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MNDO Analysis of Reactivity Parameters of Pyran and its Amido Derivatives

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Abstract: ***MNDO method is widely used for the study of molecular electronic parameters. Analytical calculations of the gradient are key to efficient geometry optimization. The IP, EA and q at O in Pyran and its derivatives have been calculated with the help of MNDO calculations and by substituting these values in Klopmann equation the softness indicators have been evaluated. The core-core repulsion and softness parameters of the compounds indicate the comparative donor capacity of Pyran and its Amido derivatives.***

Keywords: MNDO, Gradient, Geometry optimization, softness indicators.

I. INTRODUCTION

The MNDO calculation have recently been used for study of molecular electronic structure.[1-3] The reactivity of compounds have been mainly studied with the help of the knowledge of frontier orbitals. Klopman gave a quantitative approach for explaining the reactivity of nucleophiles and electrophiles, and developed an equation for evaluating the quantitative values of reactivity.[4-7] Klopman calculations were based upon the perturbation theory of charge and frontier controlled reactions. The charge controlled reactions were used to explain the ionic interactions and frontier controlled reactions to explain the covalent interactions.[8] A chemical system may be an atom, molecule, ion or radical or several such units in a state of interaction. The chemical potential must be constant everywhere in such a system and is defined by

$$\mu = \left(\frac{\delta E}{\delta N}\right)_v = \left(\frac{\delta E}{\delta P}\right)_v \quad (1)$$

Analytical calculations of the gradient are key to efficient geometry optimization. The SCF energy expression is given by

$$E_{HF} = \Sigma_{i-1}^{N12} E_i + \frac{1}{2} \Sigma_{v=1}^{b} \Sigma_{v=1}^{b} P_{vs} H_{rs}^{core} + V_{N,N} \quad (2)$$

The geometry optimization schemes are those of Mclver and Komornicki and force method due to Pulay.[9-12]

The optimization method developed by Pulay is based on Newton Raphson minimization algorithms. The method required some approximation to force constant matrix k, which is assumed to diagonal. Force constant calculation requires the determination of forces in the neighborhood of the equilibrium. Ki value is used to quantify ligand receptor interaction[13-15]. If the i^{th} force F_i is changed by ΔF_i arising from internal coordinate change Δq_i then

$$k_{ij} = -\frac{\Delta F_i}{\Delta q_i} \quad (3)$$

II. METHODOLOGY

The LCAO approximation, from Hartee-Fock orbitals to Roothm equation served as theoretical basis for approximate molecular orbital theories.[16-18] The molecular properties in semi empirical methods are not only derived from the principles of quantum mechanics but are also used to interpret and correlate the theoretical data with the experimental data. MNDO method involves the use of atomic parameters instead of pair parameters. The data and statistics obtained by using MNDO approximation for heat of formation, molecular geometries, ionization potential, dipole moment were quite close to experimental observation. The data obtained for MNDO method about bond length, bond angle and core-core repulsion are very accurate when compared to experimental values. The negative orbital energies are the calculated values of ionization potentials i.e. the validity of Koopman theorem which neglects the electronic reorganization and the charge in correlation of energies upon ionization. The mean absolute error for first ionization energies is reduced from 0.71 ev in MINDO/3 to 0.48 ev in MNDO. To identify difficult problems recent studies have introduced data modelability[19-21]. The limitation of MNDO method is an over estimation of the ionization energies corresponding to molecular orbitals with high coefficient.

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The ionization potential, election affinity and q at O in Pyran. Pyran 2-amide, Pyran 3-amide and Pyran 4-amide have been calculated with the help of MNDO calculations. Substituting these values in Klopman equation the softness parameters have been evaluated in Table-1.

The values of bond lengths between various atoms in Pyran and its derivatives are given in the Table 2. The sequence of bond lengths are given in Table 3. The bond orders of different bonds present in Pyran and the three isomeric amido Pyrans as calculated by MNDO method is given in Table 4.

