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ELECTRONIC STATE PROPERTIES: BOND LENGTH AND BOND ANGLE OF PHENOL AND ITS SOME DERIVATIVES

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ABSTRACT

We have studied bond length and bond angle of a series of phenols. For present study the molecular modelling and geometry optimization of all the compounds were carried out with MOPAC software using MINDO/3 methods. We have conclude that the order of bond lengths between C-O, C-C, C-H and O-H atoms have been changed by changing the position of the substituents i.e., from ortho to para substitution. The C-C-C band angles have the same value while the C-C-O and C-O-H band angles differ from their normal values on substitution.

Key words: Phenol, MINDO/3, MOPAC, Electronic state properties.

INTRODUCTION

Computational chemistry have been introduced the methods of analysis of reaction mechanisms and prediction of the reactivity in synthetic chemistry. Therefore, computational chemistry is used to predict the reactivates of a wide variety of chemicals[1-4]. In this work, we have selected few derivatives of phenol for such study. MINDO/3 methods were used to study the effects of substitution of phenols[5,6]. The electronic structure of molecules is to explain the nature of classical chemical bond in terms of quantum chemical parameters by molecular orbital theory[7]. The bond length and bond angle are important characteristics of covalent bonding in molecules. The concept of bond length and bond angle permits us to get an immediate insight into the bonding situation in different molecules. In general, these parameters may be useful in correlating the quantum mechanics and ordinary chemistry and also useful in giving better results and getting deeper understanding of the results of the actual quantum chemical calculation for particular system.

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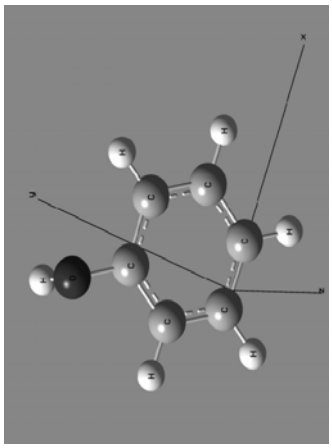
EXPERIMENTAL

The experimental materials of this paper are phenol and its few derivatives. For present study the molecular modeling and geometry optimization[8] of all the compounds were carried out with MOPAC software using MINDO/3 methods[9]. The bond length and bond angle of every atom of the derivatives have been calculated by softness calculators.

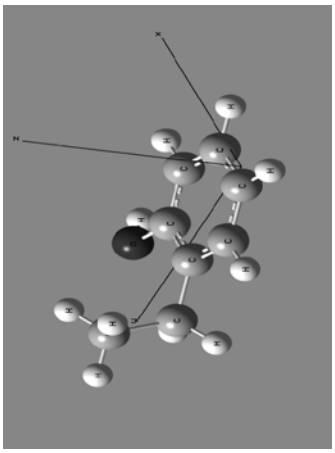
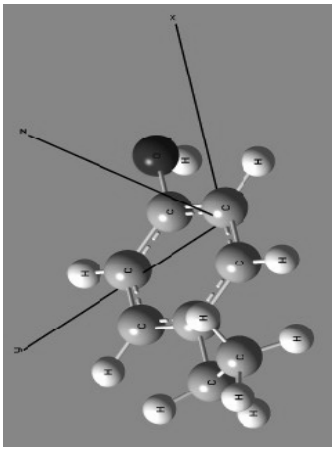
RESULTS AND DISCUSSION

The bond length and bond angle of phenol and its derivatives by MINDO/3 method which is presented in Table 1 below.

