Bond Order Indices, Valence Indices and Chemical Reactivity o-, m-, p-Nitro Phenol And o-, m-, p-Nitro Aniline

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Abstract- We have applied MINDO/3 method to o-, m-, p-Nitro Phenol, o-, m-, p-Nitro Aniline for calculating Bond Order Indices, Valence Indices and Chemical Reactivity. These parameters have been computed by MOPAC software. The concept of the bond order (multiplicity) and valence indices calculated from the semi-empirical bond order matrix is of direct chemical significance because they can be put well into correspondence with the corresponding classical chemical notions. They may be useful both in studying the links between quantum mechanics and ordinary chemistry in general and in giving better interpretation and a getting deeper understanding of the results. Gopinathan and Jug provided a quantum chemical definition of valence index as the sum of bond indices defined between two atoms since it represents the total extent of electron sharing between the atoms. We have used Gopinathan and Jug's suggestion for the study of chemical reactivity; i.e. tendency for covalent bond formation excluding nucleophilic or electrophilic reactivity.

Indexed Terms- MINDO/3, MOPAC, Bond Order Indices, Valence Indices and Chemical Reactivity

I. INTRODUCTION

The electronic structure of molecules aims to elucidate the nature of the classical chemical bond in terms of quantum chemical parameters. These parameters evaluated by MOPAC software [1] using Modified intermediate neglect of differential overlap /3 (MINDO/3) method.

