



Estd. 2005

JOURNAL OF ULTRA CHEMISTRY

An International Open Free Access Peer Reviewed Research Journal of Chemical Sciences and Chemical Engineering

website:- www.journalofchemistry.org

Calculation of Angle of Twist, Eigen values and Atomic Orbital Election Population in 2, 3 & 4 Amido Pyrans by DFT method

M.B. KALHANS

P.G. Department of Chemistry Bareilly College, Bareilly, (U.P.) 243005 (India)

Corresponding Author E-mail : drmbkalthans@gmail.com<http://dx.doi.org/10.22147/juc/150401>

Acceptance Date 01st August, 2019,

Online Publication Date 3rd August, 2019

Abstract

Density functional theory (DFT) emerged as an important tool in quantum chemistry calculation. Parr introduced a term electronic chemical potential for every chemical entity or system which was given by

$\mu = \left(\frac{\partial E}{\partial N} \right)_v$. Some important molecular parameters viz angle of twist, eigen values and AOEP were calculated

in Pyran and its derivatives which are helpful in predicting the coordination capacity of the said compounds. Since the energies of HOMO and LUMO are popular quantum mechanical descriptors therefore by comparing the energies of HOMO and LUMO in these compounds the ability of better coordination can be predicted.

Keywords : DFT, electronic chemical potential, Eigen values, AOEP, coordination capacity, HOMO, LUMO.

Introduction

The concept of reactivity of acid and base got advance treatment when Parr et al; published a paper on the application of density functional theory to chemical systems.¹ Density functional theory is a quantum mechanical method which focuses on the one electron density function ρ instead of on wave functions.²

Parr showed that for every chemical system there is a quantity μ , called the electronic chemical

potential. A chemical system is an atom, molecule, ion or radical or several such units in a state of interaction.

The chemical potential must be constant every where in such as system. μ is given by the relationship

$-\mu = -\left(\frac{\partial E}{\partial N} \right)_v = \left(\frac{I+A}{2} \right) = \chi_m$. It should be

realized that χ_m or just χ is now quite different from Pauling's original meaning of electro negativity, which was a property of an atom in a molecule. χ is a property of the entire molecule, atom, ion or radical. Chemical hardness η and density functional theory was given

by Parr. Pearson and Parr defined η and gave an empirical method of evaluating it³

$$\eta = \frac{1}{2} \left(\frac{\partial \mu}{\partial N} \right)_v = \frac{1}{2} \left(\frac{\partial^2 E}{\partial N^2} \right)$$

For the two reactants A and B

$$\mu_A = \mu_A^0 + 2\eta_A \Delta N$$

$$\mu_B = \mu_B^0 + 2\eta_B \Delta N$$

$$\text{and } \Delta N = \frac{\mu_B^0 - \mu_A^0}{2(\eta_A + \eta_B)} = \frac{\chi_A^0 - \chi_B^0}{2(\eta_A + \eta_B)}$$

While χ and η are global properties of the system, the electron transfer between two molecules will still involve definite filled orbitals on the donor and definite empty orbitals on the acceptor.⁴ The most important donor orbital will usually be the highest occupied molecular orbital (HOMO) and the most important acceptor orbital will usually be the lowest unoccupied molecular orbital (LUMO). The normalized electron densities of these frontier orbitals are called Fukui functions f .

Material and Methodology :

Angle to twist is defined as the angle ω between one half plane, RSTV, and the other half plane, STV, of a molecule. Precisely, the angle of twist is angle RSX, where lines RS and SX are both perpendicular to line ST. In dealing with a molecular dihedral angle D involving four atoms ABCD and AB & CD bonds are not likely to be perpendicular to BC bond, so we have to project AB and CD into a plane perpendicular to line BC.⁵⁻⁶ The multipole model has been used to calculate the molecular electrostatic potential for MNDO like wave function and the definitions for all the multipoles for the 4s charge distribution that rise with an s-p-d basis set have been listed⁷⁻⁹. MNDO calculation of the angle of twist of Pyran and its Amido derivatives are given in the table no. 1.

