Study of the Effect of Methyl and Hydroxyl Subgroups on the Electronic Structure of Biphenyl Molecule

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Abstract

Theoretical study of the effect of methyl and hydroxyl subgroups on the electronic structure of biphenyl molecule was performed using DFT with B3LYP/6-31G(d, p)basis set. The optimized structures, total energies, energy gaps, electrochemical hardness, Fermi level, molecular symmetry, dipole moment, dipole polarizability and the infrared spectrum frequencies were calculated. The results showed that the total energy of the two groups of molecules is independent on the position of the subgroup in the molecule but depends only on the number of the added subgroups. On the other hand, the energy gap, Fermi level and the electrochemical hardness are varied with the position of the added subgroups.

Keywords: Koopman^s theorem, Energy gap, Fermi level and polarizability.

الخلاصة

دراسة نظرية لتأثير مجاميع المثيل والهيدروكسيل على التركيب الالكتروني لجزيئة ثنائي فينيل بتطبيق نظرية دالية الكثافة مع الدالة الهجينة لي–يانغ–بار ذات المعاملات الثلاث ودوال اساس 6−31G(p, d). تم حساب التراكيب المثلى, الطاقات الكلية, فجوات الطاقة, الصلادة الكهروكيميائية, مستوي فيرمي, التماثل الجزيئي, عزم ثنائي القطب, الاستقطابية وترددات طيف الاشعة تحت الحمراء. بينت النتائج ان الطاقة الكلية لمجموعتي الجزيئات لا تعتمد على موضع المجموعة المضافة وانما تعتمد فقط على عدد المجاميع المضافة. من جانب آخر فأن فجوة الطاقة, مستوي فيرمي والصلادة الكهروكيميائية تتغير مع تغير موقع المجاميع المضافة.

الكلمات المفتاحية: نظرية كوبمان, فجوة الطاقة, مستوي فيرمي والاستقطابية.

Introduction

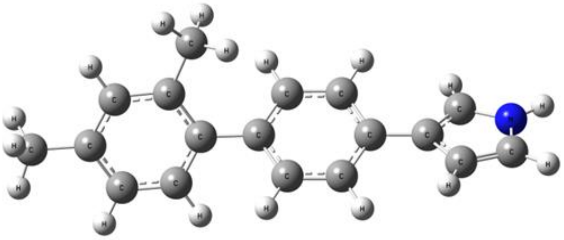
In the last years, wide interest in organic materials are growing in view of their ability to many kinds of applications [Denniston, *et al*., 2007]. Organic material is a material that contains carbon and hydrogen and usually other elements such as nitrogen, sulfur and oxygen covalently bound to other atoms[Ponce-Espinosa, *et al*., 2014]. From organic compounds which studied in the present work is biphenyl compound. Biphenyl compound is an aromatic hydrocarbon with a molecular formula $(C_6H_5)_2$. It is used in organic syntheses, heat transfer fluids, dye carriers, food preservatives, as an intermediate for polychlorinated biphenyls, and as a fungistat in the packaging of citrus fruits [Yoshitane Imai, *et al*., 2006]. The aim of the present work is study the effect of methyl and hydroxide subgroups on the electronic structure of biphenyl compound.

Computational details

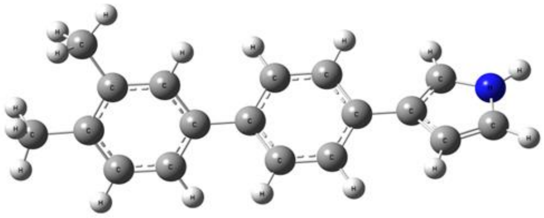
In the present work, the effect of methyl (CH_3) and hydroxide (OH) subgroups on the electronic structure of biphenyl compound is studied by using Density functionl theory (DFT) employing Gaussian 09 suite of programs [Frisch, *et al*., 2009]. Density functional theory (DFT) is a quantum mechanical modeling method used in physics and chemistry to investigate the electronic structure (principally the ground state) of many-body systems, in particular atoms, molecules, and the condensed phases. With this theory, the properties of many-electron system can be determined by using functionals, which in this case is the spatially dependent electron density [Dreizler, *et al*., 1990]. DFT is an extremely successful approach for the description of ground state properties of metals, semiconductors, and insulators [Klaus capelle, 2006]. Figure (1) represents the molecules under this study. The molecular properties of the compounds have been computed by DFT using the standard 6-31G(d,p) basis set. In the DFT calculations the Lee, Yang and Parr correlation functional [Lee *et al*.,1988] is used together with Becke's three parameters [Becke, 1988] exchange functional B3LYP. Conformational analysis of the molecules has been performed to have an idea about the lowest energy structures of the species. The geometry optimization was performed at the B3LYP density functional theory with the same basis set [Frisch, *et al*., 2009; Becke, 1993]. Harmonic vibration frequencies were computed at the same level of theory. The hybrid functional B3LYP has shown to be highly successful

for calculation the electronic properties such as ionization potentials, electronic states and energy gaps [Engelberts, *et al*;2005;.Santos, *et al*.,2004; Santos, *et al*., 2005].

