{10}	> C_7=C_8-N_9	>
	124.147814	122.017438	121.154079	
	C_2=C_1-H_{11}	> C_3-C_4-N_{14}	> C_2-C_3=C_4	>
	121.126616	121.100319	120.83033	
	C_1=C_2-C_3	> C_4-C_5=C_6	> C_1=C_2-H_{12}	>
	120.727728	120.325402	120.19336	

	C_6-C_7-H_{15}	> C_3=C_4-C_5	> C_2-C_3-H_{13}	>
	119.796556	119.060396	119.013131	
	C_5-N_{10}-N_9	C_6-C_7=C_8	> C_5=C_6-C_7	>
	118.432721	118.201713	117.55325	
Quinoxaline	C_7=C_8-H_{17}	> C_8-N_9-N_{10}	> N_7-C_8-C_9	>
	121.4546	121.3397	121.2978	
	C_9=N_{10}-C_9	C_2-C_1-H_{11}	> C_3-C_4=H_{14}	>
	121.227512	121.1387	121.1284	
	C_2-C_3=C_4	C_1=C_2-C_3	> C_1=C_2-H_{12}	>
	121.0034	120.9996	120.0686	
	C_5-C_6-N_9	C_4-C_5-C_6	> C_3-C_4-C_5	>
	119.9217	119.8997	119.0985	
	C_2-C_3=H_{13}	C_6-N_7=C_8	> N_7=C_8-H_{16}	>
	118.9092	118.7789	117.1959	
Quinazoline	N_8-C_9=N_{10}	> C_6-N_7=H_{18}	> C_2=C_1-H_{11}	>
	123.1558	121.6552	121.1436	
	C_3-C_4=H_{14}	C_6-N_7=N_8	> C_2-C_3=C_4	>
	121.0936	120.9673	120.9418	
	C_1-C_2=C_3	C_1-C_2-H_{12}	> C_4-C_5=C_6	>
	120.6282	120.2769	120.0163	
	C_7=N_8-C_9	> C_5-N_{10}-C_9	> C_3=C_4-C_5	>
	119.4301	119.382421	119.1316	
	C_2-C_3-H_{13}	N_8=C_9-H_{17}	> C_5-C_6=C_7	
	118.9777	117.6507	117.4928	

Angle of twist [16] for the three compounds is calculated in Table 5.

Table 5: Twist angle among various atoms of benzodiazines

Type of Bond	Cinnoline	Quinoxaline	Quinazoline
C_1=C_2-C_3=C_4	0.032272	0.014820	0.06418
C_2-C_3=C_4-C_5	0.012183	0.031052	0.017035
C_3=C_4-C_5=C_6	0.029823	0.001301	0.039254
C_4-C_5=C_6-C_7	179.963365	179.9494 C_4-C_5=C_6-N_7	179.94164
C_5=C_6-C_7=C_8	0.011461	0.007252 C_5=C_6-N_7=C_8	0.024419 C_5=C_6-C_7=N_8
C_6-C_7=C_8-N_9	0.003190	0.024215 C_6-N_7=C_8-C_9	0.014804 C_6-C_7=N_8-C_9
C_7=C_8-N_9-N_{10}	0.005773	0.02444 N_7-C_8-C_9-N_{10}	0.003563 C_7-N_8-C_9-N_{10}
C_3-C_2=C_1-H_{11}	179.9922	179.96849 C_3-C_2=C_1-H_{11}	179.9614
C_3-C_1=C_2-H_{12}	179.9896	179.97185	179.9727
C_4-C_2-C_3-H_{13}	179.9943	179.99450	179.98582
C_5-C_3-C_4-H_{14}	179.9969	179.9959	179.98235
C_8-C_6-C_7-H_{15}	179.9946	179.9966 C_9-N_7-C_8-H_{16}	179.9894 N_{10}-N_8-C_9-H_{17}
N_9-C_7-C_8-H_{16}	179.9944	179.97384 N_{10}-C_8-C_9-H_{17}	179.9912 N_8-N_6-C_7-H_{18}

Result and Discussion

Table 1 & 2 clearly shows that $E_m^{\neq}$ values for both the ring nitrogens (N_1 & N_2) in the three isomeric benzodiazenes have the following sequence,

Quinoxaline	>	Quinazoline	>	Cinnoline
5.263387		5.202122		3.146653 (N_1)
5.361873		5.200671		3.173428 (N_2)

The sequence of softness values $E_m^{\neq}$ for the three isomeric benzodiazines clearly shows that the basic softness $E_m^{\neq}$ i.e. tendency to donate electrons is maximum in Quinoxaline and minimum in Cinnoline. In case of Quinoxaline the two ring nitrogen are at para position i.e. at maximum distance to each other therefore there is no chance for steric hindrance in between them and therefore the lone pair of electrons available on both the ring nitrogens are completely free for donation which gives the highest basic softness value. In case of quinzoline the two ring nitrogens are at meta position to each other i.e. in this case although they are far apart enough but there will be some steric hindrance between them and the donation of the lone pair of electrons is somewhat difficult in comparison to the case when they are at para position. But since in this case the distance between the two ring nitrogen is enough therefore $E_m^{\neq}$ values of Quinoxaline and Quinazoline are almost same. In case of cinnoline the two ring nitrogen are at ortho-position to each other so electrons available at both the ring nitrogens feel a strong steric hindrance which makes the

donation of electrons difficult giving the minimum value of $E_m^{\neq}$ for cinnoline.

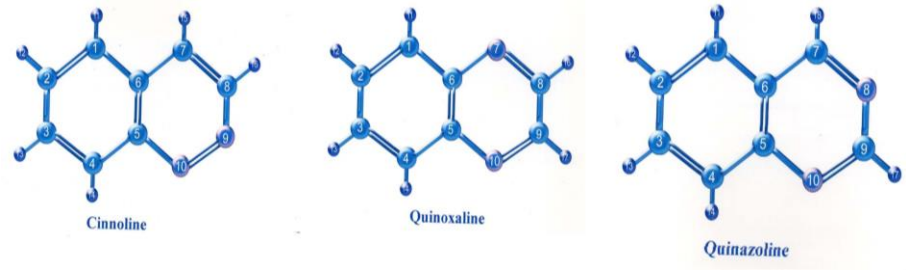

Fig 1

Conclusions

The order of bond angle in the three isomeric benzodiazines reveals the fact that angle $C_5 - N_{10} - C_9$ is highest in Quinoxaline (121.227) and lowest in Cinnoline (118.432). Thus on the basis of steric hindrance Quinoxaline should be most reactive and cinnoline should be least reactive. Depending upon the observation of the $E_m^{\neq}$ values cinnoline has least tendency of coordination and the rest two have nearly same tendency of coordination. Angle of twist only gives an idea of the comfortness of molecular structure. So by applying DFT to larger molecules having many electrons system we can predict their comparative activity for further reaction.

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