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Prediction of coordination ability of amides using eigen vector analysis

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ABSTRACT

It is well known fact that the amides coordinates through their carbonyl oxygen. In order to prove this fact we have considered twelve amides and calculated their eigen vectors using Cache software. With the help of eigen vectors, the concentrations of electrons on carbonyl oxygen and nitrogen atoms of amides have been calculated. In each amide, we have found that the sum of concentrations of electrons on carbonyl oxygen is greater than that on oxygen atom indicating the coordination ability through carbonyl oxygen. Again, as the sum of concentration on carbonyl oxygen increases, its reactivity increases. On this basis we have arranged the amides in increasing order of reactivity. Diethylbenzamide is most reactive and formamide is least reactive.

KEYWORDS

Eigen vector;
Coordination ability;
Molecular orbital;
Density functional theory.

INTRODUCTION

In the last decade, there has been a phenomenal advancement in theoretical chemistry, much faster computers are available and commercial programs incorporating the latest methods have become widely available and are capable of providing more information about molecular orbitals, with a simple input of chemical formula. The focus of attention has been on computational chemistry[1,2]. This is largely due to the successful employment of gradient corrected density functional theory in calculating molecules; particularly of the heavier atoms[3-6] and in the use of small-core relativistic effective core potential[7-9] which set the stage for calculation of geometries, bond energies, and chemical reaction and other important properties of transition metal compounds with impressive accuracy[6,10,11]. Application of molecular mechanics to organomettalic and transition metal compounds is growing[12]. Molecular orbital parameters such as eigenvectors, overlap matrix and eigen values are well calculated with this method. In this chapter we present the calculations of eigenvector, overlap matrix, and population analysis of amides, in order to study the magnitude of contribution of electron at carbonyl oxygen and amino nitrogen of amides. Such a study will help in finding the site of coordination site in amides.

MATERIAL AND METHOD

The study materials of this chapter are a set of amides given in TABLE 1. The 3D modeling and geometry optimization of the amides have been done by CAChe software using molecular mechanics with EHT option. Eigen values, eigenvectors and overlap matrix values have been obtained with the same software, using the same option. With the help of these values, eigenvector analysis, magnitude of contribution of atomic orbital in MO

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TABLE 1: Concentration of electrons at nitrogen and oxygen in formamide

MO (ϕ_i)	χ	Atomic orbital	Eigen vector	Number of electrons	Contribution $n_{r,i} = n_i c^2_{ri}$
3	10	N-2px	0.2583		
5	10	N-2px	0.4591		
8	10	N-2px	0.3169		
			1.0343	2	2.13955298
4	11	N-2py	0.5350		
7	11	N-2py	0.2327		
8	11	N-2py	0.1610		
			0.9287	2	1.72496738
6	12	N-2pz	0.2424		
9	12	N-2pz	0.8580		
			1.1004	2	2.42176032
5	6	O-2px	0.5007		
8	6	O-2px	0.8291		
			1.3298	2	3.53673608
3	7	O-2py	0.2966		
7	7	O-2py	0.8044		
4	7	O-2py	0.1773		
			1.2783	2	3.26810178
6	8	O-2pz	0.7922		
9	8	O-2pz	0.4534		
			1.2456	2	3.10303872

Summation of contribution/concentration of electrons in formamide

Orbital	Sum of eigen vectors	Orbital	Sum of eigen vectors
N-2px	2.13955298	O-2px	3.53673608
N-2py	1.72496738	O-2py	3.26810178
N-2pz	2.42176032	O-2pz	3.10303872
Summation	6.28628068		9.90787658

formation and population analysis have been made and discussed. The method adopted for various calculations is based on the following principles.

