Theoretical study of the Structure, Electronic Properties and Intramolecular Hydrogen Bonding (IHB) of the Pyrocatechol

2695 ـ1817 ISSN

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((Received 9/12/2009, Accepted 30/3/2010))

Abstract

The theortical calculations for pyrocatechol with and without intramolecular hydrogen bonding (I, II and III) were performed by quantum chemical methods. The optimized structures of the compounds(I,II and III) were obtained by using the Density functional theory (DFT /Slater) level of theory using the basis set 6-311G(d,p). Study Showed that the value of total energy for form (II) is less than compounds (I and III), which strongly indicates the stability of form(II). Also the dipole moment of form (II) is high compare with the forms (I and III). The calculation also shows a decrease in the length of hydrogen bond in form (II) compare with that of form (III). The thermodynamic calculation were carried out for (I,II andIII)and showed that favorable state is form (II)(more stable).

Keywords. Pyrocatechol , Intramolecular Hydrogen Bonding (IHB), Slater/6-311G(d,p).

Introducation

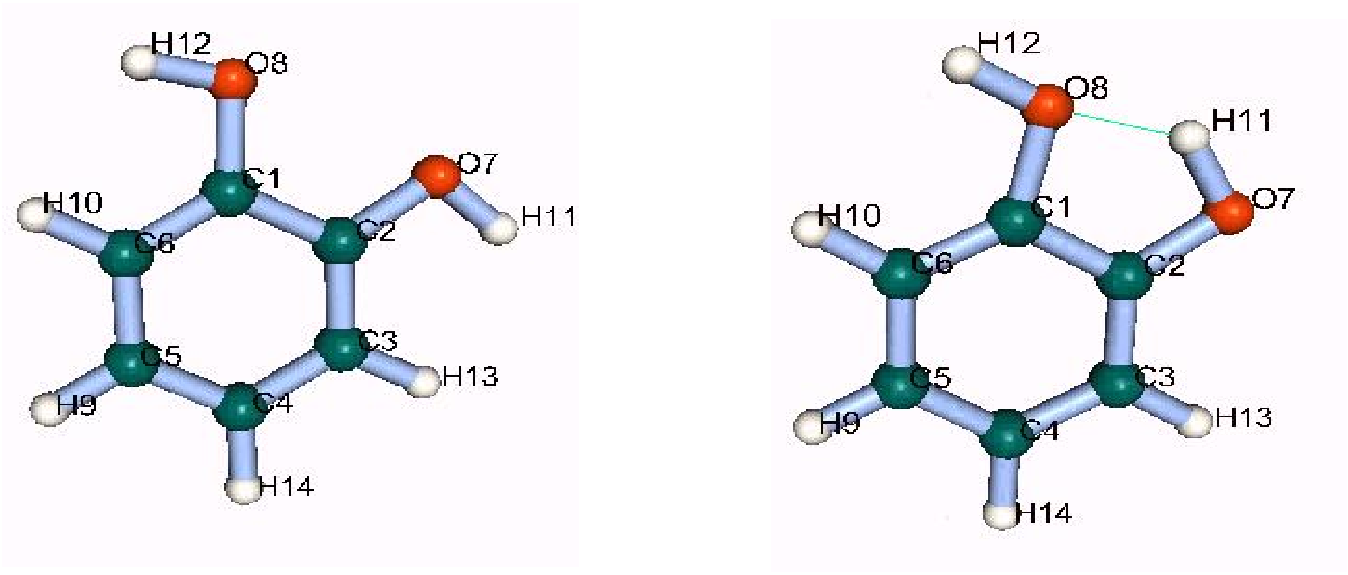
Catechol is the active center for natural phenolic antioxidants(1,2). Phenolic antioxidants have been extensively used in chemical industry, food industry, and pharmaceutical industry(3-5). Therefore, the study of intramolcular hydrogen bonding in catechole(Pyrocatechol) is very important because, as known to all, the boiling and melting points ,vapour pressure, solubility, density , viscosity, heat conductivity, heat expansion, dielectric constant, dipole moment, electro conductivity, ionization, another optical properties, spectra, acid-base, tautomeric and biological activity of chemical compound contributed essentially to helix and to double-helix stability depends on the presence of intramolecular hydrogen bond (IHB). For the directive synthesis of compounds, the quantam chemical evaluation of the IHB effect on the electronic structure of molecules is of great interest(6-11). Theoretical foundations for modern chemistry have been well developed through 70 years ago and in principle it become possible to be used for the predication of the interaction of atoms in molecule. Theoretical calculation methods are helpful tools for elucidating structure and behavior of molecules , atoms and electrons. One of the software packge for computational chemistry is PCGAMESS, it is a powerful computational package , and it offers many types of molecular and quantum mechanical calculations(11-14).In this work we attempt to study the intramolecular hydrogen bonding, electronic properties, and relative stabilities in pyrocatechol by performing Density functional theory (DFT /Slater) level of theory using the basis set 6-311G(d,p) .

