



# MINDO/3 EVALUATION OF BOND ORDER AND BOND LENGTH IN SOME HETRO-DI-SUBSTITUTED BENZENES

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## ABSTRACT

A similarity transformation is applied to the MINDO/3 density matrix to evaluate bond orders in some hetro-di-substituted benzenes involving  $-NH_2$  &  $-Cl$  as substituent. The bond orders so evaluated are used to estimate bond lengths using Coulson's bond order-bond length relationship in the ground state. The computed values of bond length are found very close to their classical values. It seems that bond orders could be used for the qualitative prediction of molecular geometry.

**Keywords:** Bond length, bond order, density matrix, geometry optimization, MINDO/3.

## I. INTRODUCTION

In a theoretical approach to determine molecular geometry, one may either use minimization of energy with respect to internal co-ordinates or a bond order-bond length relationship. Using the former approach, molecular geometries have been predicted both at semi-empirical and ab-initio levels employing gradient techniques for complete geometry optimization.<sup>1-3</sup> Even bigger size molecules like benzene and naphthalene derivatives have been studied.<sup>4-7</sup> These studies are very important because they are very helpful in understanding the chemical reactions and the transition state structures of molecules.<sup>8,9</sup> Although these studies are very important, they are very expensive and alternative methods of predicting the molecular geometries are, therefore, desirable.

In previous studies, Coulson's bond order – bond length relationship<sup>10-11</sup> coupled with the usual virtual orbital description of the excited states has been used to estimate changes in bond-lengths occurring during molecular excitation of some substituted benzenes involving F, OH and  $NH_2$  as substituents. The agreement between the calculated and experimental results was quite satisfactory. The results were helpful in resolving some ambiguities in the results of a band contour analysis by Cvitas et al.<sup>12</sup>

The MNDO method has been found to be reliable for calculating potential energy surfaces of larger molecules in the semi-empirical formalism.<sup>13, 14</sup> Schroder and Thiel<sup>15</sup> have shown that this method usually qualitatively reproduces the features of ab initio potential surfaces and transition structures for some thermal reactions.<sup>16</sup>

It was therefore, thought worthwhile to use modified intermediate neglect of differential overlap, third version (MINDO/3) bond orders, obtained by using a similarity transformation,<sup>17-19</sup> to estimate the bond lengths of some

hetro-di-substituted benzens by using Coulson's bond order-bond length relationship. It should be mentioned that the present bond order expression, due to Mulliken<sup>20</sup> for orthogonalized AOs is not invariant under co-ordinate transformation. Several papers on the concentration of the charges in the regions of classical bonds have been published which refer to bond quantities, bond order, bond indices or bond overlap but actually mean a property other than the valence multiplicity. Further-more, Jug in his consequent papers<sup>21-23</sup> distinguished the bond order from the bond index.<sup>24</sup> The former is based on the calculation of the eigen values by diagonalising the inter-atomic part of the density matrix whereas the later is the function of the square of the density matrix elements.

## II. COMPUTATIONAL DETAILS

The matrix P' is constructed from P by making it's similarity transformation. The use of hybrid orbitals in place of atomic orbitals provides maximum overlap charge along a bond.

All the molecules were considered to be planar with all bond angles at 120<sup>0</sup>. The carbon atoms were considered to be in an sp<sup>2</sup> hybridized state. Nitrogen, Chlorine and Hydrogen atoms were considered in unhybridized states to reduce the complexity of calculation. Calculations were performed on a personal computer using the MOPAC program obtained from Q.C.P.E. at the computer center of Paliwal (P.G.) College, Shikohabad.

The total bond order were obtained by summing the  $\sigma$  and  $\pi$  components. The  $\pi$ -bond orders were taken directly from the matrix P as they were unaffected by the similarity transformation. The  $\sigma$ -bond orders were taken from the matrix P'. The sum of all the off-diagonal-terms of matrix P' between two-bonded atoms provide the required  $\sigma$ -bond order between them. The bond lengths were computed from total bond orders using Coulson's bond order-bond length relationship. This relationship is given by :

$$x = s - \frac{(s - d)}{[1 + K(2 - p)/(p - 1)]}$$

Where : x is the required bond length corresponding to the total bond order p; s and d are the lengths of single and double bonds respectively for a given pair of atoms and K = 0.765 for C – C pairs.

## III. RESULT AND DISCUSSIONS

The calculated semiempirical MINDO/3  $\sigma$  and  $\pi$  bond orders using similarity transformation have been reported in Table-1 for hetro di- substituted benzenes involving – Cl and – NH<sub>2</sub> as substituents. It is clear from the table that the  $\sigma$  bond orders for C – C bonds for all the molecules are less than 1, which is the bond order for these bonds in benzene. This indicates some lengthening of C – C bonds in these molecules as compared to benzene itself. The lengthening of C – Cl bond in o-Chloro Amine is more pronounced as compared to their respective m – & p – Chloro Amines.

Although, the overlap between two hybrids, one belonging to each carbon atom and directed along the bond, contribute most to the total  $\sigma$  bond order, the other eight contributions, though very small, can not be neglected. These positive or negative contributions may contribute to increase or decrease the total  $\sigma$  bond orders significantly and thus affect the bond length.

The  $\sigma$  portion of C – Cl bond orders are smaller than the corresponding C – C ring bonds which justifies the polarization of C – Cl bonds. This resulted the total C – C ring bond order maximum adjacent to the carbon atom containing – Cl as substituted group.