Coulson [2] introduced a bond order parameter and gave an expression to relate it with the bond length for π-electron systems. Both in π-electron and all valence electron semi-empirical theories, Coulson's bond order-bond length relationship has been used with a fair amount of success. Mulliken in his work [3, 4] on population analysis used two quantities namely, the bond order and overlap population in order to define the strength of the chemical bond. Recently, a number of definitions of the above parameters for both semi-empirical and ab initio formalism have been given by several workers [5-11]. Several papers on the bond order concept in semi-empirical formalism have been published which refer to Bond quantities [12], Bond order [13,14], Bond indices or Bond overlap [15] but actually mean a property other than the valence multiplicity. Furthermore, Jug in his subsequent papers [16-19] distinguished the bond order from the bond order index. In the present paper, we have used Jug's definition for the calculation of valence and bond order indices and Mayer's definition of ab initio MO theory applied to the semi-empirical method for calculating the bond order and valence indices. It is found that both definitions lead to the same result for the above parameters. Coulson used in the definition of "free valence" for π-electron systems in MO theory and thus defining the valency of an atom as the sum of its calculated bond orders to the other atoms in a molecule but in such a definition, we come across problems that are usually associated with the definition of bond orders [20].
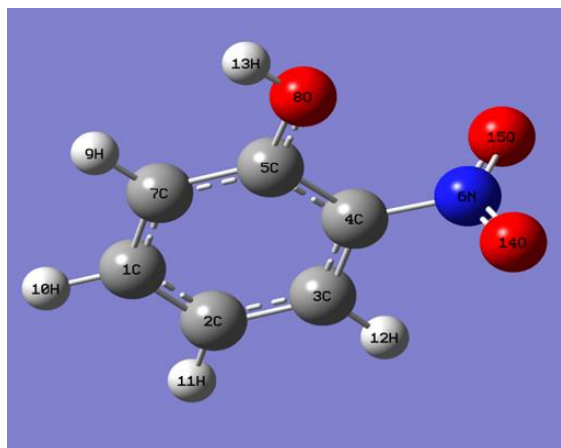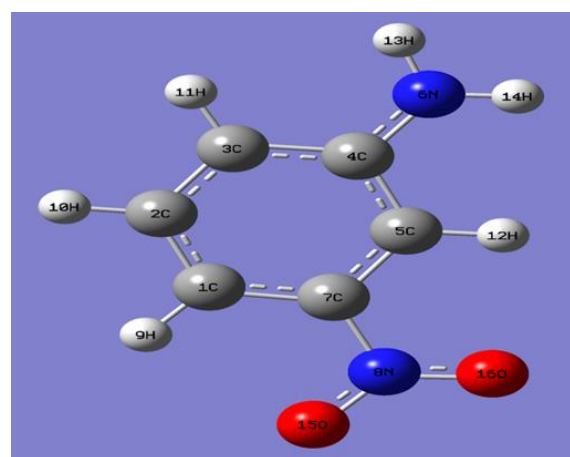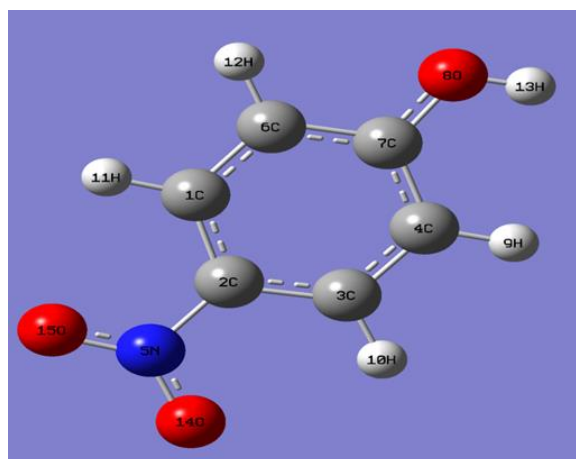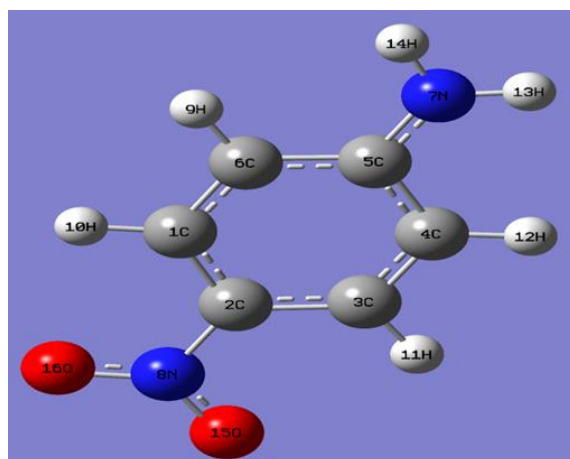
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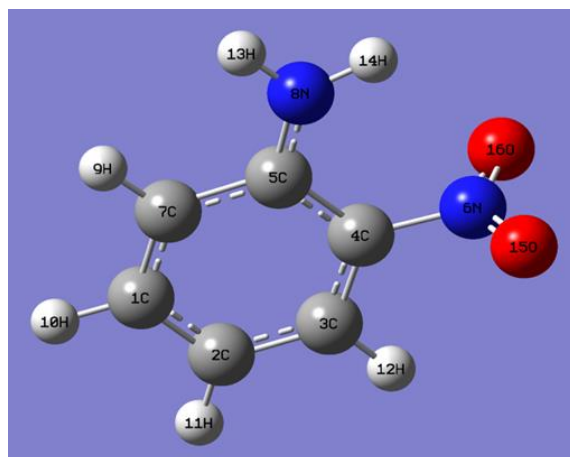
o-Nitro Aniline(iv)
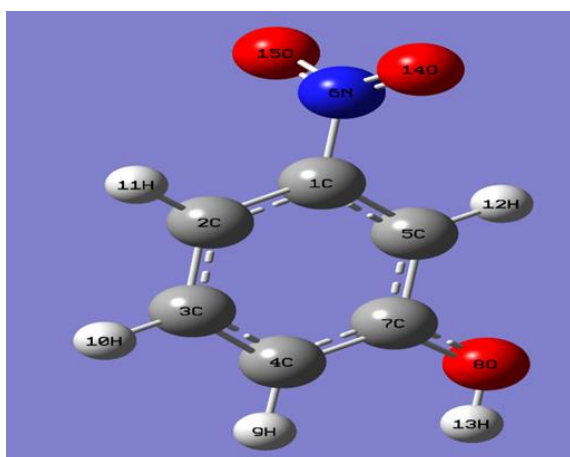
m-Nitro Phenol(ii)

m-Nitro Aniline(v)

p-Nitro Phenol(iii)

p-Nitro Aniline(vi)

Figure1(i-vi)

II. METHODOLOGY

Gopinathan and Jug defined the bond order B_{AB} between the atoms A and B as

$$B_{AB} = \sum_{i}^{+ve} \lambda_i^2 (AB)$$

And the valence index of atom A as

$$V_A = \sum_{B \neq A}^{i} \sum_{i}^{+ve} \lambda_i^2 (AB)$$

This is the first method for calculating valence indices.