Computational method

A full quantum mechanical geometry optimization was performed by PCGAMESS computational program.The calculations was done at the (DFT /Slater) level of theory use the basis set 6-311G(d,p) by using facio as interface (15) Three types of with and without intramolecular hydrogen bonding, species were optimized by the (DFT /Slater) method. All calculations were performed on the Pentium (R)4/IPM-PC- CPU 3.00GHz, 2.00GB

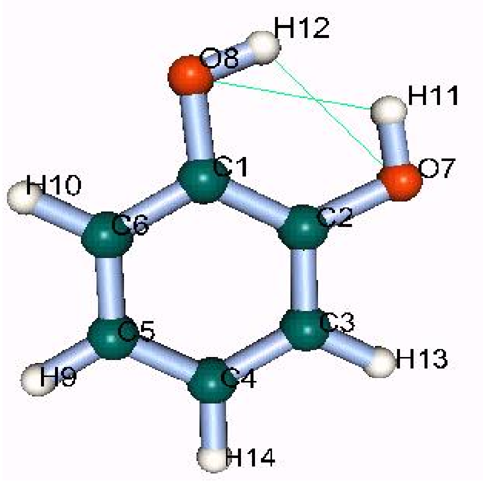
Results and Discussion

The geometry optimized structures with and without intramolecular hydrogen bonding of pyrocatechol(I, II and III) are visualized in ;Figs I, II and III and the selected structural data are summarized in Table 2.



I pyrocatechol without IHB

II pyrocatechol with IHB



III Predication of pyrocatechol with IHB

Figure 1. DFT-calculated optimized structures of the possible intramolecular hydrogen bonding and without intramolecular hydrogen bonding for the pyrocatechol in gas phase

It can be seen from Table 1 that, the total energy of the pyrocatechol with and without intramolecular hydrogen bonding have almost similar energies and thus comparable stabilities, while the form III has much more energy and accordingly less stability in comparison with the other Forms. This may be rationalized on the basis that the form III has a steric hindrance through the C—O—H------O–C and C—O----H—O—C system and this is responsible for the increase energy and less stability comparison with the forms I and II. The calculated energies show also that within the form II most stable structure more than form III, and I because have intramoleuclare hydrogen bonding by one side and with less a steric hindrance. So that the form III have more energy and less stability. On the other hand the form II has less energy and more stability. In addition the form II is more stable because of the OH group which causes intermolecular hydrogen bonding have trans configuration (the value of the dihedral angle 12-8-7-11 = 180) while the form I and III, have Cis configuration(the value of the dihedral angle 12-8-7-11 = -0.057, 0.000 sequence).

As well as the form III have high energy potential compare with form II (Trans configuration) because of electronic repulsion between H11, H12, in addition the less intermolecular distance between H11-H12 is (1.63 A). While in the form II the intermolecular distance between H11-H12 is (2.78 A) which causes decrease the energy potential. On other hand the form I have high energy potential compare with the forms II and III, because of the intermolecular distance between hydrogen atoms H11-H12 is large (4.66 A) which causes decrease electrostatic intermolecular(van der waals) forces , so the form I have high energy potential(16-18).

Table 1 Energy (Kcal/mol) of the Pyrocatechol without IHB and with IHB

Compound	***Total Energy In a.u**	***Total Potential Energy in a.u**	**Dipole moment (debye)**
I without IHB	**-375.8123**	**-751.5300**	**0.814715**
II with IHB	**-375.8187**	**-751.6562**	**2.868571**
III with IHB	**-375.8063**	**-751.5794**	**1.553794**

⋆: Minus sign denotes lower energy (stabilization)for the total energies calculated.