The molecular valence electronic energy (Uval) including nuclear repulsion is taken as the sum of the purely electronic energy (Eel.val) of the valence electrons and the core-core repulsion energy Vcc[22].

$$U_{val} = \mathrm{E_{el.val}} - \mathrm{V_{cc}} \quad (4)$$

Although this form of Vcc is used in CNDO and INDO, it is more consistent with the approximation used to evaluate the electron core interaction integrals in Dewar type theories to take –

$$V_{cc} = \sum_{B>A} \sum_{A} [C_A\, C_B\, (S_A\, S_A / S_B\, S_B) + f_{AB}] \quad (5)$$

In MNDO, the core – core repulsion is given by

$$f_{AB}^{MNDO} = C_A\, C_O\, (S_A S_A / S_B S_B)\, (e^{-\propto_A R_{AB}} + e^{-\propto_B R_{AB}}) \quad (6)$$

Where $\propto_A$ and $\propto_B$ are the parameters for atoms A and B. Core-core repulsion is calculated on the basis of above equation and given in Table 5.

III. RESULTS AND DISCUSSION

Although the stability or strength of individual bonds can be predicted in Pyran and the three isomers but these data do not furnish any comprehensive information which could be related to their comparative activity. However, it can be emphatically said that measurement of bond length has provided the information about the distance of amido group from ring oxygen in case of three isomers i.e. ortho, meta and para amido pyrans. Since the bond order and bond length of a particular bond is inversely proportional to each other the numerical values obtained for the two parameters by MNDO technique support the fact.

Core-Core repulsion in Pyran and three isomeric amido Pyrans have the sequence Pyran 2-admide (5375.48511) Pyran 3-admide (5341.42977) > Pyran 4-amide (5331.36629) > Pyran (2719.24801). In Pyran 2-amide the atomic cores of substituents – $CONH_2$ are nearest from ring oxygen this gives maximum core-core repulsion. In case of Pyran 3-amide the atomic cores of substituents – $CONH_2$ is at intermediate distance from O, this gives intermediate value of core-core repulsion and in Pyran 4 amide, the atomic cores of the substituent are at maximum distance from atom O so it has minimum core-core repulsion except Pyran which has not atomic cores of an additional substituent group thereby giving least value of core-core repulsion.

IV. CONCLUSION

Core-core repulsion gives a measure of the comfortability of the various atomic nuclei constituting the 3D molecular structure. The core-core repulsion order of the three isomeric amido pyrans with pyran itself is; Pyran 2 amide > Pyran 3-amide > Pyran 4 amide > Pyran. Analysis of table-1 reveals that $E_m^{\#}$ values of Pyran and three isomeric Amido Pyrans are in the sequence Pyran (1.793441) > 4-Amido Pyran (1.012191) > 3-Amido Pyran (0.9439262) > 2-Amido Pyran (0.599695). So the tendency to act as legand is maximum in Pyran and minimum in 2-Amido Pyran. So the study may be helpful in predicting the donor capacity of a particular site in larges molecules to make an easy route for synthesising useful derivatives.

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Table.1.
Values of different parameters of Pyran and three isomeric Amido pyrans at (O)

Parameter	Pyran	Pyran 2-amdie	Pyran 3-amide	Pyran 4-amide
Lonisation potential	13.92951	17.17413	17.88749	18.04708
Electron Affinity	-4.966315	-7.679936	-8.527449	-8.635807
Charge	-0.013952	-0.160161	-0.192525	-0.199776
Atom electron density	1.82356	1.83843	1.83798	1.84038
Electronegativity	4.481595	4.747095	4.680021	4.705635
Radius of atom	0.74	0.74	0.74	0.74
Fukui function	0.230035	0.2298038	0.2297475	0.2300475
Density distribution fn	12.5536	12.65596	12.65287	12.63939
Softness of atom $E_m^{\#}$	1.793441	0.599695	0.9439262	1.012191