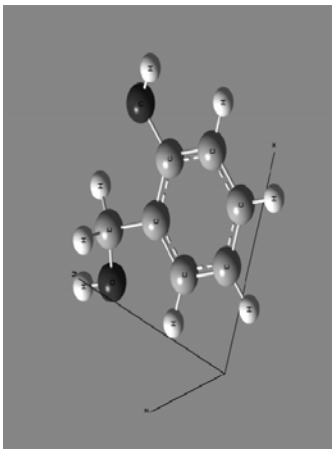
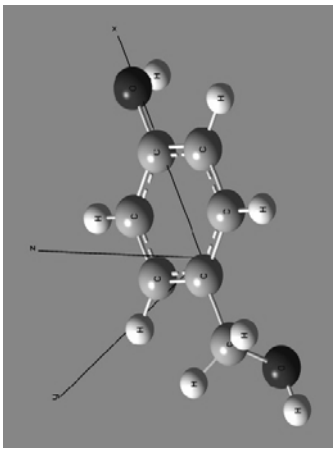
Table 1: Bond length and bond angles of phenol and its derivatives

Molecule	Bond	Bond length (A^0)	Bond	Bond angle (degree)
 phenol	C_1-C_2	1.403	C_1-C_2-C_3	118.53
	C_2-C_3	1.424	C_2-C_3-C_4	120.22
	C_3-C_4	1.418	C_2-C_3-O_5	115.05
	C_3-O_5	1.427	C_3-C_4-C_6	119.89
	C_4-C_6	1.407	C_3-C_4-H_7	120.95
	C_4-H_7	1.105	C_4-C_6-C_8	120.25
	C_6-C_8	1.405	C_6-C_8-H_9	120.25
	C_8-H_9	1.103	C_2-C_1-H_{10}	118.54
	C_1-H_{10}	1.107	C_3-C_2-H_{11}	121.88
	C_2-H_{11}	1.104	C_4-C_6-H_{12}	119.88
	C_6-H_{12}	1.106	C_3-O_5-H_{13}	114.00
	O_5-H_{13}	0.951		
	H_7-C_{14}	1.011		
	C_1-C_2	1.398	C_1-C_2-C_3	119.43
	C_2-C_3	1.425	C_2-C_3-C_4	123.22
	C_3-C_4	1.440	C_2-C_3-O_5	121.83
	C_3-O_5	1.324	C_3-C_4-C_6	113.11
	C_4-C_6	1.430	C_3-C_4-C_7	127.76
	C_4-C_7	1.480	C_4-C_6-C_8	124.87

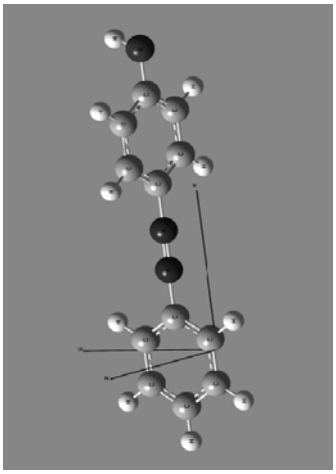
Cont…

Molecule	Bond	Bond length (A^0)	Bond	Bond angle (degree)
 o- ethyl phenol	C_6-C_8	1.403	C_4-C_7-C_9	139.72
	C_7-C_9	1.330	C_3-C_2-H_{10}	120.89
	C_2-H_{10}	1.105	C_2-C_1-H_{11}	120.04
	C_1-H_{11}	1.106	C_4-C_6-H_{12}	117.62
	C_6-H_{12}	1.109	C_6-C_8-H_{13}	120.40
	C_8-H_{13}	1.105	C_3-O_5-H_{14}	114.30
	O_5-H_{14}	0.951	C_4-C_7-H_{15}	101.80
	C_7-H_{15}	4.210	C_4-C_7-H_{16}	109.80
	C_7-H_{16}	1.118	C_7-C_9-H_{17}	128.06
	C_9-H_{17}	1.097	C_7-C_9-H_{18}	126.49
	C_9-H_{18}	3.330	C_2-C_3-H_{19}	122.10
	C_9-H_{19}	1.100		
 p- ethyl phenol	C_1-C_2	1.502	C_1-C_2-C_3	145.92
	C_2-C_3	1.478	C_2-C_3-C_4	71.70
	C_3-C_4	1.308	C_2-C_3-O_5	139.03
	C_3-O_5	1.301	C_3-C_4-C_6	124.05
	C_4-C_6	2.835	C_4-C_6-C_7	113.77
	C_6-H_7	1.335	C_6-C_7-C_8	155.86
	C_7-C_8	1.449	C_7-C_8-C_9	137.50
	C_8-C_9	1.328	C_2-C_1-H_{10}	111.16
	C_1-H_{10}	1.126	C_3-C_2-H_{11}	104.67
	C_2-H_{11}	1.134	C_3-C_4-H_{12}	141.73
	C_4-H_{12}	1.134	C_4-C_6-H_{13}	92.23
	C_6-H_{13}	1.091	C_7-C_8-H_{14}	109.48
	C_8-H_{14}	1.115	C_7-C_8-H_{15}	71.36
	C_8-H_{15}	2.278	C_8-C_9-H_{16}	127.62
	C_9-H_{16}	1.097	C_8-C_9-H_{17}	122.63
	C_9-H_{17}	1.099	C_8-C_9-H_{18}	86.89
	C_9-H_{18}	2.753	C_3-O_5-H_{19}	115.61
	O_5-H_{19}	0.953		

