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Quantum Mechanical Study of Coordination Ability of Amides Using Eigen Value Parameters

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Abstract: It is well known fact that the bonding occurs at oxygen atom in the Amides compounds. In order to prove this fact we have considered eighteen Amides compounds. Present study deals to calculate their Eigen value using Quantum Mechanical descriptors via Cache software. With the help of Eigen values, the concentrations of electrons on oxygen and nitrogen atoms of Amides compounds have been calculated. In Amides compounds, the sum of contributions of p-orbitals of oxygen atom in the formation of molecular orbitals is smaller as compared to other atoms. This indicates that the bonding takes place at oxygen atom.

Keywords: Eigen value, coordination ability, Amides compounds, molecular orbital, density functional theory.

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Introduction

The coordinating ability of Amides Compounds has been a matter of great controversy. 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 complexes of Lewis acid but the question whether these donor molecules are coordinated to the Lewis acids through the nitrogen or the oxygen atom is still a debatable subject in some cases. Packages incorporating latest methods for obtaining such deeper information about molecular structure are now available which were not possible earlier. Fast computers can provide information through packages within a reasonable span of time. Quantum mechanical information about electronic structure of complexes even today is available.

The experimental results of Amides complexes are available but their correlation with quantum mechanical parameters has not been made so far. Our main aim is to evaluate theoretical parameters with the 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 Amides. In this paper

we have presented the calculations of Eigen values analysis of Amides Compounds in order to determine the site of coordination. Such a quantitative study has provided the correct information about the coordinating site.

Material and Methods

Material

The study materials are the four groups of amides are as follows:

A. Alkyl Group Amide:		
1	HCONH ₂	Formamide
2	HCONHCH ₃	N-Methyl-formamide
3	HCON(CH ₃) ₂	N, N-Dimethyl-formamide
4	CH ₃ CONH ₂	Acetamide
5	CH ₃ CONHCH ₃	N-Methyl-acetamide
6	CH ₃ CON(CH ₃) ₂	N, N-Dimethyl-acetamide

B. Phenyl Group Amide:		
7	$C_6H_5CONH_2$	Benzamide
8	$C_6H_5CONHCH_3$	<i>N</i> -Methyl-benzamide
9	$C_6H_5CON(CH_3)_2$	<i>N,N</i> -Dimethyl-benzamide
10	$C_6H_5CONHC_2H_5$	<i>N</i> -Ethyl-benzamide
11	$C_6H_5CON(C_2H_5)_2$	<i>N,N</i> -Diethyl-benzamide
12	$C_6H_5CONHC_6H_5$	<i>N</i> ,-Phenyl-benzamide
13	$C_6H_5CON(C_6H_5)_2$	<i>N,N</i> -DiPhenyl-benzamide

C. Amide with Sulphonyl Group:		
14	$SO_2NH_2C_6H_4NHCOCH_3$	<i>N</i> -(4-Sulfanoyl-phenyl)-acetamide
15	$NH_2-C_6H_4SO_2NHCOCH_3$	<i>N</i> -Acetyl-4-amino-benzenesulfonamide

D. Pyridine Group Amide:		
16	$C_5H_4NCONH_2$	Pyridine-2-carboxylic acid amide
17	$C_5H_4NCONH_2$	Pyridine-3-carboxylic acid amide
18	$C_5H_4NCONH_2$	Pyridine-4-carboxylic acid amide

3D Structure

The 3D modeling and geometry optimization of Amides compounds and its derivatives under study have been done by Cache software using molecular mechanics with EHT option. The 2d structures of Amides compounds and its derivatives proposed for study is shown in Fig.-1. Eigenvalues have been obtained with the same software using the same option. With the help of these values magnitude of contribution of atomic orbital in Molecular Orbital formation have been discussed. The molecular orbitals are formed by the linear combination of basis functions.

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

$$\Phi_i = \sum_i c_{ri} \chi_r \quad \dots\dots\dots (1)$$

Where, the χ_r 's are the STO basis functions. Here 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 orbitals. 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 population's n_r in the basis functions χ_r and overlap populations n_{r-s} for all possible pairs of basis functions.