The Hamiltonian from of Schrodinger wave equation is

$$H\Psi = E\Psi - (1)$$

So, a general equation can be written in the following form.

$$O\Psi = \chi\Psi - (2)$$

Eigen function is that wave function which when operated by an operator generates the same function multiplied by a constant. This constant is known as eigen value of that particular function. For a general square matrix A of order n, the corresponding equation satisfied by the eigen values is

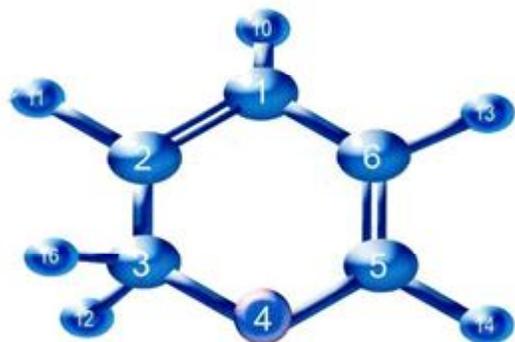
$$\det(A_{ij} - \delta_{ij}\lambda) = 0 - (3)$$

when a n^{th} order determinant is expanded it gives a polynomial in λ whose highest power is λ^n . This characteristic polynomial has n roots for λ , so a square matrix of order n has n eigen values.¹⁰ The eigen values of different molecular orbitals of the sample compounds as calculated by MNDO method are given in table 2.

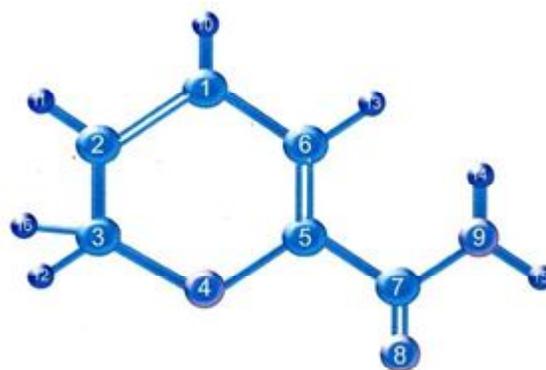
Atomic orbital electron population represents the density of electrons in various orbitals of an atom in bonded state. The contribution of electrons in each occupied molecular orbital are calculated by using the population analysis method of Mulliken.^{11,12} AOEP values of different molecular orbitals of Pyran and its derivatives are calculated by MNDO technique Table 3.

Results and Discussion

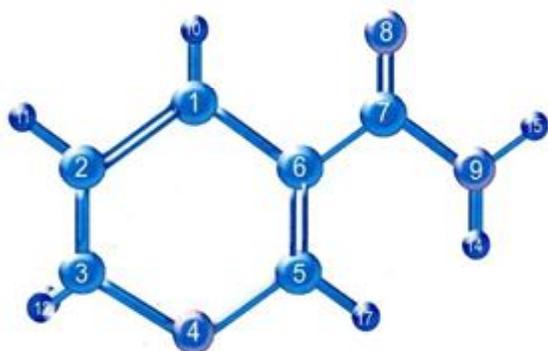
The angle between the planes passing through atoms C₁-C₂-C₃ and C₂-C₃-O₄ in Pyran 2-amide, Pyran 3-amide and Pyran 4-amide is approximately zero, i.e. the two half planes are parallel where as the angle between planes passing through atoms C₇-C₅-O₄ and C₅-O₄-C₆ in the three derivatives is 180° i.e. the two half planes are mutually linear. Also the angle between the planes passing through atoms H₁₂-C₃-C₂ and C₃-C₂-O₄ in Pyran 2-amide, atoms C₁-C₇-N₉ and C₇-N₉-H₁₃ in Pyran 4-amide, atoms C₆-O₄-C₅ and O₄-C₅-H₁₇ and in Pyran 3-amide is 120°.