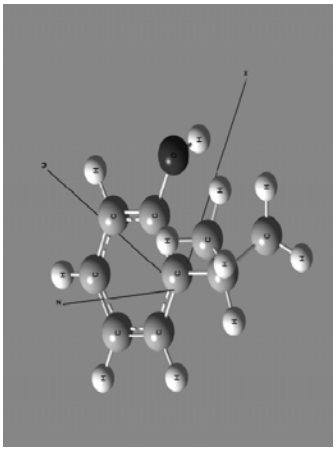
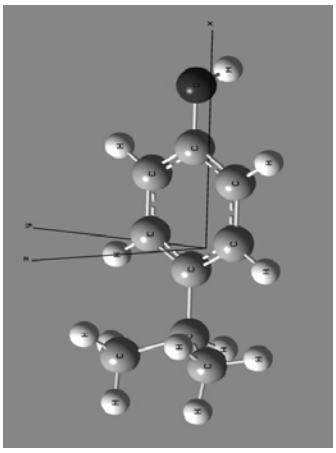
Cont…

Molecule	Bond	Bond length (A^0)	Bond	Bond angle (degree)
 o- hydroxyl benzyl alcohol	C_1-C_2	1.371	C_1-C_2-C_3	120.00
	C_2-C_3	1.460	C_2-C_3-C_4	121.15
	C_3-C_4	1.350	C_3-C_4-C_5	122.68
	C_4-C_5	1.493	C_4-C_5-C_6	117.37
	C_5-C_6	1.528	C_5-C_6-C_7	122.58
	C_6-C_7	1.363	C_6-C_7-O_8	131.04
	C_7-O_8	1.311	C_2-C_1-O_9	124.58
	C_1-O_9	1.326	C_3-C_2-H_{10}	117.83
	C_2-H_{10}	1.103	C_2-C_3-H_{11}	117.16
	C_3-H_{11}	1.106	C_3-C_4-H_{12}	121.65
	C_4-H_{12}	1.105	C_4-C_5-H_{13}	108.31
	C_5-H_{13}	1.126	C_1-O_9-H_{14}	113.94
	O_9-H_{14}	0.952	C_6-C_7-H_{15}	50.74
	C_7-H_{15}	2.775	C_6-C_7-H_{16}	124.64
	C_7-H_{16}	1.118	C_7-O_8-H_{17}	115.68
	O_8-H_{17}	0.952		
 p- hydroxyl benzyl alcohol	C_1-C_2	1.402	C_1-C_2-C_3	118.68
	C_2-C_3	1.421	C_2-C_3-C_4	119.51
	C_3-C_4	1.419	C_2-C_3-O_5	115.52
	C_3-O_5	1.324	C_3-C_4-C_7	119.65
	C_4-C_6	1.403	C_4-C_6-C_7	123.24
	C_6-C_7	1.427	C_7-C_8-O_9	122.70
	C_7-C_8	1.507	C_2-C_1-H_{10}	114.87
	C_8-O_9	1.354	C_2-C_1-H_{11}	116.91
	C_1-H_{10}	1.108	C_3-C_2-H_{11}	122.14
	C_2-H_{11}	1.104	C_3-C_4-H_{12}	121.24
	C_4-H_{12}	1.105	C_4-C_6-H_{13}	117.25
	C_6-H_{13}	1.108	C_3-O_5-H_{14}	114.21
	O_5-H_{14}	0.951	C_7-C_8-H_{15}	110.13
	C_8-H_{15}	1.133	C_7-C_8-H_{16}	111.19
	C_8-H_{16}	1.130	C_8-C_9-H_{17}	111.72
	O_9-H_{17}	0.951		