A widely used method to analyze SCF wave function[13-18] is population analysis, introduced by Mulliken[19,20]. He proposed a method that apportions the electrons of an n-electron molecule into net populations 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 $\chi_1, \chi_2 \ldots\ldots \chi_b$, each molecular orbital ϕ_i has the form $_i = \sum_s c_{si}\chi_s = c_{1i}\chi_1 + c_{2i}\chi_2 + \ldots + c_{bi}\chi_b$. For simplicity, we shall assume 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.)

$$|\phi_i|^2 = c_{1i}^2\chi_1^2 + c_{2i}^2\chi_2^2 + \ldots + 2c_{1i}c_{2i}\chi_1\chi_2 + 2c_{1i}c_{3i}\chi_1\chi_3 + 2c_{1i}c_{3i}\chi_2\chi_3 + \ldots$$

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

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

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 (A) 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 MO ϕ_i ($n_i = 0, 1, 2$) and let $n_{r,i}$ and $n_{r-s,i}$ electrons in the MO ϕ_i to the net population in χ_r and to the overlap population between χ_r and χ_s, respectively. We have

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

Based on the above principle, the contribution of electrons in each occupied MO has been calculated with the help of eigenvector values for the following amides.

1. Formamide; 2. Methylformamide; 3. Dimethyl formamide; 4. Acetamide; 5. Methylacetamide; 6. Dimethylacetamide; 7. Benzamide; 8. Methyl benzamide; 9. Dimethylbenzamide; 10. Ethylbenzamide; 11. Diethylbenzamide; 12. Benzylbenzamide

The above study provide informations about the involvement of each atomic orbital in the formation of molecular orbital, hence detail knowledge of coordinating ability of amides. Information that has been obtained, enables us to evaluate the comparative coordinating ability of a series of amides.

RESULT AND DISCUSSION

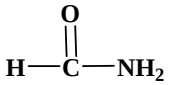
In order to evaluate the contribution/concentration of electrons at carbonyl oxygen and amino nitrogen of amides the following equation-1 has been solved for all the twelve amides

$$n_{r,i} = {}_{ni}\, c^2_{ri}$$
$$\text{and } n_{r-s,i} = n_i(2c_{ri}\, c_{si}\, S_{rs})$$

The number of valence electrons of each amide has been evaluated by adding the valence electrons of the constituent atoms. The numbers of electrons have been considered as two for each occupied molecular orbitals. The data relating to c_{ri} have been taken from eigen

vector values obtained by Cache software.

Compound (1): Formamide



The number of valence electrons in formamide is 18 as given below: -

1C	=	4
1O	=	6
1N	=	5
3H	=	3
		18

			1	2	3	4	5	6	7	8
1	1 C	2S	0.3155	0.1738	-0.4324	-0.0513	-0.0084	0.0000	0.0048	-0.0136
2	1 C	2Px	-0.0048	0.0545	0.1276	-0.1729	-0.3485	-0.0000	-0.0264	0.2295
3	1 C	2Py	0.0653	-0.1220	0.1930	-0.0324	0.0352	0.0000	-0.2635	0.0233
4	1 C	2Pz	0.0000	-0.0000	0.0000	0.0000	0.0000	-0.3759	-0.0000	0.0000
5	2 O	2S	0.7830	-0.3069	0.2566	0.0805	-0.0358	-0.0000	0.1214	0.0088
6	2 O	2Px	0.0004	0.0030	0.0386	-0.1913	-0.5007	-0.0000	-0.0815	-0.8291
7	2 O	2Py	0.0251	-0.0412	0.2966	0.1773	-0.0792	-0.0000	0.8044	-0.0627
8	2 O	2Pz	0.0000	-0.0000	-0.0000	0.0000	0.0000	-0.7922	-0.0000	0.0000
9	3 N	2S	0.1444	0.6993	0.1833	0.0106	-0.0204	0.0000	0.0231	0.0846
10	3 N	2Px	0.0011	0.0021	0.2583	-0.1445	0.4591	0.0000	-0.1019	-0.3169
11	3 N	2Py	-0.0032	-0.0003	-0.1156	-0.5350	0.0188	-0.0000	0.2327	0.1617
12	3 N	2Pz	-0.0000	-0.0000	0.0000	0.0000	0.0000	-0.2434	0.0000	0.0000
13	4 H	1S	-0.0035	0.0132	-0.3312	0.1003	0.2313	-0.0000	0.2067	-0.3511
14	5 H	1S	0.0001	0.1302	0.1951	-0.2634	0.3056	-0.0000	0.0552	-0.1002
15	6 H	1S	-0.0004	0.1309	0.1532	0.3982	-0.0491	0.0000	-0.1671	-0.0404