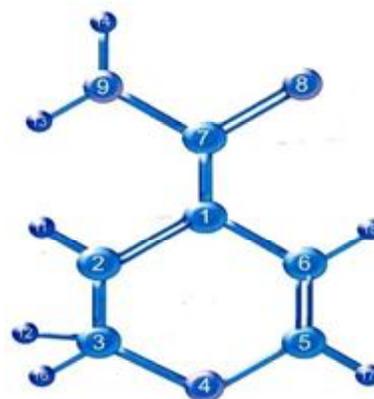
Pyran



Pyran 2-amide



Pyran 3-amide



Pyran 4- amide

Table – 1
Angle of twist among various atoms of Pyran and its Amido derivatives

Type of twist angle	Pyran	Pyran 2-amide	Pyran 3-amide	Pyran 4-amide
$C_1=C_2-C_3-C_4$	0.551385	0.052459	0.039737	.043995
$C_2=C_3-C_4-C_5$	0.382648	0.049509	0.041002	0.057183
$C_3-O_4-C_5=C_6$	0.070017	0.010957	0.039061	0.030752
$C_7-C_5-O_4=C_6$	-	179.996983	179.936897	179.983626
			($O_4-C_5-C_6-C_7$)	($C_3-C_2=C_1-C_2$)
			($C_5=C_6-C_7=O_8$)	($C_2=C_1-C_7=O_8$)

$O_6=C_7-C_5-O_4$	-	0.85373	179.898527	179.991973
			($O_8-C_6-C_7-N_9$)	($O_8-C_1-C_2-N_9$)
$N_9-C_7-C_5-O_8$	-	179.962740	179.987468	179.997240
			($C_3-C_2-C_1-H_{10}$)	($C_3-C_1-C_2-H_{11}$)
$N_{10}-C_1=C_2-C_3$	179.819483	179.978373	179.966095	179.97555
			($C_3-C_1-C_2-H_{11}$)	($O_4-C_2-C_3-H_{12}$)
$N_{11}-C_3-C_2-O_4$	179.960649	179.973738	179.956093	120.188949
			($O_4-C_2-C_3-H_{12}$)	($C_1-C_7-N_4-H_{13}$)
$N_{12}-C_3-C_2-O_4$	119.869918	120.111709	119.638111	0.001902
			($C_6-C_7-N_9-H_{13}$)	($H_{12}-C_7-N_9-H_{12}$)
$N_{13}-C_6=C_5-O_4$	179.524901	179.983234	0.053890	179.999329
			($H_{14}-C_7-N_9-H_{15}$)	($H_{11}-C_2-C_3-H_{16}$)
$N_{14}-N_9-C_7-C_5$	-	0.020596	179.978770	119.705045
			($H_{12}-C_2-C_8-H_{16}$)	($C_6-O_4-C_3-H_{12}$)
$N_{15}-N_9-C_7-C_3$	-	179.991924	120.747094	179.975048
			($C_6-O_4-C_5-H_{17}$)	($O_4-C_5-C_6-H_{18}$)
$N_{16}-C_3-C_2-H_{12}$	-	119.898783	179.964786	179.9847

Table – 2
Eigen values of different molecular orbitals or Pyran and three isomere of Amido pyran

Molecular Orbitals	Pyran	Pyran 2-amide	Pyran 3-amide	Pyran 4-admide
$C_7=O_8$ (π)	—	-40.78948	-41.08462	40.94303
$C_7=O_8$ (σ)	—	-37.15869	-37.40032	-37.52654
$C_1=C_2$ (π)	-40.32947	-33.91172	-33.59811	-33.66005
$C_1=C_2$ (σ)	-13.56268	-31.89434	-31.89885	-31.00465
$C_5=C_6$ (σ)	-30.50352	-29.09630	-29.10272	-29.85259
$C_5=C_6$ (π)	-24.63152	-24.89583	-24.9004	-25.16948
C_7-N_9 (σ)	—	-23.70734	-23.68524	-23.25748
O_4-C_5 (σ)	-22.66538	-20.39413	-20.52658	-20.49090
C_6-C_1 (π)	-18.56633	-18.96295	-18.97873	-18.94298
C_2-C_3 (π)	-17.59068	-18.17607	-18.29335	-18.23735
C_1-H_{10} (π)	-16.49420	-17.16775	-17.15281	-17.08550
				(C_7-H_{10})
C_3-O_4 (π)	-10.39740	-16.67775	-16.85387	-16.71839
C_3-H_{16} (π)	-15.08827	-16.54076	-16.35448	-16.55776
C_3-H_{12} (σ)	-14.40873	-16.03363	-15.84583	-16.19971

