

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.

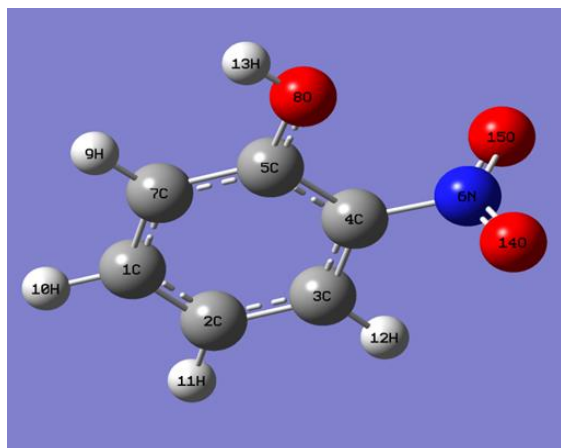
Indexed Terms- MINDO/3, MOPAC, Bond Order Indices, Valence Indices and Chemical Reactivity

I. INTRODUCTION

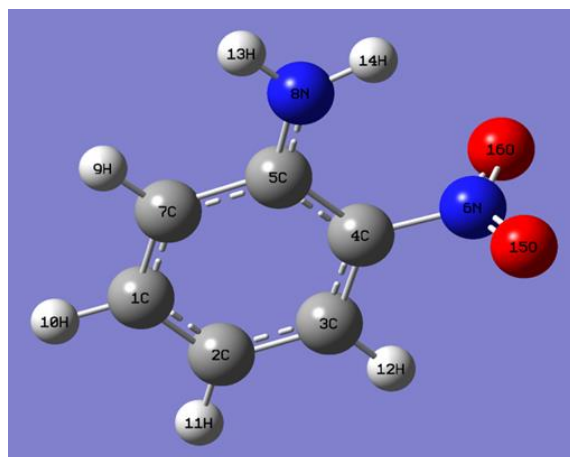
The electronic structure of molecules aims to elucidate the nature of the classical chemical bond in terms of quantum chemical parameters. These parameters evaluated by MOPAC software [1] using Modified intermediate neglect of differential overlap /3 (MINDO/3) method.

Coulson [2] introduced a bond order parameter and gave an expression to relate it with the bond length for

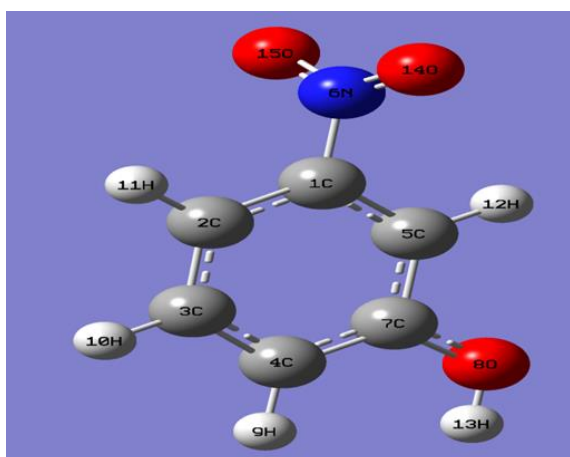
π -electron systems. Both in π -electron and all valence electron semi-empirical theories, Coulson's bond order-bond length relationship has been used with a fair amount of success. Mulliken in his work [3, 4] on population analysis used two quantities namely, the bond order and overlap population in 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].



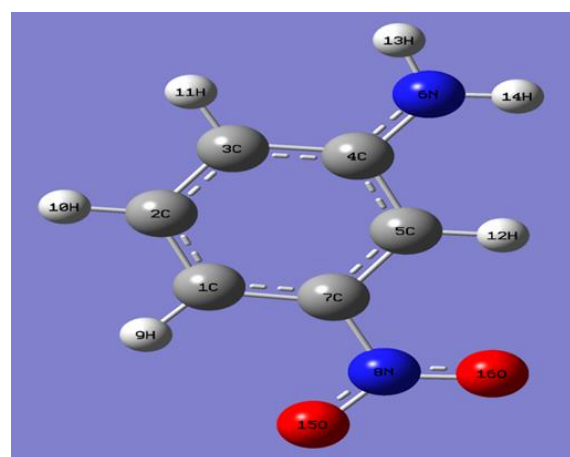
o-Nitro Phenol(i)



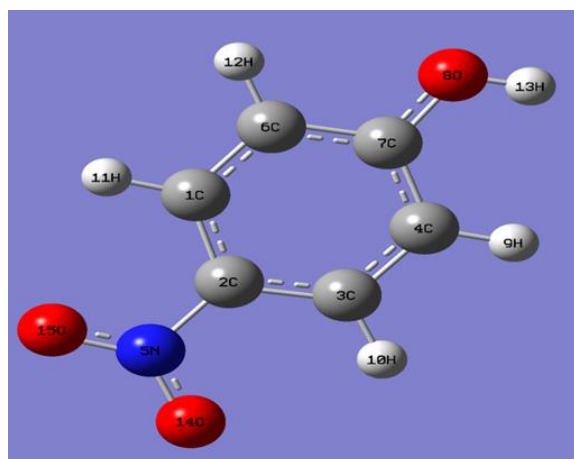
o-Nitro Aniline(iv)



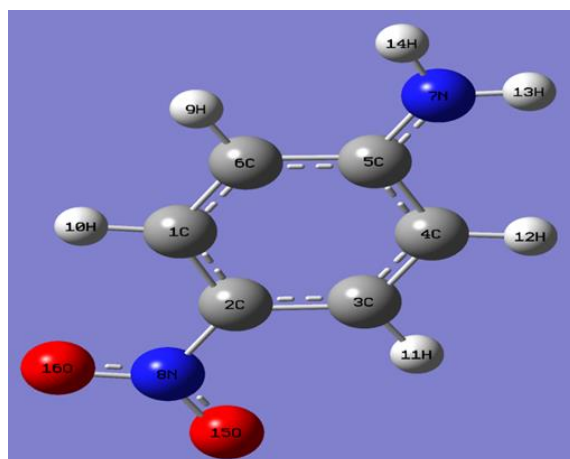
m-Nitro Phenol(ii)



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 $\lambda \in A$ and $\omega \in B$ 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

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

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

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

and hence,

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

and

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

Where $P_{\square\square} = P_{\square\square}$ is a diagonal matrix.

Accordingly, the “free valence” of an atom A of the molecule is defined as

$$F_A = (V_A^r - V_A)$$

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

$$F_A = \left(\frac{V_A^r - V_A}{V_A^r} \right) \times 100$$

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.

Gopinathan 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 -NH₂ group departs from ortho to meta to para positions w.r.t. the substituents -NO₂ group, the bond order indices of C-C bonds adjacent to C-N (-NO₂) 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.



However, the bond order indices of N(-NO₂) -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 separability [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 -NO₂ 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 –NH₂ 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

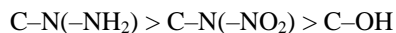
S.No.	Molecules	Atoms	Excess Valence (%)			Predicted Affinity for Covalent Bond Formation
			Hyper	Normal	Sub	
1	2	3	4	5	6	7
1	o-Nitro Phenol	C ₁	-----	-----	+2.45	”
		C ₂	-----	-----	+3.31	”
		C ₃	-----	-----	+2.69	”
		C ₄	-----	-----	+4.07	”
		C ₅	-----	-----	+5.59	”
		N ₆	-28.1	-----	-----	Reactive
		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.



- However, the bond order indices of N(–NO₂)–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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