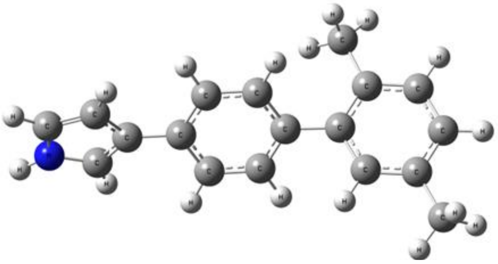
Iso methylbiphenyl



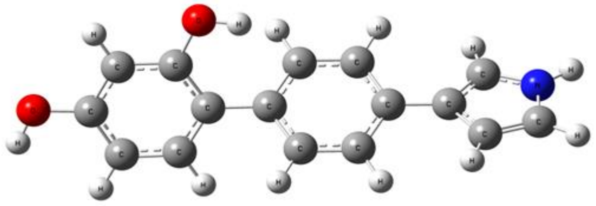
Meta methylbiphenyl

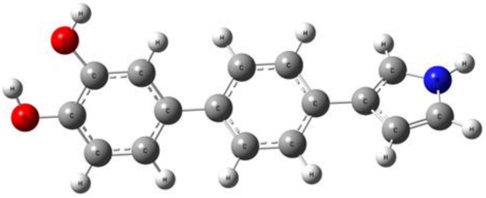


Para methylbiphenyl

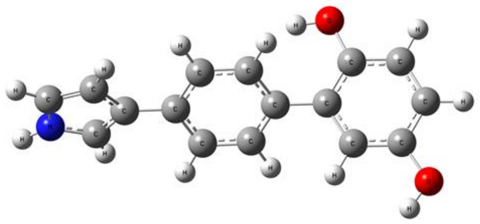


Iso hydroxide biphenyl





Meta hydroxide biphenyl



Para hydroxide biphenyl

Figure 1. Structures of methylbiphenyl and hydroxide biphenyl.

Results and Discussion

The total energies, symmetry of structures, Fermi level, hardness and energy gaps for molecules calculated by DFT-B3LYP levels with the 6-31G(d, p) basis set are listed in table (1).

Table (1) Total energy, Energy gap, Fermi level, Hardness and Symmetry.

Properties	CH_3 mol.			OH mol.		
	Iso	Meta	Para	Iso	Meta	Para
Total energy (a.u)	-750.7406	-750.744	-750.7405	-822.5084	-822.5101	-822.5062
Energy gap (eV)	4.822	4.633	4.827	4.699	4.554	4.508
Fermi level (eV)	5.449	5.425	5.483	5.640	5.436	5.681
Hardness (eV)	5.031	4.897	5.046	5.013	4.848	4.899
Symmetry	C1	C1	C1	C1	C1	C1

From Table (1), we can see that the total energies for methyl-biphenyl molecules are approximately the same, also the group of hydroxide-biphenyl molecules have approximately the same value of total energy in which this refers to that the total energy depends on the number of radicals added to the ring and independent on the position of the CH_3 and OH radicals in the ring, as we see in figure (2). The influence of the effects of the subgroups added to the biphenyl molecules on the energy gap was illustrated in figure (3), we showed that the calculated value of energy gap depends on the type of the subgroup and it is position in the biphenyl ring. Meta methylbiphenyl has the smallest value of energy gap in comparison with iso- and para- methylbiphenyl. While for hydroxyl biphenyl molecules group, we observed that the para hydroxyl biphenyl has the lowest value of energy gap. In short wards, the orders of energy gap of the two groups are meta methylbiphenyl < iso methylbiphenyl < para methylbiphenyl, and para hydroxyl biphenyl < meta hydroxyl biphenyl < iso hydroxyl biphenyl. The calculated theoretical values of Fermi energy for the two groups of molecules showed that they are in the order of meta < iso < para, as shown in figure (4). These results are not coming from the HOMO and LUMO of the molecules but reflect of the effect of the position of the subgroup in the molecule. The results of electrochemical hardness in figure (5) also indicate to the effect of the position of subgroups in the molecule. Table 1 shows also the symmetry of studied molecules, Were we can see that the type of the symmetry is C1, this means that studied molecules have only one symmetry operation.