$C_2-H_{11} (\sigma)$	-13.0109	-5.15358	-15.34944	-14.80089
$N_9-H_{14} (\sigma)$	—	-14.58341	-14.51163	-14.67536
$N_9-H_{15} (\sigma)$	—	-14.47394	-14.49954	-14.58371
$C_6-H_{13} (\sigma)$	-12.64873	-13.66437	-13.76427	13.30649
$C_5-C_7 (\sigma)$	—	-12.76067	(C_1-H_{12}) -13.03172	(C_1-C_2) -13.07965
Non bonding	-12.37308	-12.63452	(C_2-H_7) -12.58268	(C_2-C_3) -12.90852
Non bonding	-11.53419	-11.85847	-11.63288	-11.67836
Non bonding (HOMO)	-8.66676	-10.85911	-10.75323	-10.81228
Non bonding	0.21695	-9.87272	-9.74968	-9.81875
Non bonding (HOMO)	—	-9.01278	-8.97187	-8.94906
$C_5-C_7 (\sigma^*)$	—	-0.52232	(C6-C7) -0.34726	(C_1-C_2) -0.46221
$C_6-H_{13} (\sigma^*)$ (LUMO)	1.91540	1.12574	1.00268 (C_1-H_{14})	1.09315
$N_9-H_{15} (\sigma^*)$	—	1.19.979	1.50153	1.41435
$N_9-H_{14} (\sigma^*)$	—	2.04850	1.97369	2.19792
$C_2-H_{11} (\sigma^*)$	2.57904	2.28599	2.27036	2.35448
$C_3-H_{12} (\sigma^*)$	3.05142	2.66663	2.57889	2.43966
$C_3-H_{16} (\sigma^*)$	3.18041	2.81645	2.94165	2.86005
$C_3-O_4 (\sigma^*)$	0.6703	3.23328	3.14505	3.18128
$C_1-H_{10} (\sigma^*)$	3.83884	3.49680	3.52095	3.64772
$C_2-C_3 (\sigma^*)$	4.24308	3.99090	3.92328	3.89037
$C_6-C_1 (\sigma^*)$	4.28153	4.04763	0.95436	3.89901
$O_4-C_5 (\sigma^*)$	4.43102	4.05382	0.16862	4.01731
$C_7-N_9 (\sigma^*)$	—	4.46131	4.39414	4.53197
$C_5=C_6 (\sigma^*)$	5.15644	4.91350	5.03935	4.97619
$C_5=C_6 (\pi^*)$	5.15644	4.91350	5.03935	4.97619
$C_1=C_2 (\pi^*)$	5.79029	5.34644	5.44814	5.41304
$C_1=C_2 (\sigma^*)$	6.47050	5.75848	5.89306	5.9521
$C_7=C_8 (\pi^*)$	—	0.19151	6.19730	6.24654
$C_7=O_8 (\sigma^*)$	—	7.28922	7.45596	7.34484

Table – 3
 AOEP values of different molecular orbitals of Pyran and three isomeric amido pyrans

