Bond Order, Oxidation Number and Dipole Moments Of o–, m–, p–Cresol – A Semi–Empirical Calculations

DEEPAK KULSHRESHTHA[1], RAJEEV GUPTA[2], P. K SINGH[3], O. P. SINGH[4]

[1, 2, 4]*Department of Physics, Paliwal (P.G.) College, Shikohabad*
[3]*Department of Physics, M. L. K. (P.G.) College, Balrampur*

Abstract- We have applied MINDO/3 method to o–, m–, p– Cresol for calculating bond order, oxidation number and dipole moments. These properties have been calculated by MOPAC software and Gaussian 03. The study concluded that bond order indices of o–, m–, p– Cresol calculated by MINDO/3 are similar to the bond order index defined by Mayer [2,3] and the MINDO/3 C–H bond order indices are found to be less than this classical value 1. Oxidation number calculated by Giambiagi's method [4]. It seems to be indicative of their orientational behavior. The dipole moment should increase with decreasing electronegativity of substituent [5].

Indexed Terms- Cresol, MINDO/3, MOPAC, Bond Order, Oxidation Number, Dipole Moment.

I.   INTRODUCTION

The concept of bond order 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. Coulson [1] introduced a bond order parameter and gave an expression to relate it with the bond length for π electron system. Mulliken in his work [2,3] on population analysis used two quantities namely, the bond order and overlap population in order to define the strength of chemical bond. A number of definitions of the bond order given by several workers [4-9-]. Mayer can be considered as ab intio generalization of Wiberg's bond index.

In the present study we have used Jug's definition for the bond order indices and Mayer's definition of ab initio MO theory applied to semi–empirical method for calculating the bond order. It is found that both the definitions lead to the same result for the above parameters. Bond border is a measure of net number of bonding electron pair [10]. Another approach of bond order calculations was in 1939, when Coulson derived a definition of bond order based on the molecular orbital theory (MOT) that said ''the electrons are allocated to orbitals which spread over the molecule as a whole, subsequently the sharing and delocalization of the electrons are emphasized'' [11].

when two atoms share a pair of the electrons, it is generally true, unless the atoms are identical that the electrons will be drawn more closely to one of the atoms than to the other. As a result, the electrical centres of the negative charges do not coincide with the centre of the positive charges. In general, therefor, every covalent bond between two atoms will associated with a dipole moment; the value of this moment is equal to the product of the electronic charge and the relative displacement of the positive and negative electrical centres.

II.   METHODOLOGY

For present study the molecular modeling and geometry optimization were carried out with MOPAC software [12] using MINDO/3 program to evaluate various parameter e.g., bond order and dipole moment of every atom of o–, m–, p–Cresol have been calculated by softness calculators. Oxidation number calculation carried out with Gaussian 03[13] abinitio software using MINDO/3 program.

Gopinathan and Jug (1983 a) defined the bond order B_{AB} between the atoms A and B as

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

Mayer [14, 15] defined the bond order, B_{AB}, between atoms A and B in the molecule for a closed shell system as,

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

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

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

For symmetrical matrix
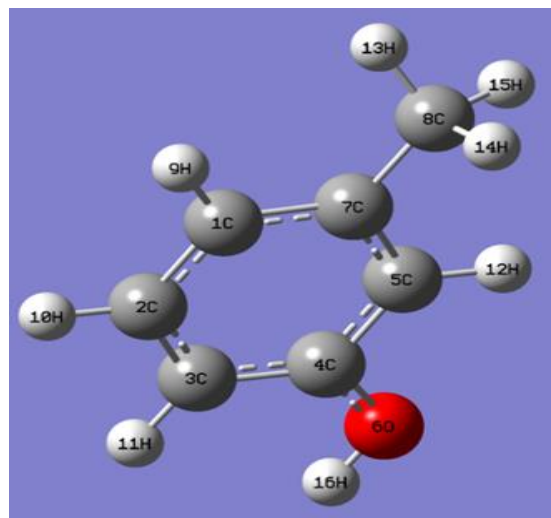
$$(P)_{\mu\nu} = (P)_{\nu\mu}$$