Mayer defined the bond order, B_{AB}, between atoms A and B and the actual total valence, V_A, of an atom A in the molecule for a closed-shell system as,

$$B_{AB} = \sum_{\lambda \in A} \sum_{\omega \in B} (PS)_{\omega\lambda} (PS)_{\lambda\omega}$$

where the notations $\square \in A$ and $\square \in B$ indicate that the summations have to be carried out for all the basis orbitals centered on atoms A and B, respectively, P and S are the density and overlap matrices, respectively[21].

$$V_A = 2 \sum_{\mu \in A} (PS)_{\mu\mu} - \sum_{\substack{\mu,\nu \in A \\ \mu \neq \nu}} (PS)_{\mu\nu} (PS)_{\nu\mu}$$

Or

$$V_A = \sum_{\mu \in A} (2P_\mu - P_\mu^2) - \sum_{\substack{\mu,\nu \in A \\ \mu \neq \nu}} (PS)_{\mu\nu} (PS)_{\nu\mu}$$

In the present MINDO/3 semi-empirical calculations, overlap matrix S is a unit matrix, therefore,

$$B_{AB} = \sum_{\lambda \in A} \sum_{\omega \in B} (P)_{\omega\lambda} (P)_{\lambda\omega}$$

and

$$V_A = \sum_{\mu \in A} (2P_{\mu\mu} - P_{\mu\mu}^2) - \sum_{\substack{\mu,\nu \in A \\ \mu \neq \nu}} (P)_{\mu\nu} (P)_{\nu\mu}$$

For symmetrical matrix

$$(P)_{\mu\nu} = (P)_{\nu\mu} \qquad \text{and} \qquad P_{\omega\lambda} = P_{\lambda\omega}$$

and hence,

$$B_{AB} = \sum_{\lambda \in A} \sum_{\omega \in B} P_{\omega\lambda}^2$$

and

$$V_A = \sum_{\mu \in A} (2P_\mu - P_\mu^2) - \sum_{\substack{\mu,\nu \in A \\ \mu \neq \nu}} P_{\mu\nu}^2$$

Where $P_\square = P_{\square\square}$ is a diagonal matrix. Accordingly, the "free valence" of an atom A of the molecule is defined as

$$F_A = \left(V_A^r - V_A \right)$$

and the percentage "free valence" of an atom A in the molecule is defined as

$$F_A = \left(\frac{V_A^r - V_A}{V_A^r} \right) x100$$

Where V_A^r is the "reference" valency and V_A is its valency in the molecule under consideration. The reference valency is chosen to be the integer values (For example, 1 for H, 4 for C, 3 for N, and so on) around which the computed valency of A is distributed in a large number of compounds.

Gopinahtan and Jug [22, 23] in their paper suggested that if $F_A = 0$, the atom is said to have "normal valency" which is the same as the "reference valency" of the atom. When F_A is positive, the valency of atom A is not fully satisfied and this situation is called "sub valent". Similarly, when F_A is negative, the computed valency of A is exceeding the reference valency of A and the atom A is then said to be "hyper valent". In other words, an atom having zero "free valence" would be "unreactive", one with high subvalence would be "reactive" and one with high "hyper valence" value would be "anti-reactive" in the sense that it would not normally form further covalent bonds but would tend to reduce its hyper valency by breaking

or weakening the existing bonds. We have used Gopinathan and Jug's suggestion for the study of chemical reactivity; i.e., tendency for covalent bond formation excluding nucleophilic or electrophilic reactivity.