For the set of basis functions $\chi_1, \chi_2, \dots, \chi_b$, each molecular orbital Φ_i has the form $\Phi_i = \sum_s c_{si} \chi_s = c_{1i} \chi_1 + c_{2i} \chi_2 + \dots + c_{bi} \chi_b$. For simplicity, we have assumed that the c_{si} 's and χ_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) $|\Phi_i|^2 = c_{1i}^2 \chi_1^2 + c_{2i}^2 \chi_2^2 + \dots + 2c_{1i}c_{2i} \chi_1 \chi_2 + 2c_{1i}c_{3i} \chi_1 \chi_3 + 2c_{2i}c_{3i} \chi_2 \chi_3 + \dots$. Integrating this equation over three-dimensional space and using the fact that Φ_i and the χ_s 's are normalized, we get

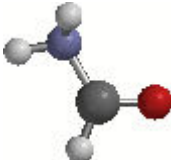
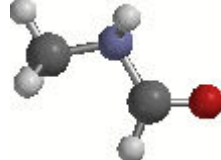
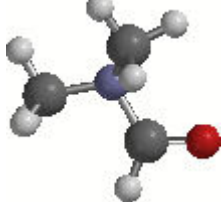
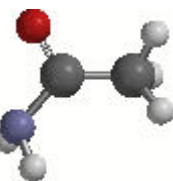
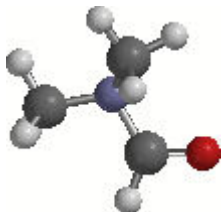
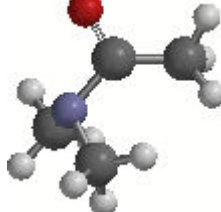
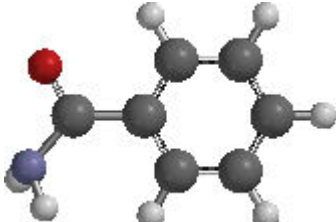
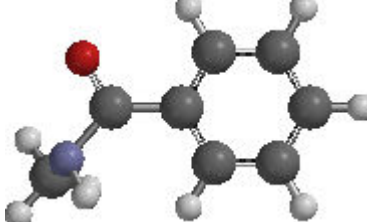
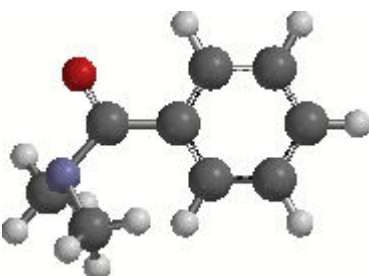
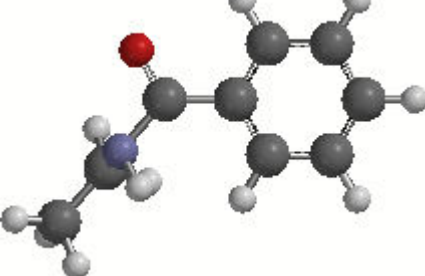
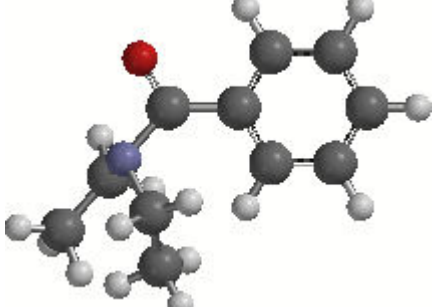
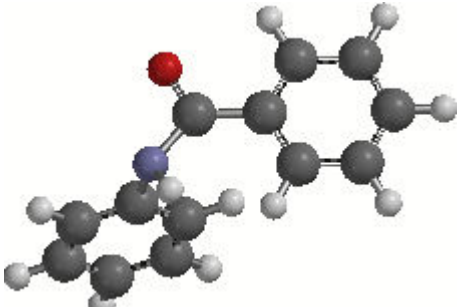
$$1 = c_{1i}^2 + c_{2i}^2 + \dots + 2c_{1i}c_{2i} S_{12} + 2c_{1i}c_{3i} S_{13} + 2c_{2i}c_{3i} S_{23} + \dots (2)$$