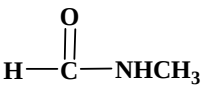
			9	10	11	12	13	14	15
1	1 C	2S	0.0000	0.0000	0.0173	-0.1603	0.5068	0.2338	-1.3407
2	1 C	2Px	0.0000	-0.0000	-0.4305	-0.7349	-0.7470	0.5209	-0.1866
3	1 C	2Py	0.0000	0.0000	-0.1512	0.2524	-0.6414	-1.0372	-0.5905
4	1 C	2Pz	0.1959	-0.9573	0.0000	0.0000	-0.0000	0.0000	0.0000
5	2 O	2S	-0.0000	-0.0000	0.0955	-0.0896	0.1623	0.4833	0.8609
6	2 O	2Px	0.0000	-0.0000	0.1119	0.1663	0.1700	-0.1127	0.0493
7	2 O	2Py	-0.0000	-0.0000	-0.0906	0.0659	-0.0820	-0.3642	-0.7036
8	2 O	2Pz	-0.4534	0.4683	-0.0000	-0.0000	-0.0000	0.0000	0.0000
9	3 N	2S	-0.0000	-0.0000	-0.0195	-0.2610	0.3692	-1.0982	0.5610
10	3 N	2Px	-0.0000	-0.0000	-0.6982	-0.5571	0.4805	0.3471	-0.1958
11	3 N	2Py	-0.0000	-0.0000	-0.6353	0.8211	0.2093	-0.0517	0.3280
12	3 N	2Pz	0.8580	0.4976	-0.0000	-0.0000	0.0000	0.0000	-0.0000
13	4 H	1S	-0.0000	-0.0000	-0.4267	-0.3011	-1.0327	-0.1748	0.3885
14	5 H	1S	-0.0000	0.0000	0.9161	0.3370	-0.5874	0.3939	-0.1779
15	6 H	1S	0.0000	-0.0000	-0.6254	0.9111	-0.1177	0.4937	-0.0864

18 Electrons are accommodated in first nine molecular orbitals. Since our interest is confined to the study of those molecular orbitals in which oxygen and nitrogen orbitals are involved, molecular orbital 3 - 9 are of our interest. The contributions of electrons in 2px, 2py, 2pz orbitals of nitrogen and oxygen are presented in TABLE 1, under n_i, $i=n_i c^2_{ri}$. Eigen vectors different molecular orbitals of formamide are shown above-

A reference to TABLE 1 constructed using above eigen vectors indicates that total contribution of N-2px electrons is 2.13, of N-2py and N-2pz are 1.72 and 2.42 respectively. The sum of contribution of N-2px, 2py, 2pz electron is 6.28. The contribution of electrons in corresponding oxygen atom is 3.53 in O-2px; 3.26 in O-2py and 3.10 in O-2pz. The sum of electron is 9.90. In such a way to concentration of electrons at carbonyl oxygen is much more (9.90) as compared to concentration at nitrogen (6.28). The higher concentration at oxygen is the possible reason of $HCONH_2$ to coordinate through its carbonyl oxygen.

In other compounds, we have shown only summation of concentration of electrons instead of showing eigen vectors of each molecular orbitals.

