COORDINATING ABILITY OF ETHYLUREA BY USING EIGEN VECTORS ANALYSIS

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Abstract
The concentration of electrons on carbonyl oxygen and nitrogen atoms of ethylurea and its derivatives have been calculated with the help of Cache software. In Ethylurea, we have found that the sum of concentration of electrons on carbonyl oxygen is greater than that on Nitrogen atom indicating the coordination through carbonyl oxygen.

Keywords: Eigenvector Values, Ethylurea, Quantum Chemical Parameters.

Introduction
There are a large number of cases where the coordination has been reported by carbonyl oxygen but in many cases it is through amino nitrogen. There   has been fairly large amount of work on the amide and ethylurea complexes of Lewis acid such as $CdCl_2$, BCl_3, BBr_3, $SbCl_5$, $TiCl_4$, $TiBr_4$, TiI_4 but the question whether these donor molecules are coordinated to the Lewis acids through the nitrogen or the oxygen atom is still undecided in some cases. Packages incorporating latest methods for obtaining such deeper information about molecular structure are now available which were earlier not possible. Fast computers can provide information through packages within a reasonable span of time. Quantum mechanical information about electronic structure of complexes even today is hardly available.

Our main aim is to evaluate theoretical parameters with help of computational packages and to correlate them with experimental results. The result will help in predicting the coordinating ability and in resolving the controversy of site of bonding in Ethylurea.. Such a quantitative study will provide the correct information about the coordinating site.

Material and Methods
The 3D modeling and geometry optimization of Ethylurea under study have been done by Cache software using molecular mechanics with EHT option. Eigen values and Eigen vectors values have been obtained with the same software using the same option. With the help of these values, eigenvector analysis and magnitude of contribution of atomic orbital in Molecular Orbital formation have been discussed.

The molecular orbital are formed by the linear combination of basic functions. Most molecular quantum-mechanical methods (such as- SCF, CI etc.) begin the calculation with the choice of a basis functions $_r$, which are used to express the MOs ϕ_i as $\phi_i = {}_i c_{ri} {}_r$ (c = coefficient of , r = number of atomic orbital, i = molecular orbital number). The use of an adequate basis set is an essential requirement for the calculation. The basic functions are usually taken as AOs. Each AO can be represented as a linear combination of one or more Slater-type orbital $(STOs)^{(1–3).}$ Each molecular orbital ϕ_i is expressed as_

$$\phi_i = {}_i c_{ri} {}_r \qquad (1)$$

Where, the $_r$'s are the STO basis functions. Here we use the STO–6G basis set (which is contracted Gaussian) $^{(4–7)}$ for the SCF calculation. The coefficients in linear combination for each molecular orbital being found by solution of the Roothaan equation.$^{(8)}$ The most efficient way to solve the Roothaan equation is to use matrix–algebra methods. In matrix–algebra methods, the matrix elements are computed,$^{(9)}$ and the secular equation is solved to give the set of orbital energies (i.e. eigen values). These orbital energies $^{(10-12)}$ are used to solve Roothaan equations for the set of coefficients (*i.e.* eigenvectors) giving a set of molecular orbital. The calculations are done using a computer.

By the above calculation, the values of orbital energies (eigen values) and eigenvectors (coefficients) have been calculated.

A widely used method to analyze SCF wave function is population analysis, introduced by Mulliken.$^{(13, 14)}$ He proposed a method that apportions the electrons of an n–electron molecule into net populations n_r in the basic functions $_r$ and overlap populations $n_{r–s}$ for all possible pairs of basic functions.

For the set of basic functions $_1$, $_{2,}$ $_b$, each molecular orbital ϕ_i has the form $\phi_i = {}_s c_{si} {}_s = c_{1i} {}_1 + c_{2i} {}_2 +...+ c_{bi} {}_b$. For simplicity, we shall assume that the c_{si}'s and $_s$'s are real. The probability density associated with one electron in ϕ_i is (s and b are the number of the atomic orbital other than r)

$$| \phi_i |^2 = c_{1i}^2 \phi_1^2 + c_{2i}^2 \phi_2^2 + ... + 2c_{1i}c_{2i} \phi_1 \phi_2 + 2c_{1i}c_{3i} \phi_1 \phi_3 + 2 c_{2i}c_{3i} \phi_2 \phi_3 + ...$$

Integrating this equation over three-dimensional space and using the fact that ϕ_i and the ϕ's are normalized, we get

$$1 = c_{1i}^2 + c_{2i}^2 + ... + 2c_{1i} c_{2i} S_{12} + 2c_{1i} c_{3i} S_{13} + 2c_{2i} c_{3i} S_{23} + ... \qquad (2)$$