RESULT AND DISCUSSION

The Bond Order Indices, Valence Indices and Chemical Reactivity o-, m-, p-Nitro Phenol and o-, m-, p-Nitro Aniline are described separately as below:

2.1 Bond Order Indices: The values of net atomic charges at various atomic sites in units of electrons are presented in *Figure1(i-vi)*. The following conclusions are drawn from Table 1:

In all Nitro Aniline molecules, it has been seen that as the $-NH_2$ group departs from ortho to meta to para positions w.r.t. the substituents $-NO_2$ group, the bond order indices of C–C bonds adjacent to C–N ($-NO_2$) one being modified. Similar observations are also found for the other two groups of molecules. This is supported by the fact that the C–C bond, which is farthest from the C–X bond and hence almost free from the substituents effect, have the largest value of the bond order indices.

Bond order [24] in non-bonded atoms (not shown in table) is maximum for diagonal atoms in ring carbon. It is due to the migration of charge cloud from the diagonally non-bonded C–H bonds that take place to more attractive diagonally non-bonded C–C bonds.

The magnitudes of the bond order indices of the ring carbons attached with the substituent are found to have smaller values as compared to that of the C–C bonds of the ring carbons in all the molecules taken for the present study. However, this difference is nearly the same in all the molecules.

The magnitude of bond orders of N–H bonds in all the molecules taken for the study is larger than the bond orders of C (ring carbon) –H bonds. The bond order values of the substituents bond are in the order.

$C–N(–NH_2) > C–N(–NO_2) > C–OH$
However, the bond order indices of $N(–NO_2)$ –O, in o–, m–, p–Nitro Aniline and o–, m–, p–Nitro Phenol, are in the order of m–Nitro Phenol > o–Nitro Phenol > m-Nitro Aniline > p–Nitro Phenol > p-Nitro Aniline > o-Nitro Aniline, respectively.

2.2 Valence Indices: On inspection of Table 1, We notice the following features of the above parameters.

The values of valence indices of molecules considered for the present study by MINDO/3 method are found to be consistent with the classical magnitudes and are close to the integers. It is to be mentioned here that σ and π separatibility [25] is maintained as one of the NHOs remains an unchanged 2p orbital as is seen from the fact that the diagonalization does not change the occupancy of the orbital. These results are similar to earlier results obtained by MNDO and ab initio results [26, 27].

Table-1 indicates that each of the carbon atoms to which substituents are bonded has a smaller valency than the other ring carbon atoms in the same molecule. All the hydrogen atoms are found to have a valence almost equal to unity as required classically.

Table-1

Calculated Values of Bond Order indices and Valence indices

S.No.	MOLECULE	BONDS	BOND ORDER INDICES	ATOM	VALENCE INDICES
1	2	3	4	5	6
1	o-Nitro Phenol	C_1-C_2	1.3189	C_1	3.9019

		C_2-C_3	1.4663	C_2	3.9078
		C_3-C_4	1.2872	C_3	3.8924
		C_4-C_5	1.3056	C_4	3.8372
		C_5-C_7	1.2631	C_5	3.7764
		C_7-C_1	1.4635	N_6	3.843
		C_1-H_{10}	0.9369	C_7	3.8968
		C_2-H_{11}	0.9392	O_8	2.0579
		C_3-H_{12}	0.937	H_9	0.9978
		C_4-N_6	0.9135	H_{10}	1
		C_5-O_8	1.0069	H_{11}	0.9995
		N_6-O_{14}	1.4354	H_{12}	1
		N_6-O_{15}	1.4323	H_{13}	0.9307
		C_7-H_9	0.9389	O_{14}	1.7298
		O_8-H_{13}	0.8986	O_{15}	1.7261
2	m-Nitro Phenol	C_1-C_2	1.3772	C_1	3.9002
		C_2-C_3	1.3656	C_2	3.9005
		C_3-C_4	1.4304	C_3	3.9088
		C_4-C_7	1.2941	C_4	3.9058
		C_5-C_7	1.3403	C_5	3.8993
		C_5-C_1	1.3433	N_6	3.8431
		C_1-N_6	0.9089	C_7	3.8064
		C_2-H_{11}	0.9395	O_8	2.0468
		C_3-H_{10}	0.9371	H_9	0.9984
		C_4-H_9	0.9398	H_{10}	1
		C_5-H_{12}	0.9398	H_{11}	0.9997
		N_6-O_{14}	1.4351	H_{12}	0.9995
		N_6-O_{15}	1.4349	H_{13}	0.9346
		C_7-O_8	0.9935	O_{14}	1.7335
		O_8-H_{13}	0.9067	O_{15}	1.7334
3	p-Nitro Phenol	C_1-C_2	1.3463	C_1	3.892
		C_2-C_3	1.3163	C_2	3.8684
		C_3-C_4	1.4446	C_3	3.894