Compound (2): Methyl formamide



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The number of valence electrons in methyl formamide is 24 as given below: -

2C	=	8
1O	=	6
1N	=	5
5H	=	5
		24

24 Electrons are accommodated in first twelve molecular orbitals. Since our interest is confined to the study of those molecular orbitals in which oxygen and nitrogen orbitals are involved, molecular orbital 1 and 2 have no involvement of oxygen and nitrogen hence left over. Molecular orbital 3-12 are of our interest. The contributions of electrons in 2px, 2py, 2pz orbitals of nitrogen and oxygen are presented in TABLE 2. The number of electrons in each orbital is two. The coefficient of eigen vector are given under eigen vector. The molecular orbitals in which 2px, 2py, 2pz orbitals of nitrogen and oxygen are involved are shown under M.O. (ϕ).

A reference to TABLE 2 indicates that total contribution of N-2px electrons is 3.609, of N-2py and N-2pz are 4.09 and 2.72 respectively. The sum of contribution of N-2px, 2py, 2pz electron is 10.42. The contribution of electrons in corresponding oxygen atom is 7.54 in O-2px; 6.84 in O-2py and 4.47 in O-2pz. The sum of electron is 18.87. In such a way to concentration of electrons at carbonyl oxygen is much more (18.87) as compared to concentration at nitrogen (10.42). The higher concentration at oxygen is the possible reason of $HCONHCH_3$ to coordinate through its carbonyl oxygen.

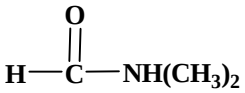
TABLE 2: Summation of contribution/concentration of electrons in methylformamide

Orbital	Sum of eigen vectors	Orbital	Sum of eigen vectors
N-2px	3.60944712	O-2px	7.54972082
N-2py	4.09208832	O-2py	6.8487005
N-2pz	2.72284448	O-2pz	4.47244232
Summation	10.42437992		18.87086364

TABLE 3: Summation of contribution/concentration of electrons in dimethylformamide

Orbital	Sum of eigen vectors	Orbital	Sum of eigen vectors
N-2px	5.89892552	O-2px	7.63076178
N-2py	5.17904928	O-2py	7.45829442
N-2pz	2.75796098	O-2pz	2.22942728
Summation	13.83593578		17.31848348

Compound (3): N, N-dimethylformamide



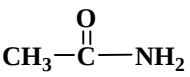
The number of valence electrons in N, N-dimethyl formamide is 30 as given below: -

3C	=	12
1O	=	6
1N	=	5
7H	=	7
		30

30 Electrons are accommodated in first nine molecular orbitals. Since our interest is confined to the study of those molecular orbitals in which oxygen and nitrogen orbitals are involved, molecular orbital 3 - 15 are of our interest. The contributions of electrons in 2px, 2py, 2pz orbitals of nitrogen and oxygen are presented in TABLE 3.

A reference to TABLE 3 indicates that total contribution of N-2px electrons is 3.6, of N-2py and N-2pz are 4.09 and 2.72 respectively. The sum of contribution of N-2px, 2py, 2pz electron is 10.42. The contribution of electrons in corresponding oxygen atom is 7.5 in O-2px; 6.8 in O-2py and 4.47 in O-2pz. The sum of electron is 48.87. In such a way to concentration of electrons at carbonyl oxygen is much more (18.87) as compared to concentration at nitrogen (10.42). The higher concentration at oxygen is the possible reason of $HCON(CH_3)_2$ to coordinate through its carbonyl oxygen.

Compound (4): Acetamide



The number of valence electrons in acetamide is 24 as given below: -

2C	=	8
1O	=	6
1N	=	5
5H	=	5
		24

24 Electrons are accommodated in first nine molecular orbitals. Since our interest is confined to the study

of those molecular orbitals in which oxygen and nitrogen orbitals are involved, molecular orbital 3-12 are of our interest. The contributions of electrons in 2px, 2py, 2pz orbitals of nitrogen and oxygen are presented in TABLE 4.

A reference to TABLE 4 indicates that total contribution of N-2px electrons is 3.01, of N-2py and N-2pz are 2.78 and 2.81 respectively. The sum of contribution of N-2px, 2py, 2pz electron is 8.62. The contribution of electrons in corresponding oxygen atom is 8.1 in O-2px; 5.16 in O-2py and 4.86 in O-2pz. The sum of electron is 18.23. In such a way to concentration of electrons at carbonyl oxygen is much more (18.23) as compared to concentration at nitrogen (8.62). The higher concentration at oxygen is the possible reason of CH_3CONH_2 to coordinate through its carbonyl oxygen.