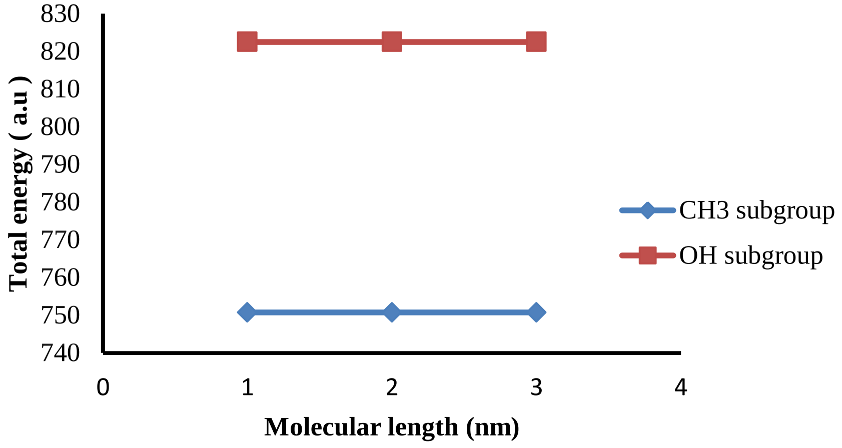


Figure (2) The relation between total energy and molecular length for studied molecules.

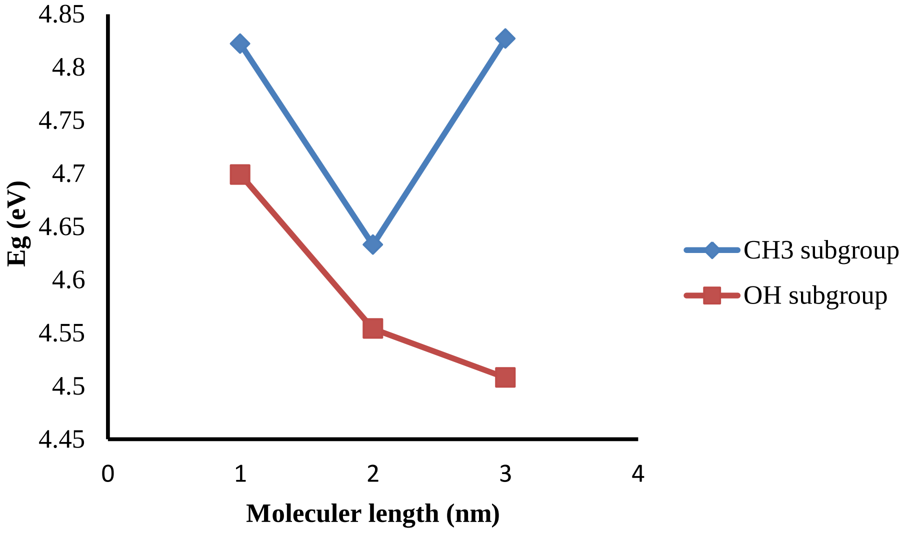


Figure (3) The relation between energy gap and molecular length for studied molecules.

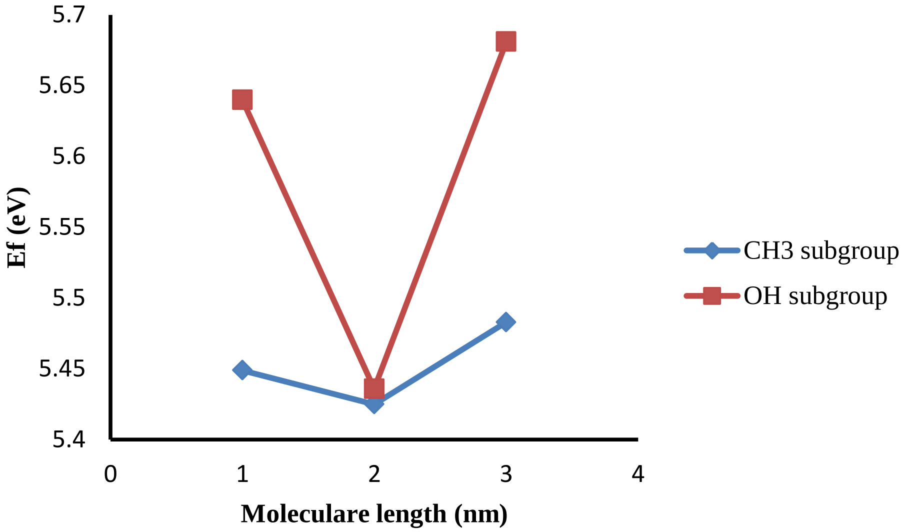


Figure (4) The relation between Fermi level and molecular length for studied molecules.