		C_4-C_7	1.2854	C_4	3.8971
		C_6-C_7	1.3121	N_5	3.8441
		C_6-C_1	1.414	C_6	3.8923
		C_1-H_{11}	0.9369	C_7	3.79
		C_2-N_5	0.9152	O_8	2.0581
		C_3-H_{10}	0.9371	H_9	0.9979
		C_4-H_9	0.9391	H_{10}	1
		N_5-O_{14}	1.4331	H_{11}	1
		N_5-O_{15}	1.4333	H_{12}	0.999
		C_6-H_{12}	0.9393	H_{13}	0.9342
		C_7-O_8	1.0042	O_{14}	1.7285
		O_8-H_{13}	0.9061	O_{15}	1.7283
4	o-Nitro Aniline	C_1-C_2	1.2502	C_1	3.8935
		C_2-C_3	1.5327	C_2	3.9019
		C_3-C_4	1.2123	C_3	3.8857
		C_4-C_5	1.2252	C_4	3.7894
		C_5-C_7	1.1813	C_5	3.8391
		C_7-C_1	1.5333	N_6	3.8492
		C_1-H_{10}	0.9361	C_7	3.8831
		C_2-H_{11}	0.939	N_8	3.3271
		C_3-H_{12}	0.9376	H_9	0.9997
		C_4-N_6	0.9937	H_{10}	0.9999
		C_5-N_8	1.2293	H_{11}	0.9995
		N_6-O_{15}	1.4041	H_{12}	0.9997
		N_6-O_{16}	1.3759	H_{13}	0.9925
		C_7-H_9	0.9395	H_{14}	0.9835
		N_8-H_{13}	0.9559	O_{15}	1.6959
		N_8-H_{14}	0.9416	O_{16}	1.6703
5	m-Nitro Aniline	C_1-C_2	1.428	C_1	3.8984
		C_2-C_3	1.373	C_2	3.9084
		C_3-C_4	1.3556	C_3	3.8979
		C_4-C_5	1.3691	C_4	3.9006
		C_5-C_7	1.2935	C_5	3.885

		C_7-C_1	1.2771	N_6	3.8415
		C_1-H_9	0.9397	C_7	3.878
		C_2-H_{10}	0.9368	N_8	3.2056
		C_3-H_{11}	0.9393	H_9	0.9998
		C_4-N_6	0.9097	H_{10}	1
		C_5-H_{12}	0.9396	H_{11}	0.9998
		N_6-O_{15}	1.4334	H_{12}	0.9998
		N_6-O_{16}	1.4339	H_{13}	0.9919
		C_7-N_8	1.1194	H_{14}	0.9918
		N_8-H_{13}	0.9547	O_{15}	1.7303
		N_8-H_{14}	0.9543	O_{16}	1.7308
6	p-Nitro Aniline	C_1-C_2	1.3163	C_1	3.893
		C_2-C_3	1.3198	C_2	3.8591
		C_3-C_4	1.4468	C_3	3.8932
		C_4-C_5	1.26	C_4	3.8859
		C_5-C_6	1.2589	C_5	3.8645
		C_6-C_1	1.4495	C_6	3.8863
		C_1-H_{10}	0.9366	N_7	3.2417
		C_2-N_8	0.9205	N_8	3.8426
		C_3-H_{11}	0.9367	H_9	0.9996
		C_4-H_{12}	0.9392	H_{10}	1
		C_5-N_7	1.1508	H_{11}	1
		C_6-H_9	0.9394	H_{12}	0.9996
		N_7-H_{13}	0.9543	H_{13}	0.9918
		N_7-H_{14}	0.9545	H_{14}	0.9919
		N_8-O_{15}	1.429	O_{15}	1.722
		N_8-O_{16}	1.4297	O_{16}	1.7227

In all the molecules taken for the present study, the valence index of the ring carbon to which the substituent group is attached is found to be the least than other ring carbon atoms.