TABLE 4: Summation of contribution/concentration of electrons in acetamide

Orbital	Sum of eigen vectors	Orbital	Sum of eigen vectors
N-2px	3.01793312	O-2px	8.19882018
N-2py	2.78574408	O-2py	5.16746952
N-2pz	2.81841282	O-2pz	4.86782402
Summation	8.62209002		18.23411372

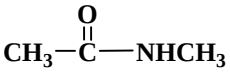
TABLE 5: Summation of contribution/concentration of electrons in methylacetamide

Orbital	Sum of eigen vectors	Orbital	Sum of eigen vectors
N-2px	5.04857088	O-2px	8.44687202
N-2py	3.9762	O-2py	7.64092232
N-2pz	3.37168512	O-2pz	3.612672
Summation	12.39645600		19.70046634

TABLE 6: Summation of contribution/concentration of electrons in dimethylacetamide

Orbital	Sum of eigen vectors	Orbital	Sum of eigen vectors
N-2px	5.33076552	O-2px	10.93061768
N-2py	4.33062450	O-2py	9.88701512
N-2pz	3.41754368	O-2pz	7.66361250
Summation	13.078934		28.4812453

Compound (5): N-methylacetamide



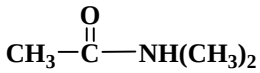
The number of valence electrons in methyl formamide is 30 as given below: -

3C	=	12
1O	=	6
1N	=	5
7H	=	7
		30

30 Electrons are accommodated in first N-methylacetamide molecular orbitals. Since our interest is confined to the study of those molecular orbitals in which oxygen and nitrogen orbitals are involved, molecular orbital 3-15 are of our interest. The contributions of electrons in 2px, 2py, 2pz orbitals of nitrogen and oxygen are presented in TABLE 5.

A reference to TABLE 5 indicates that total contribution of N-2px electrons is 5.04, of N-2py and N-2pz are 3.97 and 3.37 respectively. The sum of contribution of N-2px, 2py, 2pz electron is 12.39. The contribution of electrons in corresponding oxygen atom is 8.44 in O-2px; 7.64 inO-2py and 3.61 in O-2pz. The sum of electron is 19.70. In such a way to concentration of electrons at carbonyl oxygen is much more (19.70) as compared to concentration at nitrogen (12.39). The higher concentration at oxygen is the possible reason of $CH_3CONHCH_3$ to coordinate through its carbonyl oxygen.

Compound (6): N, N-dimethylacetamide



The number of valence electrons in N, N-dimethylacetamide is 36 as given below:

4C	=	16
1O	=	6
1N	=	5
9H	=	9
		36

36 Electrons are accommodated in first eighteen molecular orbitals. Since our interest is confined to the study of those molecular orbitals in which oxygen and nitrogen orbitals are involved, molecular orbital 3-18 are of our interest. The contributions of electrons in 2px, 2py, 2pz orbitals of nitrogen and oxygen are presented in TABLE 6.

A reference to TABLE 6 indicates that total contribution of N-2px electrons is 5.33, of N-2py and N-2pz are 4.33 and 3.41 respectively. The sum of contribution of N-2px, 2py, 2pz electron is 13.07. The contribution of electrons in corresponding oxygen atom is 10.93 in O-2px; 9.88 in O-2py and 7.66 in O-2pz.

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The sum of electron is 28.48. In such a way to concentration of electrons at carbonyl oxygen is much more (28.48) as compared to concentration at nitrogen (13.07). The higher concentration at oxygen is the possible reason of $CH_3CON(CH_3)_2$ to coordinate through its carbonyl oxygen.