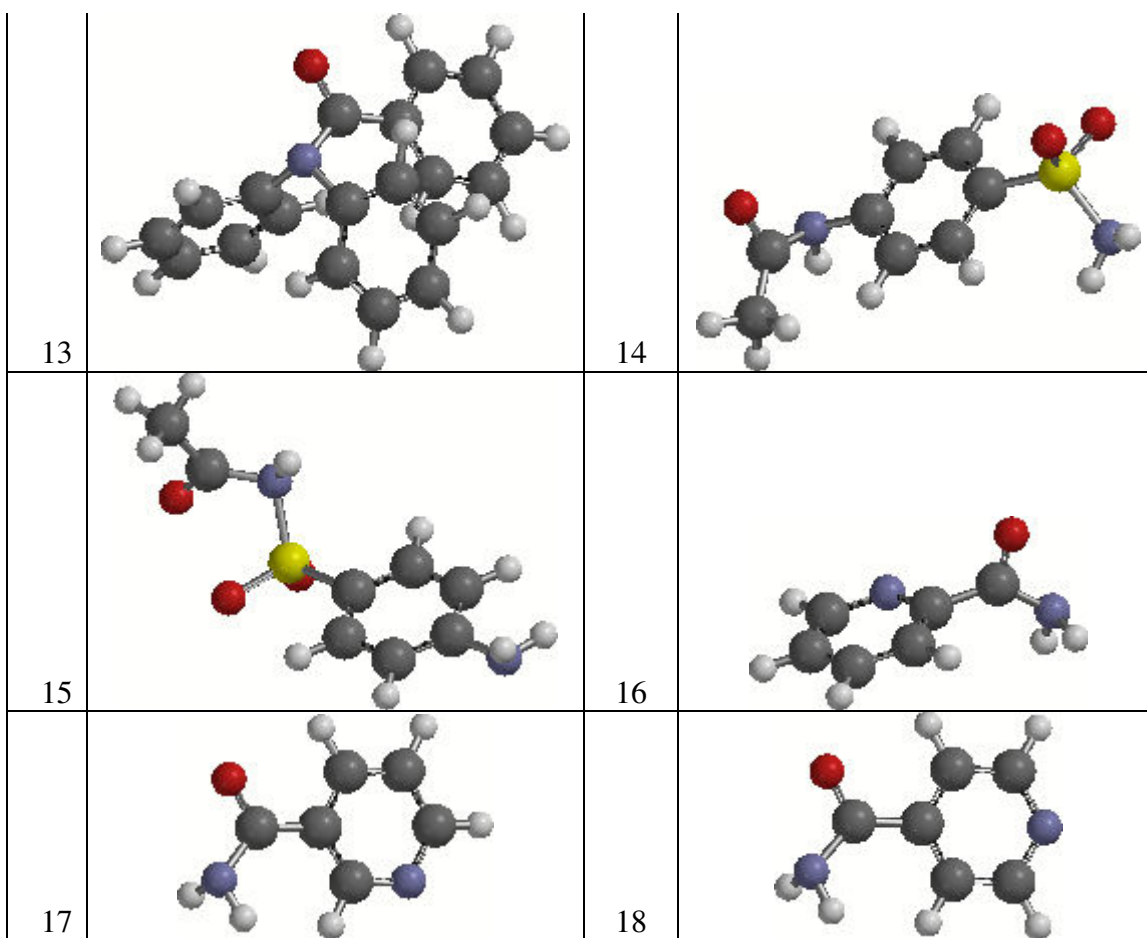
Where the S 's are overlap integrals: $S_{12} = \int \chi_1 \chi_2 dv_1 dv_2$, etc. Mulliken proposed that the terms in Eq.2 be apportioned as follows. One electron in the molecular orbital Φ_i contributes c_{1i}^2 to the net population in χ_1 , c_{2i}^2 to the net population in χ_2 , etc., and contributes $2c_{1i}c_{2i}S_{12}$ to the overlap population between χ_1 and χ_2 , $2c_{1i}c_{3i}S_{13}$ to the overlap population between χ_1 and χ_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 contributions of electrons in the molecular orbital Φ_i to the net population in χ_r and to the overlap population between χ_r and χ_s , respectively. We have

$$n_{r,i} = n_i c_{ri}^2 \quad \dots\dots\dots (3)$$

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

Based on the above principle, the contributions of electrons in each occupied molecular orbital have been calculated with the help of eigenvector values overlap matrix for distinguishing the bonding, nonbonding and antibonding nature of molecular orbital.

No	3D	No	3D
1		2	
3		4	
5		6	
7		8	
9		10	
11		12	



Results and Discussion

Amides Compounds

Molecular orbital calculations of all the compounds have been done with the help of CAChe software using the following Input Control Parameters-
 EHT option: Normal EHT
 Basis Contraction: ST0-6G

Parameter K: 1.7500
 Request MOs: All molecular

The Eigen values of amides and their derivatives have been evaluated for resolving the controversy of site of bonding.