The valence index of Nitrogen and Oxygen atoms departs from its normal valency in all the molecules having $-NO_2$ group. However, where the nitrogen valence indices are found large than its normal valency, the oxygen valence index is found to be less than its normal valency. The reason depends upon the electronegativity of oxygen and nitrogen atoms.

2.3 Chemical Reactivity: The percentage "excess valence" or "valence defect" of different atoms in molecules taken for study and their affinity for

covalent bond formation are listed in Table .2. In most "normal" compounds the valency of carbon is close to the traditional value of 4, which we, therefore, consider as the reference valency of a carbon atom. Similarly, the reference valence of oxygen, nitrogen and hydrogen atoms are taken as 1, 3 and 1 respectively, for computing "excess valence" or "valence defect". It is observed that the valency of carbon atom in all the molecules considered for the present study is close to (but less) its traditional value 4. In other words, there is no hypervalency of carbon and the octet rule is not violated in molecules taken for the present study. All the hydrogen atoms in each molecule have either normal valency or they have very small sub-valence values and as such these atoms are also "unreactive". The nitrogen atoms in all the molecules containing –NH$_2$ group have been observed to possess the "hypervalency" but the amount of hyper valency is so small that they are not supposed to weaken or break the existing bonds and hence have been termed as "unreactive".

Table-2
Calculated Values of Chemical Reactivity

S.No.	Molecules	Atoms	Excess Valence (%)			Predicted Affinity for Covalent Bond Formation
			Hyper	Normal	Sub	
1	2	3	4	5	6	7
1	o-Nitro Phenol	C$_1$	------	------	+2.45	"
		C$_2$	------	------	+3.31	"
		C$_3$	------	------	+2.69	"
		C$_4$	------	------	+4.07	"
		C$_5$	------	------	+5.59	"
		N$_6$	-28.1	------	------	Reactive
		C$_7$	------	------	+2.58	Unreactive
		O$_8$	-2.90	------	------	"
		H$_9$	------	------	+0.22	"
		H$_{10}$	------	------	+0.00	"
		H$_{11}$	------	------	+0.05	"
		H$_{12}$	------	------	+0.00	"
		H$_{13}$	------	------	+6.93	"
		O$_{14}$	------	------	+13.51	Slightly reactive
		O$_{15}$		------	+13.70	"
2	m-Nitro Phenol	C$_1$	------	------	+2.50	Unreactive
		C$_2$	------	------	+2.49	,,
		C$_3$	------	------	+2.28	,,
		C$_4$	------	------	+2.36	,,
		C$_5$		------	+2.77	,,
		N$_6$	-28.1	------	------	Reactive
		C$_7$	------	------	+4.84	Unreactive
		O$_8$	-2.34	------	------	"
		H$_9$	------	------	+0.16	"
		H$_{10}$	------	------	+0.00	"
		H$_{11}$	------	------	+0.03	"
		H$_{12}$	------	------	+0.05	"
		H$_{13}$	------	------	+6.54	"
		O$_{14}$	------	------	+13.33	Slightly reactive