Compound (7): Benzamide

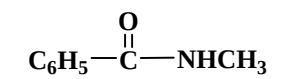
The number of valence electrons in methyl formamide is 46 as given below: -

7C	=	28
1O	=	6
1N	=	5
7H	=	7
		46

46 Electrons are accommodated in first twenty-three molecular orbitals. Since our interest is confined to the study of those molecular orbitals in which oxygen and nitrogen orbitals are involved, molecular orbital 3 - 23 are of our interest. The contributions of electrons in 2px, 2py, 2pz orbitals of nitrogen and oxygen are presented in TABLE 7.

A reference to TABLE 7 indicates that total contribution of N-2px electrons is 6.11, of N-2py and N-2pz are 6.24 and 4.88 respectively. The sum of contribution of N-2px, 2py, 2pz electron is 17.23. The contribution of electrons in corresponding oxygen atom is 11.34 in O-2px; 13.33 in O-2py and 6.77 in O-2pz. The sum of electron is 31.45. In such a way to concentration of electrons at carbonyl oxygen is much more (31.45) as compared to concentration at nitrogen (17.23). The higher concentration at oxygen is the possible reason of $C_6H_5HCONH_2$ to coordinate through its carbonyl oxygen.

Compound (8): N-methylbenzamide



The number of valence electrons in methyl formamide is 52 as given below: -

8C	=	32
1O	=	6
1N	=	5
9H	=	9
		52

TABLE 7: Summation of contribution/concentration of electrons in benzamide

Orbital	Sum of eigen vectors	Orbital	Sum of eigen vectors
N-2px	6.1117072	O-2px	11.34499
N-2py	6.2459917	O-2py	13.332415
N-2pz	4.8821875	O-2pz	6.778562
Summation	17.23988640		31.45596700

TABLE 8: Summation of contribution/concentration of electrons in methylbenzamide

Orbital	Sum of eigen vectors	Orbital	Sum of eigen vectors
N-2px	6.069128	O-2px	17.6596245
N-2py	9.03295008	O-2py	16.52780018
N-2pz	6.18042482	O-2pz	12.28394178
Summation	21.28250290		46.47136646

52 Electrons are accommodated in first twenty-six molecular orbitals. Since our interest is confined to the study of those molecular orbitals in which oxygen and nitrogen orbitals are involved, molecular orbital 3 - 26 are of our interest. The contributions of electrons in 2px, 2py, 2pz orbitals of nitrogen and oxygen are presented in TABLE 8.

A reference to TABLE 8 indicates that total contribution of N-2px electrons is 6.06, of N-2py and N-2pz are 9.03 and 6.18 respectively. The sum of contribution of N-2px, 2py, 2pz electron is 21.28. The contribution of electrons in corresponding oxygen atom is 17.65 in O-2px; 16.52 inO-2py and 12.28 in O-2pz. The sum of electron is 46.47. In such a way to concentration of electrons at carbonyl oxygen is much more (46.47) as compared to concentration at nitrogen (21.28). The higher concentration at oxygen is the possible reason of $C_6H_5HCONHCH_3$ to coordinate through its carbonyl oxygen.

Compound (9): N,N-demethylbenzamide

The Number of valence electrons in methyl formamide is 58 as given below: -

9C	=	36
1O	=	6
1N	=	5
11H	=	11
		58

58 Electrons are accommodated in first twenty-nine

molecular orbitals. Since our interest is confined to the study of those molecular orbitals in which oxygen and nitrogen orbitals are involved, molecular orbital 3 - 29 are of our interest. The contributions of electrons in 2px, 2py, 2pz orbitals of nitrogen and oxygen are presented in TABLE 9.

A reference to TABLE 9 indicates that total contribution of N-2px electrons is 9.49, of N-2py and N-2pz are 10.38 and 6.96 respectively. The sum of contribution of N-2px, 2py, 2pz electron is 26.84. The contribution of electrons in corresponding oxygen atom is 12.03 in O-2px; 20.50 inO-2py and 14.57 in O-2pz. The sum of electron is 47.11. In such a way to concentration of electrons at carbonyl oxygen is much more (47.11) as compared to concentration at nitrogen (26.84). The higher concentration at oxygen is the possible reason of $C_6H_5CON(CH_3)_2$ to coordinate through its carbonyl oxygen.