The bond lengths of C – C in o-, m- & p- Chloro Amine computed from the present MINDO/3 bond orders using Coulson's bond order – bond length relationship have been presented in Table 2.

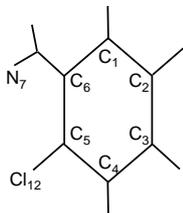
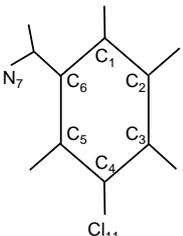
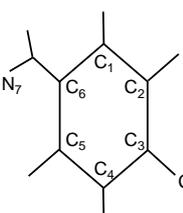
The inspection of the table shows that in all chloro amines, the bond lengths of bonds C<sub>5</sub> – C<sub>6</sub> and C<sub>6</sub> – C<sub>1</sub> are approximately same and larger in comparison to the other ring C – C bond lengths. Another fact concluded from the table is that as the substituent – Cl departs from ortho to meta to para positions with respect to – NH<sub>2</sub> group, the bond length of the bond C<sub>5</sub> – C<sub>6</sub> tends to decrease.

Generally, there is a fundamental difficulty in predicting bond lengths while discussing the molecular geometry and molecular angles by considering overlaps. This, of course does not contradict the existence of bond overlap – bond length correlation. Since, the criterion of maximum overlapping deals with attractive forces and says nothing about repulsive forces that operate in a bond, It is not able to predict bond lengths, which depend upon the equilibrium between these two sets of forces. Because, it is necessary to assume the geometrical shape of a molecule before applying the maximum overlap method, this does not mean that the method is not capable for discussing lengths starting with a standard set of bond lengths and using a bond order – bond length correlation one can get information on the variations of the calculated bond lengths from the assumed values.

#### **IV. CONCLUSION**

It is rather preposterous to believe that the process adopted in the present calculations of bond lengths is superior or may replace a careful geometry optimization but can be considered as a useful guide for structural determination of these ring shaped molecules.

TABLE –1

MINDO/3 Bond Orders <sup>a</sup>			BOND ORDER		
S.No.	MOLECULE	BOND	$\sigma$	$\pi$	Total
1.	o-Chloro Amine 	C <sub>1</sub> – C <sub>2</sub>	0.919464	0.665539	1.585003
		C <sub>2</sub> – C <sub>3</sub>	0.919628	0.670952	1.590580
		C <sub>3</sub> – C <sub>4</sub>	0.895052	0.644675	1.539727
		C <sub>4</sub> – C <sub>5</sub>	0.926156	0.687778	1.613934
		C <sub>5</sub> – C <sub>6</sub>	0.897599	0.588020	1.485619
		C <sub>6</sub> – C <sub>1</sub>	0.901400	0.617901	1.519301
		C <sub>5</sub> – Cl <sub>12</sub>	0.853370	0.133264	0.986634
		C <sub>6</sub> – N <sub>7</sub>	1.197016	0.404894	1.601910
		2.	m-Chloro Amine 	C <sub>1</sub> – C <sub>2</sub>	0.924542
C <sub>2</sub> – C <sub>3</sub>	0.901535			0.651762	1.553297
C <sub>3</sub> – C <sub>4</sub>	0.916028			0.646804	1.562832
C <sub>4</sub> – C <sub>5</sub>	0.923510			0.667390	1.590900
C <sub>5</sub> – C <sub>6</sub>	0.891777			0.597261	1.489038
C <sub>6</sub> – C <sub>1</sub>	0.904967			0.588894	1.493861
C <sub>4</sub> – Cl <sub>11</sub>	0.859963			0.171121	1.031084
C <sub>6</sub> – N <sub>7</sub>	1.185782			0.435674	1.621456
3.	p-Chloro Amine 	C <sub>1</sub> – C <sub>2</sub>	0.912722	0.683136	1.595858
		C <sub>2</sub> – C <sub>3</sub>	0.914177	0.648489	1.562666
		C <sub>3</sub> – C <sub>4</sub>	0.914285	0.656937	1.571222
		C <sub>4</sub> – C <sub>5</sub>	0.909095	0.674785	1.583880
		C <sub>5</sub> – C <sub>6</sub>	0.913049	0.909178	1.522227
		C <sub>6</sub> – C <sub>1</sub>	0.905399	0.601641	1.507040
		C <sub>3</sub> – Cl <sub>10</sub>	0.883442	0.139621	1.023063
		C <sub>6</sub> – N <sub>7</sub>	1.192359	0.402918	1.595277

<sup>a</sup>- C – H bond orders are not listed as they assume almost identical values in all molecules.

TABLE –2

Bond	Bond Length		
	o-Chloro Amine	m-Chloro Amine	p-Chloro Amine
C <sub>1</sub> – C <sub>2</sub>	1.4103	1.4057	1.4083
C <sub>2</sub> – C <sub>3</sub>	1.4092	1.4164	1.4146
C <sub>3</sub> – C <sub>4</sub>	1.4190	1.4145	1.4129
C <sub>4</sub> – C <sub>5</sub>	1.4050	1.4092	1.4106
C <sub>5</sub> – C <sub>6</sub>	1.4295	1.4288	1.4223
C <sub>6</sub> – C <sub>1</sub>	1.4229	1.4279	1.4253



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