Table-2
Bond lengths between various atoms in Pyran and its amido derivatives

Type of Bond	Pyran	Pyran 2-amdie	Pyran 3-amide	Pyran 4-amide
C_1=C_2	1.377347	1.339642	1.338281	1.345744
C_2=C_3	1.475088	1.488549	1.487898	1.488597
C_3=O_4	1.463994	1.425947	1.431119	1.427021
C_4=C_5	1.256592	1.368518	1.350099	1.359912
C_5=C_6	1.449241	1.352891	1.355030	1.345871
C_6=C_7	-	1.501648	1.481309	1.491130 C_1=C_7
C_7=O_8	-	1.223713	1.227424	1.226641
C_7=N_9	-	1.39777	1.3996	1.397141
N_9=H_{14}	-	0.993452	0.991887	0.990522
N_9=H_{15}	-	0.99041	0.990871	0.993145 (N_9=H_{13})
C_1=H_{10}	1.095756	1.093806	1.09625	1.092723 (C_3=H_{17})
C_2=H_{11}	1.094006	1.094127	1.094173	1.098487
C_3=H_{12}	1.105382	1.106241	1.105691	1.106223
C_3=H_{16}	1.105412	1.106332	1.105752	1.106290
C_6=H_{13}	1.092492	1.097218	1.096420	1.095101 (C_6=H_{18})

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Table-3
Sequence of bond lengths in Pyran, Pyran 2-amide, Pyran 3-amide and Pyran 4-amide

Bonds	Sequence
C_1=C_2	Pyran > Pyran 4-amide > Pyran 2-amide> Pyran 3-amide 1.377347 1.345744 1.339642 1.338281
C_2=C_3	Pyran 4-amide > Pyran 2-amide> Pyran 3-amide > Pyran 1.488597 1.488549 1.487898 1.475088
C_3=O_4	Pyran > Pyran 3-amide > Pyran 4-amide> Pyran 2-amide 1.463994 1.431119 1.427021 1.425947
C_4=C_5	Pyran 2-amide > Pyran 4-amide> Pyran 3-amide > Pyran 1.368518 1.359912 1.350099 1.256592
C_5=C_6	Pyran > Pyran 3-amide > Pyran 2-amide> Pyran 2-amide 1.449241 1.355030 1.352891 1.345871
C_2=H_{11}	Pyran 4-amide > Pyran > Pyran 3-amide > Pyran 4-amide 1.098407 1.094006 1.094173 1.094127
C_3=H_{12}	Pyran 2-amide > Pyran 4-amide> Pyran 3-amide > Pyran 1.106241 1.106223 1.105691 1.105382
C_7=O_8	– Pyran 3-amide > Pyran 4-amide> Pyran 3-amide 1.227424 1.226641 1.22373
C_7=N_9	– Pyran 3-amide > Pyran 2-amide> Pyran 4-amide 1.399600 1.397770 1.397141
N_9=H_{14}	– Pyran 2-amide > Pyran 3-amide> Pyran 3-amide 0.993452 0.991887 0.990522
C_3=H_{16}	Pyran 2-amide > Pyran 4-amide> Pyran 3-amide > Pyran 1.106332 1.106290 1.105752 1.105412

Table-4
Bond order between various atoms in Pyran and its amido derivatives

Type of Bond	Pyran	Pyran 2-amdie	Pyran 3-amide	Pyran 4-amide
C_1=C_2	1.529575	1.870828	1.879819	1.824243
C_2=C_3	1.048076	0.994502	0.995467	0.996301
C_3=O_4	0.877255	0.963798	0.949721	0.962350
C_4=C_5	1.56671	1.063188	1.098160	1.061889
C_5=C_6	1.124637	1.755712	1.723492	1.797104
C_6=C_1	1.418485	1.062583	1.044245	1.054638
C_5=C_7	-	0.920321	0.955540	0.940691
C_7=O_8	-	1.762047	1.736440	1.742967
C_1=N_9	-	1.150037	1.143943	1.154905
N_9=H_{14}	-	0.958922	0.961371	0.958451
N_9=H_{15}	-	0.958247	0.958394	0.959930
C_6=H_{13}	0.976995	0.955427	0.943138	0.955126
C_1=H_{10}	0.979284	0.964261	0.956515	0.953398
C_2=H_{11}	0.978237	0.962018	0.961099	0.948261
C_3=H_{16}	0.956437	0.963003	0.964602	0.962675
C_3=H_{12}	0.956143	0.963984	0.964593	0.962662