TABLE 9: Summation of contribution/concentration of electrons in dimethylbenzamide

Orbital	Sum of eigen vectors	Orbital	Sum of eigen vectors
N-2px	9.49085312	O-2px	12.0393245
N-2py	10.38403592	O-2py	20.50048512
N-2pz	6.96988448	O-2pz	14.5746005
Summation	26.84477352		47.11441012

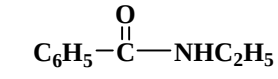
TABLE 10: Summation of contribution/concentration of electrons in ethylbenzamide

Orbital	Sum of eigen vectors	Orbital	Sum of eigen vectors
N-2px	9.48388352	O-2px	12.04030592
N-2py	10.38859362	O-2py	14.16503538
N-2pz	6.97212482	O-2pz	14.58108002
Summation	26.84460196		40.78642132

TABLE 11: Summation of contribution/concentration of electrons in diethylbenzamide

Orbital	Sum of eigen vectors	Orbital	Sum of eigen vectors
N-2px	9.30788658	O-2px	13.56788232
N-2py	9.95293728	O-2py	26.83074258
N-2pz	7.49928992	O-2pz	14.53791042
Summation	26.76011378		54.93653532

Compound (10) : N-ethylbenzamide



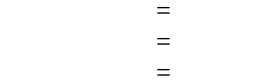
The number of valence electrons in methyl formamide is 58 as given below: -

9C	=	36
1O	=	6
1N	=	5
11H	=	11
		58

58 Electrons are accommodated in first twenty-nine molecular orbitals. Since our interest is confined to the study of those molecular orbitals in which oxygen and nitrogen orbitals are involved, molecular orbital 3 - 29 are of our interest. The contributions of electrons in 2px, 2py, 2pz orbitals of nitrogen and oxygen are presented in TABLE 10.

A reference to TABLE 10 indicates that total contribution of N-2px electrons is 9.48, of N-2py and N-2pz are 10.38 and 6.97 respectively. The sum of contribution of N-2px, 2py, 2pz electron is 26.84. The contribution of electrons in corresponding oxygen atom is 12.04 in O-2px; 14.16 inO-2py and 14.58 in O-2pz. The sum of electron is 40.78. In such a way to concentration of electrons at carbonyl oxygen is much more (40.78) as compared to concentration at nitrogen (26.84). The higher concentration at oxygen is the possible reason of $C_6H_5CONHC_2H_5$ to coordinate through its carbonyl oxygen.

Compound (11) : N, N-diethylbenzamide



The number of valence electrons in methyl formamide is 70 as given below: -

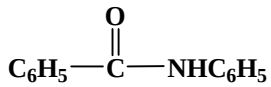
11C	=	44
1O	=	6
1N	=	5
15H	=	15
		70

70 Electrons are accommodated in first thirty-five molecular orbitals. Since our interest is confined to the study of those molecular orbitals in which oxygen and nitrogen orbitals are involved, molecular orbital 3 - 35 are of our interest. The contributions of electrons in 2px, 2py, 2pz orbitals of nitrogen and oxygen are presented in TABLE 11.

A reference to TABLE 11 indicates that total contribution of N-2px electrons is 9.30, of N-2py and N-2pz are 9.95 and 7.49 respectively. The sum of contri-

bution of N-2px, 2py, 2pz electron is 26.60. The contribution of electrons in corresponding oxygen atom is 13.56 in O-2px; 26.83 inO-2py and 14.53 in O-2pz. The sum of electron is 54.93. In such a way to concentration of electrons at carbonyl oxygen is much more (54.93) as compared to concentration at nitrogen (26.60). The higher concentration at oxygen is the possible reason of $C_6H_5CON(C_2H_5)_2$ to coordinate through its carbonyl oxygen.