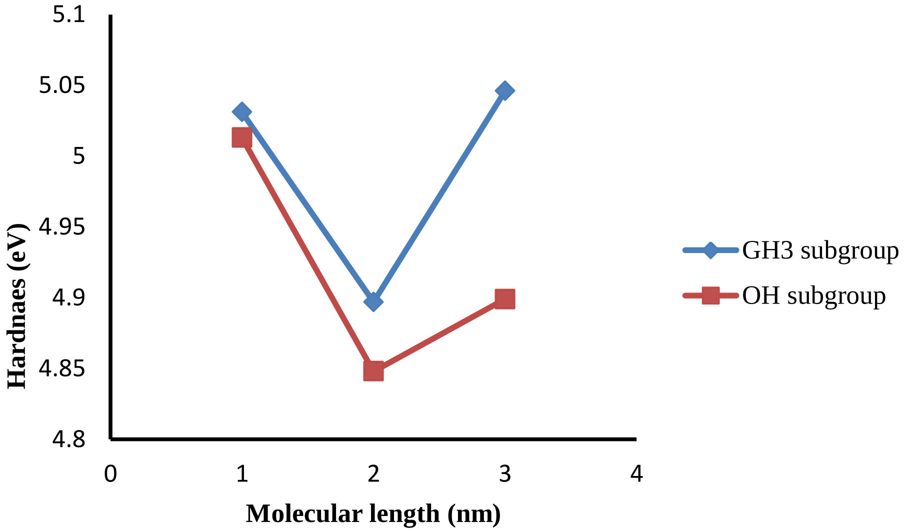


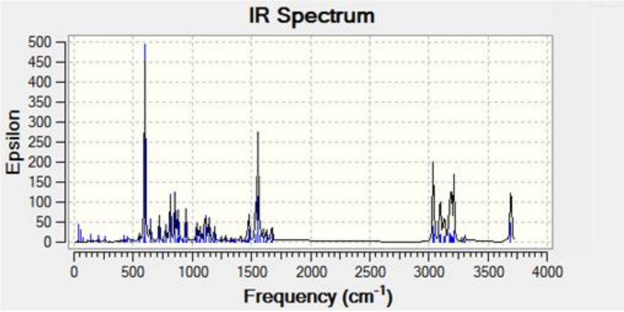
Figure (5) The relation between hardness and molecular length for studied molecules.

The molecules dipole moment represents a generalized measure of bond properties and charge densities in a molecule [Salzner, *et al*., 1997]. Molecule with electron accepter group due to better charge distribution and increasing distance have higher dipole moment[Oftadeh *et al*; 2011], from table (2) we can see that all substitution groups lead to change in the values of the dipole moments, in which the biphenyl molecule has no dipole moment and it is planar in the space, adding the subgroups leads to variety the symmetrical distribution of the electronic structure of the molecule and, therefore, change the dipole moment, as we see in Table 2. In the two groups of molecules, the para state has the highest value of dipole moment. The effect of subgroups on the polarizability of the biphenyl observed that the meta state for both groups has the high value of average polarizability.

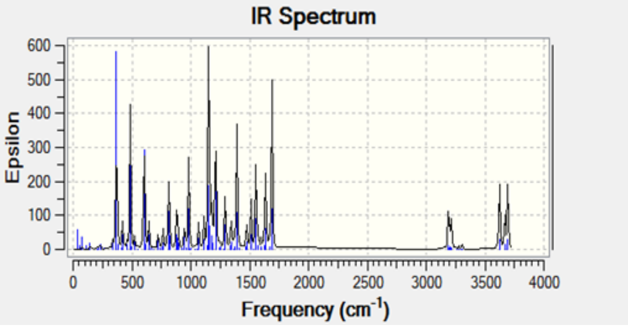
Table 2: calculated total dipole moment μ (Debye), components of αi (i = xx, yy, zz) and average of the dipole polarizability <α> in (a. u) for studied molecules.