Cont…

Molecule	Bond	Bond length (A^0)	Bond	Bond angle (degree)
 p- hydroxyl azobenzene	C_1-C_2	1.403	C_1-C_2-C_3	120.57
	C_2-C_3	1.405	C_2-C_3-C_4	121.16
	C_3-C_4	1.425	C_3-C_4-C_5	117.29
	C_3-C_5	1.424	C_3-C_4-N_6	121.06
	C_4-N_6	1.410	C_4-C_6-C_7	121.19
	C_5-C_7	1.405	C_4-N_6-N_8	142.24
	N_6-N_8	1.162	N_6-N_8-C_9	139.71
	N_8-C_9	1.424	N_8-C_9-C_{10}	120.45
	C_9-C_{10}	1.424	N_8-C_9-C_{11}	121.43
	C_9-C_{11}	1.420	C_9-C_{10}-C_{12}	122.54
	C_{10}-C_{12}	1.402	C_{10}-C_{12}-C_{13}	119.51
	C_{12}-C_{13}	1.422	C_{12}-C_{13}-C_{14}	119.31
	C_{13}-C_{14}	1.418	C_2-C_1-H_{16}	120.39
	C_{13}-O_{15}	1.327	C_3-C_2-H_{17}	119.49
	C_1-H_{16}	1.105	C_2-C_3-H_{18}	118.12
	C_2-H_{17}	1.106	C_4-C_5-H_{19}	120.71
	C_3-H_{18}	1.107	C_5-C_7-H_{20}	119.46
	C_5-H_{19}	1.107	C_9-C_{10}-H_{21}	120.42
	C_7-H_{20}	1.106	C_{10}-C_{12}-H_{22}	118.85
	C_{10}-H_{21}	1.108	C_{13}-C_{14}-H_{23}	121.26
	C_{12}-H_{22}	1.105	C_9-C_{11}-H_{24}	120.67
	C_{14}-H_{23}	1.106	C_{13}-C_{15}-H_{25}	113.72
	C_{11}-H_{24}	1.108		
	O_{15}-H_{25}	0.951		
	C_1-C_2	1.405	C_1-C_2-C_3	119.83
	C_2-C_3	1.417	C_2-C_3-C_4	121.93
	C_3-C_4	1.441	C_2-C_3-O_5	123.77
	C_3-O_5	1.327	C_3-C_4-C_6	115.39
	C_4-C_6	1.421	C_4-C_6-C_7	123.25
	C_4-C_7	1.488	C_4-C_7-C_9	122.54
	C_6-C_8	1.407	C_4-C_7-C_{10}	136.91
	C_7-C_9	1.327	C_2-C_1-H_{11}	119.66