Compound (12): N-phenylbenzamide



The number of valence electrons in methyl formamide is 74 as given below: -

13C	=	52
1O	=	6
1N	=	5
11H	=	11
		74

TABLE 12: Summation of contribution/concentration of electrons in enzylbenzamide

Orbital	Sum of eigen vectors	Orbital	Sum of eigen vectors
N-2px	8.144648	O-2px	18.072072
N-2py	8.495442	O-2py	15.49908488
N-2pz	5.8447805	O-2pz	10.59012242
Summation	22.48487050		44.16127930

TABLE 7: Summation of contribution/concentration of electrons in benzamide

Compound	Sum of concentration on nitrogen atom	Sum of concentration on oxygen atom
Formamide	6.28628068	9.90787658
Methylformamide	10.42437992	18.87086364
Dimethylformamide	13.83593578	17.31848348
Acetamide	8.62209002	18.23411372
Methylacetamide	12.39645600	19.70046634
Dimethylacetamide	13.078934	28.4812453
Benzamide	17.23988640	31.45596700
Methylbenzamide	21.28250290	46.47136646
Dimethylbenzamide	26.84477352	47.11441012
Ethylbenzamide	26.84460196	40.78642132
Diethylbenzamide	26.76011378	54.93653532
Benzylbenzamide	22.48487050	44.16127930

74 Electrons are accommodated in first thirty-seven molecular orbitals. Since our interest is confined to the study of those molecular orbitals in which oxygen and nitrogen orbitals are involved, molecular orbital 3 - 37 are of our interest. The contributions of electrons in 2px, 2py, 2pz orbitals of nitrogen and oxygen are presented in TABLE 12.

TABLE 14: Sum of concentration on oxygen atom of amides in decreasing order

Compound	Sum of concentration on oxygen atom
Diethylbenzamide	54.9365
Dimethylbenzamide	47.1144
Methylbenzamide	46.4714
Benzylbenzamide	44.1613
Ethylbenzamide	40.7864
Benzamide	31.456
Dimethylacetamide	28.4812
Methylacetamide	19.7005
Methylformamide	18.8709
Acetamide	18.2341
Dimethylformamide	17.3185
Formamide	9.90788

A reference to TABLE 12 indicates that total contribution of N-2px electrons is 8.14, of N-2py and N-2pz are 8.49 and 5.84 respectively. The sum of contribution of N-2px, 2py, 2pz electron is 22.48. The contribution of electrons in corresponding oxygen atom is 18.07 in O-2px; 15.49 in O-2py and 10.59 in O-2pz. The sum of electron is 44.16. In such a way to concentration of electrons at carbonyl oxygen is much more (44.16) as compared to concentration at nitrogen (22.48). The higher concentration at oxygen is the possible reason of $C_6H_5COH(C_6H_5)$ to coordinate through its carbonyl oxygen.

CONCLUSIONS

We have obtained the sum of concentration of electrons ($n_{r,i}$) on nitrogen and oxygen atoms of amides. As the sum concentration of electrons on an atom increases, its coordinating ability increases. Sum of concentration of electrons on nitrogen and oxygen atoms of amides is shown in the TABLE 13. In all the amides, the sum of concentration on oxygen of carbonyl group is greater than that on nitrogen atom. This indicates that the amides coordinate through their carbonyl oxygen instead of their nitrogen atom.

In order to find out the order of coordinating ability of amides, we have arranged all the amides in decreasing order of the sum of concentration of electrons on oxygen atom and given in the TABLE 14. It is clear that

the highest coordinating ability is in the diethylbenzamide and lowest coordinating ability is in the formamide. The order of coordinating ability in decreasing order is given below-

Diethylbenzamide>Dimethylbenzamide>Methyl benzamide > Benzylbenzamide > Ethylbenzamide> Benzamide > Dimethylacetamide > Methylacetamide> Methylformamide > Acetamide > Dimethylformamide > Formamide

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