and

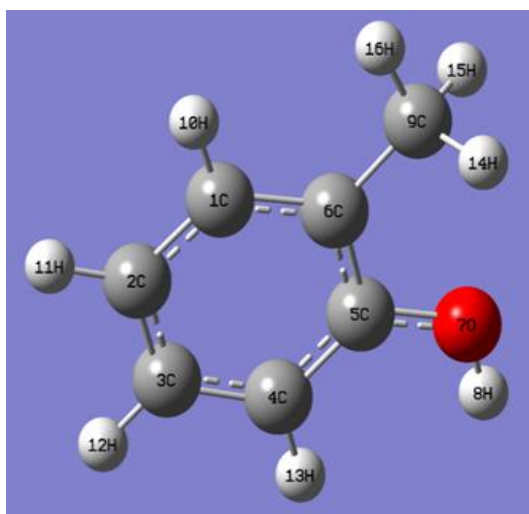$$(P)_{\omega\lambda} = (P)_{\lambda\omega}$$

and   hence,

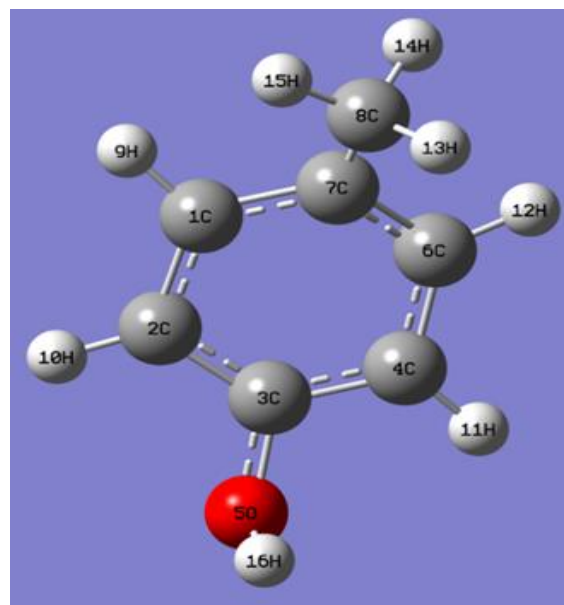$$B_{AB} = \sum_{\lambda \epsilon A} \sum_{\lambda \in B} (P^2)_{\omega\lambda}$$

Bond Order is a measure of the net number of bonding electron pairs i.e., it gives the

m–Cresol(ii)

o–Cresol(i)

p–Cresol(iii)

difference between the total number of bonding and antibonding pairs of electrons shared between the two atoms concerned.

Giambiagi, et al. (1984) [16] suggested the definition of oxidation number of an atom A in molecule as

$$\text{Oxidation number} = \left| \frac{|Q_A|}{Q_A} \right| \sum_{A \neq B} B_{AB}; A \neq B$$

Where Q_A is the net charge in A and the sum is carried over the atoms with polarity different from that of atom A

Q_A is defined as $Q_A = N_A - q_A$

Where N_A is the number of valence electrons which atom A furnishes to the molecule and q_A the electronic charge in A, i.e.

$$q_a = \sum_{a \in A} q_a$$

This sum is carried out over all the atomic orbital electronic charges of atoms A. B_{AB} is the bond order index between atoms A and B MINDO/3 program was extended to incorporate the suggestions of Giambiagi et al. (1984).

Dipole moments of bonds are regarded as vectorial in character, i.e., they have magnitude and direction both, and the direction of the bond shows its direction. The dipole moment of the molecule as a whole may be regarded as equal to vector sum of the individual bond moments. The electronic dipole moment is an important molecular property closely related to charge distribution in the various orbitals of the molecule [17].