Eigen Value Table

Table 1: Eigen values of HCONH₂ (Compound 1)

Molecular Orbital	Eigen Values (e.v.)	Molecular Orbital	Eigen Values (e.v.)
1	-1.2664	9	-0.5036
2	-1.0393	10	-0.311
3	-0.7256	11	0.0822
4	-0.6227	12	0.1721
5	-0.5864	13	0.3818
6	-0.5731	14	0.8125
7	-0.5589	15	1.1168
8	-0.514		

Table 2: Eigen values of HCONHCH₃ (Compound 2)

Molecular Orbital	Eigen Values (e.v.)	Molecular Orbital	Eigen Values (e.v.)
1	-1.2671	12	-0.4877
2	-1.0749	13	-0.3113
3	-0.8365	14	0.0439
4	-0.7188	15	0.1136
5	-0.5938	16	0.1539
6	-0.5907	17	0.2008
7	-0.5848	18	0.3877
8	-0.5666	19	0.737
9	-0.5572	20	1.0926
10	-0.5489	21	1.1409
11	-0.5113		

Table 3: Eigen values of HCON (CH₃)₂ (Compd-3)

Molecular Orbital	Eigen Values (e.v.)	Molecular Orbital	Eigen Values (e.v.)
1	-1.2678	15	-0.4762
2	-1.0991	16	-0.3124
3	-0.876	17	0.0195
4	-0.8143	18	0.0744
5	-0.6916	19	0.1442
6	-0.6003	20	0.1604
7	-0.5937	21	0.1779
8	-0.5816	22	0.1976
9	-0.5668	23	0.3537
10	-0.5648	24	0.7088
11	-0.5596	25	1.0214
12	-0.5484	26	1.0835
13	-0.5364	27	1.1739
14	-0.5087		

Eigen Values

Alkyl Group Amide:

HCONH₂:- No. 1

The molecular orbitals of HCONH₂ (Compd:-1) are formed linear combination of atomic orbitals of one carbon, one oxygen, one nitrogen and three hydrogen as detailed below:-

1 Carbon - 2s, 2px, 2py, 2pz = 4 AO
 1 Oxygen - 2s, 2px, 2py, 2pz = 4 AO

1 Nitrogen- 2s, 2px, 2py, 2pz = 4 AO
 3 Hydrogen- 1s = 3 AO
 Total Atomic Orbitals = 15 AO
 Molecular Orbitals = 15 AO

The 15 atomic orbitals gave LCAO approximation to 15 molecular orbitals.

As explained above the number of atomic orbitals and molecular orbitals in other derivative of amides are as below:

HCONHCH₃ :- No.2

Total Atomic Orbitals 21 AO
Molecular Orbitals 21 AO

The 21 atomic orbitals gave LCAO approximation to 21 molecular orbitals

HCON (CH₃)₂ :- No.3

Total Atomic Orbitals 27 AO
Molecular Orbitals 27 AO

The 27 atomic orbitals gave LCAO approximation to 27 molecular orbitals

CH₃CONH₂:- No.4

Total Atomic Orbitals 21 AO
Molecular Orbitals 21 AO

The 21 atomic orbitals gave LCAO approximation to 21 molecular orbitals

CH₃CONHCH₃:- No.5

Total Atomic Orbitals 27 AO
Molecular Orbitals 27 AO

The 27 atomic orbitals gave LCAO approximation to 27 molecular orbitals

CH₃CON (CH₃)₂:- No.6

Total Atomic Orbitals 33 AO
Molecular Orbitals 33 AO

The 33 atomic orbitals gave LCAO approximation to 33 molecular orbitals

Phenyl Group Amide:

C₆H₅CONH₂:- No.7

Total Atomic Orbitals 43 AO
Molecular Orbitals 43 AO

The 43 atomic orbitals gave LCAO approximation to 43 molecular orbitals

C₆H₅CONHCH₃:- No.8

Total Atomic Orbitals 48 AO
Molecular Orbitals 48 AO

The 48 atomic orbitals gave LCAO approximation to 48 molecular orbitals

C₆H₅CON (CH₃)₂:- No. 9

Total Atomic Orbitals 55 AO
Molecular Orbitals 55 AO

The 55 atomic orbitals gave LCAO approximation to 55 molecular orbitals

C₆H₅CONHC₂H₅:- No.10

Total Atomic Orbitals 55 AO
Molecular Orbitals 55 AO

The 55 atomic orbitals gave LCAO approximation to 55 molecular orbitals

C₆H₅CON (C₂H₅)₂:- No.11

Total Atomic Orbitals 67 AO
Molecular Orbitals 67 AO

The 55 atomic orbitals gave LCAO approximation to 55 molecular orbitals

C₆H₅CONHC₆H₅:- No. 12

Total Atomic Orbitals 71 AO
Molecular Orbitals 71 AO

The 71 atomic orbitals gave LCAO approximation to 71 molecular orbitals

C₆H₅CON (C₆H₅)₂:- No. 13

Total Atomic Orbitals 99 AO
Molecular Orbitals 99 AO

The 99 atomic orbitals gave LCAO approximation to 99 molecular orbitals.