Cont…

Molecule	Bond	Bond length (A^0)	Bond	Bond angle (degree)
 o- isopropyl phenol	C_7-C_{10}	4.541	C_3-C_2-H_{12}	120.98
	C_1-H_{11}	1.106	C_4-C_6-H_{13}	118.54
	C_2-H_{12}	1.106	C_6-C_8-H_{14}	119.88
	C_6-H_{13}	1.108	C_3-O_5-H_{15}	114.12
	C_8-H_{14}	1.104	C_4-C_7-H_{16}	111.92
	O_5-H_{15}	0.951	C_7-C_9-H_{17}	125.39
	C_7-H_{16}	1.114	C_7-C_9-H_{18}	124.27
	C_9-H_{17}	1.100	C_7-C_9-H_{19}	90.88
	C_9-H_{18}	1.099	C_7-C_{10}-H_{20}	92.12
	C_9-H_{19}	3.631	C_7-C_{10}-H_{21}	75.33
	C_{10}-H_{20}	1.102	C_7-C_{10}-H_{22}	154.08
	C_{10}-H_{21}	1.102		
	C_{10}-H_{22}	1.102		
 p- isopropyl phenol	C_1-C_2	1.509	C_1-C_2-C_3	142.98
	C_2-C_3	1.501	C_2-C_3-C_4	89.06
	C_3-C_4	1.320	C_2-C_3-O_5	146.35
	C_3-O_5	1.320	C_3-C_4-C_6	126.28
	C_4-C_6	1.663	C_4-C_6-C_7	137.33
	C_6-C_7	1.327	C_6-C_7-C_8	131.79
	C_7-C_8	1.473	C_7-C_8-C_9	96.36
	C_8-O_9	1.497	C_7-C_8-C_{10}	176.12
	C_8-C_{10}	1.346	C_2-C_1-H_{11}	140.57
	C_1-H_{11}	1.125	C_3-C_2-H_{12}	127.01
	C_2-H_{12}	1.128	C_2-C_4-H_{13}	117.28
	C_4-H_{13}	1.085	C_4-C_6-H_{14}	84.36
	C_6-H_{14}	1.088	C_3-C_6-H_{15}	77.03
	O_5-H_{15}	0.953	C_7-C_8-H_{16}	95.50
	C_8-H_{16}	3.867	C_8-C_9-H_{17}	90.94
	C_9-H_{17}	1.112	C_8-C_9-H_{18}	90.88
	C_9-H_{18}	1.112	C_8-C_9-H_{19}	178.67
	C_9-H_{19}	1.112	C_8-C_{10}-H_{20}	82.99
	C_{10}-H_{20}	3.729	C_8-C_{10}-H_{21}	90.00
	C_{10}-H_{21}	1.100	C_8-C_{10}-H_{22}	174.80
	C_{10}-H_{22}	1.100		

The bond length and bond angle of phenol and its derivatives are described separately as below -

Bond length

In a pioneering work, introduced a bond order parameter and correlated it with bond length for π-electron and all valence electron semi- empirical theories[10-15]. Ban border is a measure of net number of bonding electron pair. According to MO theory, a covalent bond between two atoms is formed by overlap of their atomic orbital. During overlapping, when the force of attraction between the two atoms is balanced by the force of repulsion between the nuclei of two atoms, the equilibrium distance between the two atomic nuclei is called bond length[16]. We have calculated the bond length of phenol and its derivatives by MINDO/3 method which is presented in Table 1. In phenol the bond length between C_2-C_3 is 1.4236 Å which is maximum it means the electronegativity difference between these atoms will be minimum. The bond length between atoms in phenol has been found in following order:

C-O > C-C > C-H > O-H

The maximum bond length is found between C-O while minimum bond length is found between O-H. Since bond length between O-H is minimum therefore the electronegativity difference between O- H maximum. It is also found that the presence of OH group at C_3 in phenol, increases the bond length between C_2-C_3 is maximum. The bond length between C_1-C_2 and C_4-C_6 is just nearly equal. Similarly the bond length between C_2-C_3 and C_3-C_4 are approximately equal in phenol. In ortho and para ethyl phenol the bond length between different atoms are found in following order:

C-H > C-C > C-O > O-H

An interesting feature is found that the bond length of C_7 –H_{16} and C_9-H-$_{18}$ are found maximum because CH_2, CH_3 group are attached at C_2 and C_9 respectively. Hence electronegativity difference between C-H will be least while electronegativity difference between O-H will be highest. In o-hydroxyl benzyl alcohol and p-hydroxyl benzyl alcohol. The bond length is found in following order:

C-C > C-O > C-H > O-H

In p-hydroxyl azobenzene, N group is attached. The bond length of C_3-C_4 is maximum and the bond length between O-H is minimum. In p-hydroxyl azobenzene the bond length between C_1-C_2, C_2-C_3, C_4-N_6, C_5-C_7 and C_{10}-C_{12} are nearly equal. In phenol and

its derivatives o-ethyl phenol, p-ethyl phenol, o-hydroxyl benzyl alcohol, p-hydroxyl benzyl alcohol, p-hydroxyl azobenzene, o-isopropyl phenol and p- isopropyl phenol, the bond length between C atom containing OH group and other C atom will be higher in comparison to the bond length between other C-C atoms, i.e., presence of OH group increases the bond length. The bond length between C-O is less than the bond length between C-N in p-hydroxyl azobenzene because the bond orders between C = O is greater than that of C- N. Hence if bond order increases than bond length decreases. It is also seen that the bond length between hydrogen and ring carbon atoms are found smaller than the bond length between hydrogen and carbon atom of substituent group.

Bond Angel

Bond angle[17] is the internal angle between the orbitals containing electron pairs in the valence shell of the central atom in a covalent molecule. Bond angles give an idea of distribution of the orbitals in three dimensional spaces around the central atom in the molecule and thus give an idea of the shape of the molecule. Bond angle will be the maximum in case if central atom has no lone pair i.e. with the decrease in magnitude of bond pair – bond pair repulsion as well as with decrease of electronegativity. Bond angle of phenol and some of its derivatives have been calculated by MINDO/3 method and presented in Table 1. In phenol, the bond angle among C_2-C_3-C_4 is exactly equal to the bond angle among C_4-C_5-C_6 due to bond pair – bond pair repulsion being same. The bond angle among C_2-C_3-O_5 is founder greater than the bond angle C_3-O_5-H_{13}, which shows that bond pair – bond pair repulsion in C_2-C_3-O_5 is greater than the bond pair – bond pair repulsion in C_3-O_5-H_{13}. In phenol, the bond angles between different bonds are found in the following order:

$$\text{C-C-H} > \text{C-C-C} > \text{C-O-H}$$

The C_3-C_2-H_{11} bond angle is about 121.88^0 while the C_3-O_5-H_{13} bond angle is about 114^0. This is due to presence of OH group at the C_3 that decreases its bond angle in side the ring. In other products of phenol the maximum bond length is formed between C_7-C_9-H_{17} but the OH group is attached with the C_3 of first ring carbon therefore the C_3-C_4-C_6 bond angel is minimum. The maximum bond angel is found about 139.72^0 while the minimum bond angle is found about 101.8^0. Similar trend is found in p – ethyl phenol and o- hydroxyl benzyl alcohol. In p – hydroxyl azobenzene bond angle C_4-N_6-N_8 and N_6-N_8-C_9 are found nearly equal. The C_{11}-O_5-H_{25} is found 113.72^0 which is minimum. The CH_3 group is attached to C_9 and C_{10} in o- isopropyl phenol. The bond angle in C_7-C_9-H_{19}, C_9-C_{10}-H_{20} and C_7-C_{10}-H_{21} are found minimum which shows that CH_3 group decreases the bond angle.

CONCLUSION

From above study we have concluded that :

(i) The bond length between C atom containing OH group and other C atom will be higher in comparison to the bond length between other C-C atoms.

(ii) The bond length between atoms in phenol has been found in the order: C-O > C-C > C-H > O-H.

(iii) In ortho- and para-ethyl phenol the bond length between different atoms are found in the order: C-H > C-C > C-O > O-H.

(iv) In o-hydroxyl benzyl alcohol and p-hydroxyl benzyl alcohol. The bond length is found in the order: C-C > C-O > C-H > O-H.

(v) The bond length between hydrogen and ring carbon atoms is found smaller than the bond length between hydrogen and carbon atom of substituent group.

(vi) In phenol, the bond angles between different bonds are found in the order: C-C-H > C-C-C > C-O-H.

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