RESULT AND DISCUSSION

The molecules taken for the present study are presented in *Figure1(i–iii)*. The bond order indices, oxidation number and dipole moment of o–, m–, p– Cresol are described separately as below:

Bond order indices: The calculated bond order indices are listed in Table 1. Magnitudes of the bond orders in between different atoms are almost close to the values required classically [18,19]. The magnitudes of C (ring carbon)–H bond orders are not identical in any of the molecules considered for the present study. These results are similar for above indices also have been reported in ab initio calculations. This is due to the fact that C–(–CH$_3$) are more electronegative than hydrogen and therefore, the electronic charge flows from C–H bond regions to attractive C–C–CH$_3$ bond regions making C–H bonds slightly less than unity. Furthermore, the magnitude of different C–H bond orders depend upon their relative positions with respect to the substituent.

In o–, m–, p– Cresol, the change in O–H bond order indices is insignificant. As far CH$_3$ group is concerned the out of plane C–H bond order indices in all the o–, m–, p– Cresol are less than the inplane C–H bond order indices. C–O bond order index are in the order of ortho < meta < para. Furthermore, as the C–X bond departs from ortho to para, the C–C (–CH$_3$) bond order index is modified and found to be in the order of para > ortho > meta.

Table 1: Bond orders of o–, m–, p– Cresol.

o–Cresol		m–Cresol		p– Cresol	
Bonds	Bond Order Indices	Bonds	Bond Order Indices	Bonds	Bond Order Indices
C$_1$–C$_2$	1.3886	C$_1$–C$_2$	1.4061	C$_1$–C$_2$	1.3974
C$_2$–C$_3$	1.3936	C$_2$–C$_3$	1.3917	C$_2$–C$_3$	1.3305
C$_3$–C$_4$	1.3918	C$_3$–C$_4$	1.3278	C$_3$–C$_4$	1.3025
C$_4$–C$_5$	1.3364	C$_4$–C$_5$	1.3202	C$_4$–C$_6$	1.4294
C$_5$–C$_6$	1.2825	C$_5$–C$_7$	1.3829	C$_6$–C$_7$	1.3435
C$_6$–C$_1$	1.3812	C$_7$–C$_1$	1.3512	C$_7$–C$_1$	1.3729
C$_1$–H$_{10}$	0.9371	C$_1$–H$_9$	0.9395	C$_1$–H$_9$	0.9365
C$_2$–H$_{11}$	0.9392	C$_2$–H$_{10}$	0.9366	C$_2$–H$_{10}$	0.9397
C$_3$–H$_{12}$	0.9363	C$_3$–H$_{11}$	0.9396	C$_3$–O$_5$	0.9818
C$_4$–H$_{13}$	0.9394	C$_4$–O$_6$	0.9806	C$_4$–H$_{11}$	0.9402
C$_5$–O$_7$	0.9798	C$_5$–H$_{12}$	0.9413	C$_6$–H$_{12}$	0.9370
O$_7$–H$_8$	0.9105	O$_6$–H$_{16}$	0.9118	O$_5$–H$_{16}$	0.9110
C$_6$–C$_9$	0.9855	C$_7$–C$_8$	0.9840	C$_7$–C$_8$	0.9858
C$_9$–H$_{14}$	0.9619	C$_8$–H$_{13}$	0.9632	C$_8$–H$_{13}$	0.9623
C$_9$–H$_{15}$	0.9539	C$_8$–H$_{14}$	0.9556	C$_8$–H$_{14}$	0.9541
C$_9$–H$_{16}$	0.9532	C$_8$–H$_{15}$	0.9555	C$_8$–H$_{15}$	0.9542