Table-5 Core-core repulsion values

Molecule	Core-Core Repulsion in (Ev)
Pyran	2719.24801
Pyran 2-amide	5375.48511
Pyran 3-amide	5341.42977
Pyran 4-amide	5331.36629

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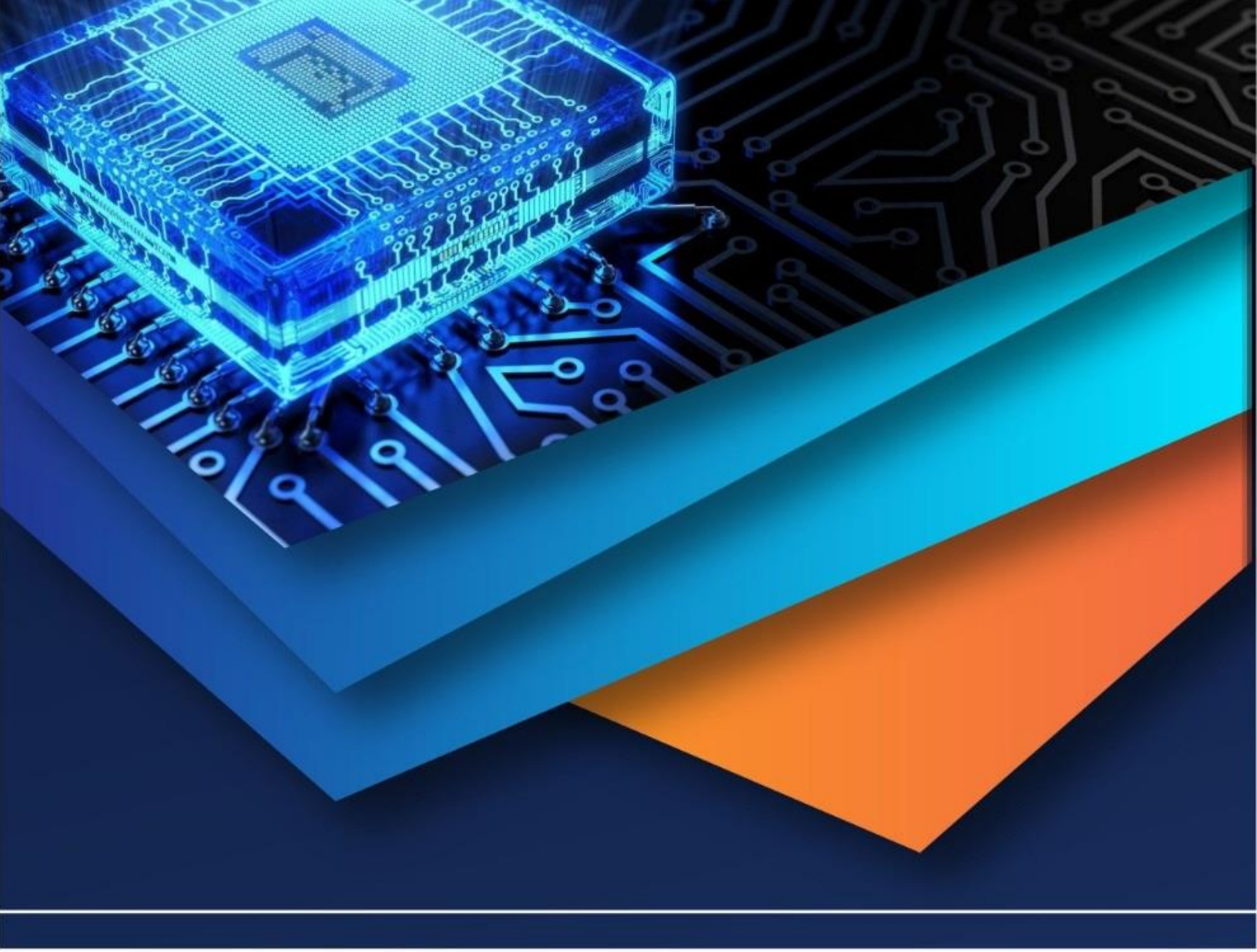

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