		O_{15}	------	------	+13.33	,,
3	p-Nitro Phenol	C_1			+2.7	Unreactive
		C_2	------		+3.29	,,
		C_3	------	------	+2.65	,,
		C_4	------	------	+2.57	,,
		N_5	-28.14	------	------	Reactive
		C_6	------	------	+2.69	Unreactive
		C_7	------	------	+5.25	,,
		O_8	-2.91	------	------	,,
		H_9	------	------	+0.21	,,
		H_{10}	------	------	+0.00	,,
		H_{11}	------	------	+0.00	,,
		H_{12}	------	------	+0.01	,,
		H_{13}	------	------	+6.58	,,
		O_{14}	------	------	+13.58	Slightly reactive
		O_{15}	------	------	+13.59	"
4	o-Nitro Aniline	C_1	------	------	+2.66	Unreactive
		C_2	------	------	+2.45	,,
		C_3	------		+2.86	,,
		C_4	------	------	+5.27	,,
		C_5	------	------	+4.02	,,
		N_6	-28.31	------	------	Reactive
		C_7	------	------	+2.92	Unreactive
		N_8	-10.9	------	------	Slightly reactive
		H_9	------	------	+0.03	Unreactive
		H_{10}	------	------	+0.01	,,
		H_{11}	------	------	+0.05	,,
		H_{12}	------	------	+0.03	,,
		H_{13}	------	------	+0.75	,,
		H_{14}	------	------	+1.65	,,
		O_{15}	------	------	+15.21	Slightly reactive
		O_{16}	------	------	+16.49	,,
5	m-Nitro Aniline	C_1	------	------	+2.54	Unreactive
		C_2	------	------	+2.29	,,
		C_3	------	------	+2.55	,,
		C_4	------		+2.49	,,
		C_5	------	------	+2.88	,,
		N_6	-28.05	------	------	Reactive
		C_7	------	------	+3.05	Unreactive
		N_8	-6.85	------	------	,,
		H_9	------	------	+0.02	
		H_{10}	------	------	+0.00	Unreactive
		H_{11}	------	------	+0.02	,,
		H_{12}	------	------	+0.02	,,
		H_{13}	------	------	+0.81	,,
		H_{14}	------	------	+0.82	,,
		O_{15}	------	------	+13.49	Slightly reactive

		O_{16}	------	------	+13.46	,,
6	p-Nitro Aniline	C_1	------	------	+2.68	Unreactive
		C_2	------	------	+3.52	,,
		C_3	------	------	+2.67	
		C_4	------	------	+2.85	,,
		C_5	------	------	+3.39	,,
		C_6	------	------	+2.84	,,
		N_7	-8.06	------	------	,,
		N_8	-28.09	------	------	Reactive
		H_9	------	------	+0.04	Unreactive
		H_{10}	------	------	+0.00	,,
		H_{11}	------	------	+0.00	,,
		H_{12}	------	------	+0.04	,,
		H_{13}	------	------	+0.82	,,
		H_{14}	------	------	+0.81	,,
		O_{15}	------	------	+13.9	Slightly reactive
		O_{16}	------	------	+13.87	,,

CONCLUSION

- The magnitude of bond orders of N–H bonds in all the molecules taken for the study is larger than the bond orders of C (ring carbon) –H bonds. The bond order values of the substituents bond are in the order.

    $C–N(–NH_2) > C–N(–NO_2) > C–OH$
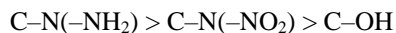
- However, the bond order indices of $N(–NO_2)$ –O, in o–, m–, p–Nitro Aniline and o–, m–, p–Nitro Phenol, are in the order of m–Nitro Phenol > o–Nitro Phenol > m-Nitro Aniline > p–Nitro Phenol > p-Nitro Aniline > o-Nitro Aniline, respectively.

- These features of valence indices in MINDO/3 study are even better than earlier studies by MNDO and ab initio methods.

- A very little deviation from the integral values is due to the bond polarity and delocalization effects though the valency depends on the orbital occupancies, the intra-atomic partial bond order terms have to be subtracted from the sum of these orbital occupancies in order to get the numerical value of the valency.

- The valency of an atomic orbital in a molecule may be defined as the sum of the squares of its density matrix elements with the orbitals on all other atoms.

- The percentage sub valences or hyper valences of all the atoms are so small that they can be treated as almost unreactive in all the cases as far as their affinity for covalent bond formation is concerned.

- The difference between the classical valence (reference valence) and the sum of the bond order indices (actual valence indices) may be attributed to delocalization and polarization effects.

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