Amide with Sulphonyl Group:

SO₂NH₂C₆H₄NHCOCH₃:- No.14

Total Atomic Orbitals 71 AO
Molecular Orbitals 71 AO

The 71 atomic orbitals gave LCAO approximation to 71 molecular orbitals

NH₂-C₆H₄SO₂NHCOCH₃:- No. 15

Total Atomic Orbitals 71 AO
Molecular Orbitals 71 AO

The 71 atomic orbitals gave LCAO approximation to 71 molecular orbitals

C₅H₄NCONH₂ :- No. 16

Total Atomic Orbitals 42 AO
Molecular Orbitals 42 AO

The 42 atomic orbitals gave LCAO approximation to 42 molecular orbitals

C₅H₄NCONH₂:- No. 17

Total Atomic Orbitals 42 AO
Molecular Orbitals 42 AO

The 42 atomic orbitals gave LCAO approximation to 42 molecular orbitals

C₅H₄NCONH₂- No. 18

Total Atomic Orbitals	42 AO
Molecular Orbitals	42 AO

The 42 atomic orbitals gave LCAO approximation to 42 molecular orbitals.

The Eigen values of molecular orbitals of eighteen amides have been evaluated in table and for brevity only three tables have given. The molecular stability of the amides can be related with the value of lowest Eigen value of the amides which are presented below for different amides, in order of their decreasing stability.

The most stable amides is NH₂-C₆H₄SO₂NHCOCH₃ (15) and the least stable of series is HCONH₂ (No.1). The sequence of stability is shown in the table 4. 15>14>12>13>9>10>8>11>7>6>16>17>18>5>4>3>2 >1

Table 4: Stability order of all the compounds with their eigen values

Compd.	Lowest Eigen value
15	-1.3243
14	-1.3242
13	-1.2736
12	-1.2725
9	-1.2721
10	-1.272
8	-1.2719
11	-1.2719
7	-1.2711
6	-1.2702
16	-1.2725
17	-1.2721
18	-1.27
5	-1.2695
4	-1.2688
3	-1.2678
2	-1.2671
1	-1.2664

The LCAO of various amides shows that the numbers of oxygen and nitrogen atom in all cases are not same. As such our interest is only in oxygen and nitrogen atoms, carbon and hydrogen atoms are kept out of our discussion. The Eigen vector tables, as discussed later shows that 2pz orbitals, of oxygen are the donor sites in all the amides. The Eigen values of 2pz orbitals show that oxygen has maximum contribution in two molecular orbitals of comp. - 2, 6, 4, 3, 5, 1, 8 molecular orbitals of comp. -

11,10,8,9,7,18,17,13,12,14,16 and 9 molecular orbitals comp. No. 14,15, The Eigen values of the molecular orbitals have been taken from the Eigen value table, and are presented in table 5.

Table 5: Eigen value table of 2pz orbitals of oxygen

Compd.	Amides	Eigen value of 2pz orbitals
15	HCONH ₂	-0.7922
14	HCONHCH ₃	-0.3894
13	HCON(CH ₃) ₂	-0.5774
12	CH ₃ CONH ₂	-0.4998
9	CH ₃ CONHCH ₃	-0.7172
10	CH ₃ CON(CH ₃) ₂	-0.4496
8	C ₆ H ₅ CONH ₂	-0.3122
11	C ₆ H ₅ CONHCH ₃	-0.2577
7	C ₆ H ₅ CON(CH ₃) ₂	-0.2618
6	C ₆ H ₅ CONHC ₂ H ₅	-0.1877
16	C ₆ H ₅ CON(C ₂ H ₅) ₂	-0.6888
17	C ₆ H ₅ CONHC ₆ H ₅	-0.5502
18	C ₆ H ₅ CON(C ₆ H ₅) ₂	-0.6933
5	SO ₂ NH ₂ C ₆ H ₄ NHCOCH ₃	-0.3915
4	NH ₂ -C ₆ H ₄ SO ₂ NHCOCH ₃	-0.4877
3	C ₅ H ₄ NCONH ₂	-0.7156
2	C ₅ H ₄ NCONH ₂	-0.6404
1	C ₅ H ₄ NCONH ₂	-0.319

Conclusion

The Eigen values of 2pz of the oxygen indicate the following order of their stability.

1>5>16>14>12>15>3>13>4>17>6>2>18>7>9>8>10>11.

The above sequence shows that most stable molecular orbital of carbonyl 2p_z is of HCONH₂ and the least stable of the series is C₆H₅CON(C₂H₅)₂. A close look at the amides indicates that increase of phenyl substitution on NH₂ increase the stability and similarity the methyl substitutions on NH₂ also increase the stability. The phenyl substitution however has greater effect.

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