From Table 2, we can see the important optimized bond lengths and bond angles which participate in forming IHB in the forms II and III. The bond length H(11)-O(8) in form II found 1.6370(A) shorter than bond length H(13)-O(8)and H(14)-O(7)in form III. Also the bond angle O(7)-H(11)-O(8) in form II largest than bond angle O(7)-H(13)-O(8)and O(8)-H(14)-O(7)in form III, The changes of the bond lengths and bond angles in the forms II and III indicate the presence electric static which participates in forming the IHB. As a result, a shortening of [H(11)-O(8)=1.6370] distances in form II compared with the form III [H(13)-O(8)= 2.3716, H(14)-O(7)= 2.3717], this showed a strong to be discordant in form III which causes more energy and less stability .On the other hand this behavior reflects the strong electrostatic attraction and the sterices effects its very important chemical bonding. So that the form III have more energy and less stability compared with the form II less energy and more stability, this indicate the shorter O·····H in form II contact is in agreement with the large stability(19-21). The energy of the hydrogen bonding has been calculated according to the equation as shown below(22-23)

$$E_{\mathbf{H\text{-}bond}} = E_{\mathbf{with\text{-}HB}} - E_{\mathbf{without\text{-}HB}}$$

The value of the energy of hydrogen bonding in form (II) was -52.5847 KJ.mol^{-1}(more stable), while in the form (III) the energy of hydrogen bonding was 15.9226 KJ.mole^{-1}, probably the most studied hydrogen bond is that in water dimmer, found to be -23 ± 3 KJ. mol^{-1} experimentally(24).

Table 2 Selected structural parameters of the optimized compounds, bond distance(A°) X1—H- - - - X2 and bond angles(°) X1—H-----X2.

Compound	Basis set	Bond	Bond Length(A°)	Bond angles(°)	Bond angles(°)
I without IHB	6-311G(d,p)	-------	--------	--------	---------
II with IHB	6-311G(d,p)	H(11)-O(8)	1.83	O(7)-H(11)-O(8)	122.5
III with IHB	6-311G(d,p)	H(11)-O(8) H(12)-O(7)	2.38 2.38	O(7)-H(11)-O(8) O(8)-H(12)-O(7)	109.6 109.7

In the Table 3; excitation energy of the pyrocatechol without IHB and with IHB calculated, it can be seen that the form I has need less energy to electronic excitation because of have high HOMO energy(-3.793 eV) compare with less of the HOMO energy to the forms II and III (-3.842 ev, -4.014 ev sequence),(20-25)

Table 3 Excitation Energy of the Pyrocatechol without IHB and with IHB

Compound	OSC. STR	λmax nm	Enrgy Kcal/mol
I without IHB	0.0416075	272	104.7608
II with IHB	0.0409871	267	106.8197
III with IHB	0.0341864	267	*107.0142*

On the basis of vibrational analysis and statistical thermodynamic, the standard thermodynamic functions, H, G, Cp, S at constant temperature 298.15 k, were obtained and listed in Table 4, it can be observed that the composition the form II have more spontaneity compare with forms I, III, because of the form II have less free energy (G), on the other hand the form II showed increase value of entropy(S) and decrease value of enthalpies(H) compare with the form III. Also increase entropy(S) to form II lead to more spontaneity compare with form I, in spite of have high enthalpies(H) value compare with form I , this is obvious in the total free energy (G) are less in form II compare with the form I, and this lead to increase entropy toward to favorable state (more stable) , this in agreement and with thermodynamic laws(22-26).

Table 4 Thermodynamic Properties with and without intramolecular hydrogen bonding of pyrocatechol at temperature 298.15 k

Compound	H Kcal/mol	G Kcal/mol	Cp cal/mol. K	S cal/mol. K
I without IHB	68.855	44.834	29.775	80.567
II with IHB	69.200	44.711	29.663	82.139
III with IHB	75.266	52.661	24.224	75.819

Conclusion

The quantum chemical calculations can be successfully used for the prediction of intramolecular hydrogen bonding, electronic properties, and relative stabilities in pyrcatechol.

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المستخلص:

تم في هدا البحث دراسة نظرية للخصائص والصفات التركيبية والالكترونية للبايروكاتيكول(I,II,III) بوجود التاصر الهيدروجيني الضمني وبعدم وجوده بواسطة كيمياء الكم. انجزت الموائمة الهندسية للتراكيب بطريقة DFT/Slater وعند المستوى المجموعة الاساسية 6-311G(d,p)

. اظهرت الدراسة أن الطاقة الكلية للجزئة II أقل من الطاقة الكلية للجزئتين I وIIIوهدا يؤكد الاستقرارية العالية للجزئة II كدلك اظهرت الدراسة القيمة العالية لعزم ثنائي القطب للجزئةII مقارنة مع الجزئات I,III وكما بينت الحسابات النظرية تناقص طول الاصرة الهيدروجينية في الجزئةII مقارنة مع طول الاصرة الهيدروجينية في الجزئة III . و تم حساب الخواص الثرموداينميكية للجزئات I,II,III ووجد ان الحالة المفضلة التي يكون فيها S اعلى ما يمكن هو ما يملكه الشكل II.