2.2 Oxidation Number: Table 2 indicates that calculated oxidation number of each atom of molecule. According to the definition the sum of the oxidation number of molecules is zero. The sign of oxidation number of the atoms depends upon the sign of their net charges. The oxidation numbers of all the ring carbons in o–, m–, Cresol have a value slightly excess to their classical valence number, i.e., 4, whereas in p-Cresol differ from their classical values of valence numbers appreciably. The signs are positive and negative in the ring carbons alternatively while the sign of substituent carbon

is found positive in all the above molecules. The oxidation numbers of carbon of substituent —CH3 in all o-, m-, p-Cresol positive and differ from their classical values of valence numbers appreciably. The oxidation numbers of the oxygen atoms in all the molecules under study with —H as substituent have a value slightly differ to 2, respectively with identical -ve signs. The oxidation numbers of the ring carbons in p-cresol are far deviated from their classical values of valence.

TABLE 2: Oxidation Number of atoms of o–, m–, p– Cresol

o–Cresol		m–Cresol		p– Cresol	
Atoms	Oxidation Number	Atoms	Oxidation Number	Atoms	Oxidation Number
C_1	4.7273	C_1	-3.8133	C_1	2.0293
C_2	-4.7616	C_2	4.8034	C_2	-4.6968
C_3	4.7708	C_3	-4.5916	C_3	4.4782
C_4	-4.6195	C_4	4.4717	C_4	-2.7027
C_5	4.3992	C_5	-4.5512	O_5	-1.6789
C_6	-4.5352	O_6	-1.7910	C_6	-2.5529
O_7	-1.7912	C_7	3.7501	C_7	1.6696
H_8	0.8290	C_8	2.7543	C_8	2.4229
C_9	3.7151	H_9	-0.0004	H_9	0.0003
H_{10}	-0.8785	H_{10}	-0.8774	H_{10}	0.8808
H_{11}	0.8826	H_{11}	0.8829	H_{11}	0.8814
H_{12}	-0.8768	H_{12}	0.8856	H_{12}	0.8834
H_{13}	0.8830	H_{13}	-0.9236	H_{13}	-0.7927
H_{14}	-0.9094	H_{14}	-0.9233	H_{14}	-0.7841
H_{15}	-0.9094	H_{15}	-0.9073	H_{15}	-0.8504
H_{16}	-0.9254	H_{16}	0.8312	H_{16}	0.8129

Dipole Moment: The calculated dipole moments of the molecules under study have been presented in Table 3. The total dipole moment of an unsaturated molecule can be divided into two parts, firstly, π– part of mesomeric moment arising from the π–electron charge distribution and secondly, the σ– part arising from the σ–electron charge distribution. The π–electron theoretical calculations of the dipole moment can not be compared directly with the experimental observations. Since, the π donating capacity of substituents tends to decreases with increasing with

decreasing electronegativity of substituent. However, Mishra and Rai [20] in their π–electron calculations have found that dipole moment is not entirely determind by the electronegativity of the substituent but also depends on the magnitude of the resonance integral. The difference between the MINDO/3 dipole moments and the experimental dipole moments can be minimized by taking extended basis set.

TABLE 3: Dipole Moments of o–, m–, p– Cresol

o–Cresol	m–Cresol	p– Cresol
1.560	1.360	1.409

CONCLUSION

- Bond order in non-bonded atoms 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 takes place to more attractive diagonally non-bonded C–C bonds.

- The magnitudes of the bond order indices of the ring carbons attached with the substituents 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 bond order values of the substituents bond are in the order.
  $C–C(–CH_3) > C–OH$

- Since *the* only thing that is physically and chemically important is the actual electron distribution, it seems that in essentially covalent bonding situations, ionic formulations with their attendant necessity *for,* or consequence of, assigning oxidation numbers are best avoided.

- The most important conclusion of the present study is that the oxidation numbers are also seen to be Indicative of their orientational behaviour like the net atomic charges but with limited utility.

- The dipole moment is calculated by the product of distance and the charge on the atoms; it indicates the polarity of the covalent bond of the molecule. [21].

- The dipole moment is found to increase with decreasing electronegativity of substituent.

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