Molecular Orbitals	Pyran	Pyran 2-amide	Pyran 3-amide	Pyran 4-admide
$C_1=C_3 (\sigma)$	1.17073	1.17137	1.17149	1.17169
$C_1=C_2 (\pi)$	0.929310	0.94640	0.93692	0.93570
$C_7=O_8 (\pi)$	—	0.95940	0.95878	0.94470
$C_7=O_8 \frac{1}{2}\sigma\frac{1}{2}$	—	0.99376	0.95948	1.00148
$C_5=C_6 \frac{1}{2}\sigma\frac{1}{2}$	0.97507	1.20055	1.20004	1.19974
$C_5=C_6 \frac{1}{2}\sigma\frac{1}{2}$	0.97682	0.96752	0.97001	0.95914
$C_7-N_9 \frac{1}{2}\sigma\frac{1}{2}$	—	0.98645	0.98337	0.99070
$O_4-C_5 \frac{1}{2}\sigma\frac{1}{2}$	1.20012	1.03101	1.06868	1.02938
$C_6-C_1 \frac{1}{2}\sigma\frac{1}{2}$	0.99201	1.14652	1.14658	1.14442
$C_2-C_3 \frac{1}{2}\sigma\frac{1}{2}$	1.2767	0.91700	0.91321	0.91797
$C_1-H_{10} \frac{1}{2}\sigma\frac{1}{2}$	0.99491	0.83506	0.83291	0.83543
$C_5-O_4 \frac{1}{2}\sigma\frac{1}{2}$	1.14488	1.00530	1.00300	1.00159
$C_3-H_{16} \frac{1}{2}\sigma\frac{1}{2}$	0.95188	1.13960	1.16509	1.17183
$C_2-H_{11} \frac{1}{2}\sigma\frac{1}{2}$	0.94731	1.29654	1.32272	1.29896
$N_9-H_{14} \frac{1}{2}\sigma\frac{1}{2}$	—	1.88561	1.86670	1.88860
$N_9-H_{15} \frac{1}{2}\sigma\frac{1}{2}$	—	1.8867	1.18178	1.18682
$C_6-H_{13} \frac{1}{2}\sigma\frac{1}{2}$	1.84028	0.85883	0.84610	0.83683
$C_5-C_7 \frac{1}{2}\sigma\frac{1}{2}$	—	0.93270	0.95745	0.96973
Non bonding	1.15154	0.96666	0.89979	0.94002
Non bonding	1.68007	1.18005	1.18149	1.18056
Non bonding	1.5311	0.99163	0.95229	1.00932
Non bonding	1.18559	0.93699	0.95932	0.91743
Non bonding	—	1.10200	1.16427	1.11820
$C_5-C_7 \frac{1}{2}\sigma^*\frac{1}{2}$	—	1.18734	1.18006	1.18857
$C_6-H_{13} \frac{1}{2}\sigma^*\frac{1}{2}$	0.88419	0.87222	0.86701	0.88581
$N_9-H_{15} \frac{1}{2}\sigma^*\frac{1}{2}$	—	0.87850	0.87536	0.86904
$N_9-H_{14} \frac{1}{2}\sigma^*\frac{1}{2}$	—	0.79735	0.77888	0.78579

Table 2, showing the eigen values of different molecular orbitals provide an important information about the energies of HOMO and LUMO. Energies of HOMO and LUMO are very popular quantum mechanical descriptors.¹³ The compounds under examination acts as ligands therefore HOMO energies have been compared which is as follows :
 Pyran > Pyran 4-amide > Pyran 3- amide > Pyran 2-amide
 -8.666 - 8.949 -8.971 -9.012

A higher value of HOMO energy indicates better ability of coordination.

Conclusion and scope of the future work

Analysis of the eigen values of pyran and its amide derivatives gives an idea about the comparative stabilities of the different pyrans i.e. higher will be the eigen value lower will be the stability and vice-versa. So

by computing the eigen values of larger molecules their stability or activity can be predicted which will be helpful in synthesizing bulkier molecules and their derivatives used in drug designing. Angle of twist and AOEP although give an idea about the 3-D structure and contribution of the atomic orbital in forming particular molecular orbital but a direct information about the activity of the molecule can not be drawn.

References

1. R.G. Parr, R.A. Donnelly, M. Levy and W.E. Palke, J. Chem. Phys. 68, 3801 (1978).
2. P. Mohenberg and W. Kohn, Phys. Rev. B, 136, 864 (1964).
3. R.G. Parr and R.G. Pearson, J. An. Chem, Soc. 105, 7512 (1983).
4. R.P. Iczkowski and J.L. Margrave, J. An. Chem, Soc. 83, 3547 (1961).
5. H.B. Schlegel, Adv. Chem. Phys. 67, 249 (1987).
6. I.N. Levine Quantum Chemistry Vth Edition Prentice Hall, New Jersey, Chapter 15 (2000).
7. Hom, A.H.C.; Lin. J.H.; Clark, T; Theor. Chem. Acc. 114, 159-168 (2005).
8. Hom, A.H.C.; Lin. J.H.; Clark, T; Theor. Chem. Acc. 117, 461-465 (2007).
9. Golbraikh, A. Muratov E., Fourches, D. Topsha J. of Chemical Inf. model 54, 1, pp 1-4 (2014).
10. Charlie Marper, 'Introductors to Mathematical Physics', Prentice Hall of India Pvt. Ltd. (1995).
11. Ira. N. Levine, Quantum Chemistry Vth edition Prentice Hall, New Jersey, P. 665 (2000).
12. E. Clementi, C. Roetti, At. Data Nud. Data Tables, 14, 177 (1974).
13. Z. Zhon, R.G. Parr, J. An. Chem. Soc. 112, 5720 (1990).