Where the S's are overlap integrals: $S_{12} = \int \phi_1 \phi_2 d\phi_1 d\phi_2$, etc. Mulliken proposed that the terms in Eq.2 be apportioned as follows. One electron in the molecular orbital ϕ_i contributes c_{1i}^2 to the net population in ϕ_1, c_{2i}^2 to the net population in ϕ_2, etc., and contributes $2c_{1i}c_{2i}S_{12}$ to the overlap population between ϕ_1 and ϕ_2, $2c_{1i}c_{3i}S_{13}$ to the overlap population between ϕ_1 and ϕ_3, etc. Let there be n_i electrons in the molecular orbital ϕ_i (n_i = 0,1,2) and let $n_{r,i}$ and $n_{r-s,i}$ symbolize the contribution of electrons in the molecular orbital ϕ_i to the net population in ϕ_r and to the overlap population between ϕ_r and ϕ_s, respectively. We have

$$n_{r,i} = n_i c_{ri}^2, \qquad (3)$$
$$n_{r-s,i} = n_i (2c_{ri} c_{si} S_{rs}) \qquad (4)$$

The least involvement is of the ϕ_{12} ($2p_z$) orbital of oxygen. The value is 1.7416. The corresponding values of two nitrogen (ϕ_4 and ϕ_{16}) are 1.9290 and 1.9290. The above observation indicates that ϕ_{12} ($2p_z$) are more available for further bonding hence ϕ_{12} ($2p_z$) orbital is most likely site of bonding. Based on the above principle, the contribution of electrons in each occupied molecular orbital have been calculated with the help of eigenvector values. The overlap population analysis has also been made with the help of the values of eigenvector and overlap matrix for distinguishing the bonding, nonbonding and anti-bonding nature of molecular orbital.

Result and Discussion
In order to evaluate the contribution concentration of electrons at carbonyl oxygen and amino nitrogen, the following equation has been solved for Ethylurea.

$$n_{r,i} = n_i c_{ri}^2,$$
$$n_{r-s,i} = n_i (2c_{ri} c_{si} S_{rs})$$

The number of valence electrons of each ethylurea has been evaluate by adding the valence electrons of the constituent's atom. The number of electrons has been considered as two for each occupied molecular orbital. The data relating to c_{ri} have been taken from eigen vector obtained by Cache software.

From geometry optimization it is clear that total contribution of 1N-2px electrons is 1.03219712 and that of 1N-2py and 1N-2pz are 0.89565728 and 0.94091762 respectively, 4N-2px electrons is 0.666311968, 4N-2py and 4N-2pz are 0.57325538 and 1.16861472 respectively. The contribution of electrons in corresponding oxygen is 1.158242 in 3O-2px, 1.21399362 in 3O-2py and 0.55989362 in 3O-2pz.

The sum of contribution of 1N-2px, 2py, 2pz electron is 2.868772. The sum of contribution of 4N-2px, 4py, 4pz electron is 2.58819 and the sum of contribution of 3O-2px, 2py, 2pz is 2.932129. In such a way to concentration of electrons at oxygen is much more (2.932129) as compared to the concentration of electron on the nitrogen. The attachment of incoming Lewis acid on oxygen atom occurs because of greater concentration of electron.

Conclusion
We have obtained the sum of concentration of electrons ($n_{r,i}$) on nitrogen and oxygen atoms of Ethylurea. As the sum concentration of electrons on an atom increases, their coordinating ability also increases in the same ratio. Sum of concentration of electrons on nitrogen and oxygen atoms of Ethylurea is shown in the Table-2. The sum of concentration on oxygen of carbonyl group is greater than that on nitrogen atom. This indicates that the coordinate through their carbonyl oxygen instead of their nitrogen atom.

Table-1: Eigen Vector Values and Concentration of Electron on Oxygen and Nitrogen Atom of Ethylurea

M.O. (ψ)		Atomic Orbital	Eigenvector Value	No. of Electron	$n_{ri}=n_i c_{ri}^2$	Summation of Concentration of e⁻ on 1N, 4N & 3O M.O.
ϕ_{27}	2	N 2Px	0.7184	2	1.03219712	2.868772
ϕ_{18}	3	N 2Py	0.6692	2	0.89565728	

ϕ_{20}	4	N 2Pz	0.6859	2	0.94091762	
ϕ_{23}	14	N 2Px	0.5772	2	0.66631968	
ϕ_{16}	15	N 2Py	0.6137	2	0.75325538	2.58819
ϕ_{25}	16	N 2Pz	0.7644	2	1.16861472	
ϕ_{15}	10	O 2Px	0.761	2	1.158242	
ϕ_{11}	11	O 2Py	0.7791	2	1.21399362	2.932129
ϕ_{12}	12	O 2Pz	0.5291	2	0.55989362	

Table-2: Sum of Concentration of Electrons on Nitrogen and Oxygen Atoms of Ethylurea

Compound	Sum of Concentration on Nitrogen Atom	Sum of Concentration on Nitrogen Atom	Sum of Concentration of E⁻ on Oxygen Atom
Ethylurea	2.868772	2.588189	2.932129

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