CH_3 mol.	μ	Polarizability				OH mol.	μ	Polarizability			
		α_{xx}	α_{yy}	α_{zz}	$<\alpha>$			α_{xx}	α_{yy}	α_{zz}	$<\alpha>$
Iso	2.508	338.703	155.954	108.072	200.909	Iso	5.149	328.298	145.466	87.897	187.220
Meta	2.175	356.742	168.908	92.190	205.946	Meta	5.063	337.453	156.745	76.108	190.102
Para	2.651	324.366	159.073	114.515	199.318	Para	6.311	316.274	148.333	92.283	185.63

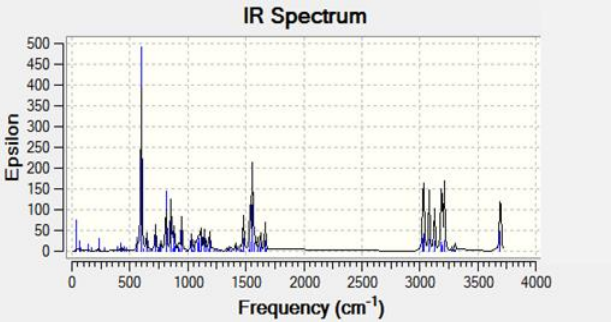
The theoretical IR spectra, calculated from the vibration frequencies at the optimized geometries of all studied molecules are given in fig. (6). The harmonic vibration frequencies calculated for molecules under study at B3LYP level using the 6-31G(d, p) basis sets. By comparing the IR spectrum of methylbiphenyl and hydroxide biphenyl molecules in figure (6), it will be noted that the differences between them, where hydroxide biphenyl molecule has vibration larger than of methylbiphenyl molecule, this result is due to the geometry of hydroxide biphenyl molecule.



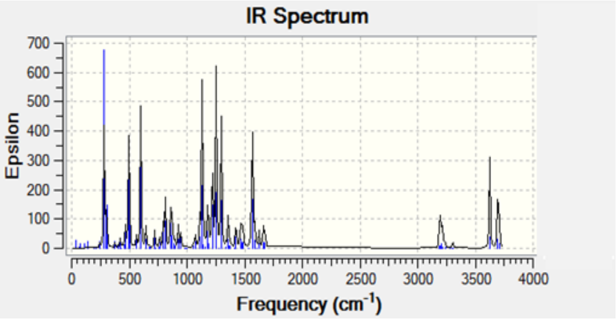
Iso methylbiphenyl



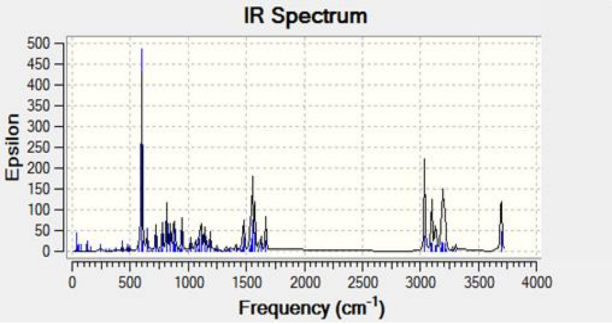
Iso hydroxidebiphenyl



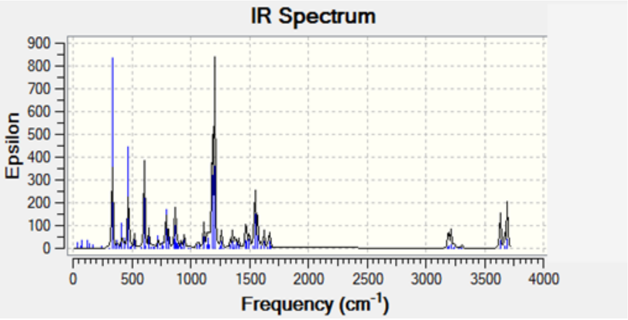
Meta methylbiphenyl



Meta hydroxidebiphenyl



Para methylbiphenyl



Para hydroxidebiphenyl

Figure 6: The calculated IR spectral frequencies for molecules under study.

Conclusions

Density Functional Theory (DFT) study has been carried out on biphenyl compound. The calculated electronic properties such as total energy, energy gap, Fermi level, electrochemical hardness and symmetry were calculated by DFT-B3LYP levels, the important conclusions are:

The total energy of the studied structures is independent on the position of the added subgroups in the biphenyl molecule, the total energy depends on the number of added subgroups only. The energy gap, Fermi level and electrochemical hardness for methyl biphenyl and hydroxide biphenyl molecules varied with the position of the methyl and hydroxyl subgroups in the molecule. The symmetry of studied molecules is C1, means adding the subgroups leads to change the symmetry of the molecule, in which, the biphenyl has high symmetry, while the new structures have C1 low symmetries. By comparing the IR spectrum of methyl biphenyl and hydroxide biphenyl molecules, we can see that hydroxide biphenyl molecules has vibrational frequencies larger than that of methyl biphenyl molecules.

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