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Density Functional Theory studies of hydroxybutanones

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Abstract: Density Functional Theory (DFT) method were applied for investigation on conformations of three constitutional isomers of Hydroxybutanone in both gas phase and aqueous solution at B3LYP/6-311++G** level. The potential energies surfaces (PES) were calculated for various conformations and the results indicated that several factors are affected on the stability of conformations. The electronic and thermodynamic parameters were also calculated for most stable and unstable conformers at B3LYP/6-311++G** level of theory and the results were consistent with PES analysis.

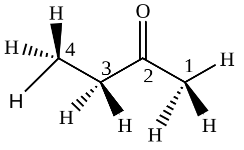
Keywords: Hydroxybutanones, DFT, Potential Energy Surface, Conformational analysis.

Introduction

3-Hydroxybutanone and 4-Hydroxybutanone are important molecules due to their application in the synthesis of α,β-unsaturated carbonyl compounds [1]. The optical active 3-Hydroxybutanone (acetoin, with a stereogenic center at C_3), is used as an external energy store by a number of fermentive bacteria and produced via metabolic processes of microorganisms [2].

Conformational analysis of carbonyl compounds is one of the subjects of interest for organic chemists. The mechanism of the reactions is highly dependent on the conformation of the participating materials and that is dependent on the stereoelectronic effects of atoms or groups. It is thus apparent that a greater understanding of the different types of conformations is essential.

The preferred conformations of linear open-chain carbonyl compounds, like 1-alkenes, are eclipsed rather than bisected. For example in propanal, it is the methyl group, rather than the hydrogen, that is eclipsed with the carbonyl group in the most stable conformation [3,4]. Ketones also favor eclipsed conformations. The preference is for the rotamer in which the alkyl group, rather than hydrogen, is eclipsed with the carbonyl group because this conformation allows the two alkyl groups to be *anti* rather than *gauche* with respect to the other carbonyl substituent. The conformational profile for 2-butanone has been developed from analysis of its infrared spectrum [5]. The dominant conformation is *anti* with a C_1–H and the C_4 methyl group eclipsed with the carbonyl group (Scheme **1**).



Scheme 1: Preferred conformation of 2-butanone

The preferred conformation of 3-methyl-2-butanone is similar [6,7]. Moreover, electron diffraction studies of 3-pentanone indicate the methyl-eclipsed conformation to be the most stable rotamer [8].

By replacement of an atom with a substituent in a molecule, some of the structural parameters such as

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*Corresponding author. Tel: (+98) 6642468320, Fax: (+98) 6642468223, E-mail: m_soleymani2007@yahoo.com bond lengths and bond angles will be changed. The preferred conformation is resulted from a balance between electronic and steric effects in molecule.

In continuous of our theoretical studies on various organic compounds [9-13], it is the purpose of our study to perform conformational analysis of 1-Hydroxybutanone (**1-HB**), 3-Hydroxybutanone (**3-HB**) and 4-Hydroxybutanone (**4-HB**). The potential energies surfaces (PES) were calculated for various conformations and the results indicated that several factors such as hydrogen bonding, electronic repulsions, steric repulsions and either bond eclipsed or bond bisected are affected on the stability of conformations. The electronic and thermodynamic parameters such as zero point energy (E_0), HOMO energy (E_{HOMO}), LUMO energy (E_{LUMO}), chemical hardness (η), chemical potential (μ), polarizability (<α>), dipole moment (μ'), heats of formation (ΔH_f) and free energies of formation (ΔG_f) were also calculated for most stable and unstable conformations of Hydroxybutanones and the results were agreement with PES analysis.

Results and discussion

Potential Energy Surface (PES) analysis:

PES scan of Hydroxybutanones was performed around selected dihedral angle (torsion angles) with 5° increment, using B3LYP/6-311++G** method. The potential energy curves of **1-HB** was plotted as a function of C1–C2–C_3–C_4 (α) and HO–C_1–C_2–O (β) dihedral angles in both gas phase and aqueous solution, as shown in Figure 1. To obtain conformers of **1-HB** molecule, when the procedure of torsional scan was performed at each of the fixed values of α and β, all other structural parameters were optimized. As shown in Figure 1, for gas phase calculations, the internal rotation of C_2–C_3 and C_1–C_2 bonds yielded global minimum (by consideration of both curves A and B), at β=0°, E= –808084.58 kJ/mol and global maximum at α=0°, E= –808050.08 kJ/mol. The corresponding structures (**1-HB-a** and **1-HB-b**, respectively) are shown in figure 2. Due to possibility of formation of intra-molecular hydrogen bonding and also C_1–OH and C_3–C_4 bonds eclipsed with the carbonyl group [5], **1-HB-a** is the overall dominant conformations of 1-Hydroxybutanone in gas phase and energetically is lowest relative to others.

In addition to global maximum and minimum, there are other relatively stable or unstable conformations, For example the energetically minima at α=180°, E = −808071.14 kJ/mol and the higher energy conformation at β=290°, E= –808052.08 kJ/mol, which the corresponding structures are illustrated in Figure 2 as **1-HB-c** and **1-HB-d,** respectively.

The *anti*-conformation of hydroxyl group with respect to the carbonyl group in **1-HB-c** and the *gauche*-conformation in **1-HB-d** is determining their relative stability or instability.

In the case of aqueous solution calculations, all potential energy surfaces are lower than the gas phase which can be attributed to the solvation stabilization of molecules. As shown in Figure 1 the global minimum is observed at α=180°, E= –808108.66 kJ/mol and two same global maximums are observed at β=75° and 275° with E= –808085.26 kJ/mol. The structures of the lowest energy conformer (**1-HB-e**) and the highest energy conformer (**1-HB-f**) are presented in Figure 2. Moreover a local minimum at β=180° with E= –808096.79 kJ/mol and a local maximum at α=0° and E= –808101.65 kJ/mol are observed which is corresponded to the **1-HB-g** and **1-HB-h** structures, respectively. In contrast to the formation of intra-molecular hydrogen bonding, **1-HB-h** is energetically unstable because the C_1–C_2 and C_3–C_4 bonds are completely eclipsed (similar to eclipsed n-butane).

To obtain conformations of 3-Hydroxybutanone (**3-HB**) the procedure of torsional scan was performed at C_1–C_2–C_3–C_4 dihedral angle (α) in both gas phase and aqueous solution.

As can be seen from Figure 1, the internal rotation of C_2–C_3 bond, yielded a global minimum at α=305°, E= –808094.79 kJ/mol and a global maximum at α=225°, E= –808066.44 kJ/mol. The corresponding conformations (**3-HB-a** and **3-HB-b**, respectively) are presented in Figure 2.

Due to the formation of intra-molecular hydrogen bonding (OH···O=C), in lowest-energy conformation **3-HB-a** and also C_1–H and C_3–OH bonds eclipsed with the carbonyl group [5], a *gauche* conformation of two C_1 and C_4 methyl groups is constrained to the molecule. The dihedral angle between C_1 and C_4 methyl groups is about 55° which consistent with a *gauche* conformation.

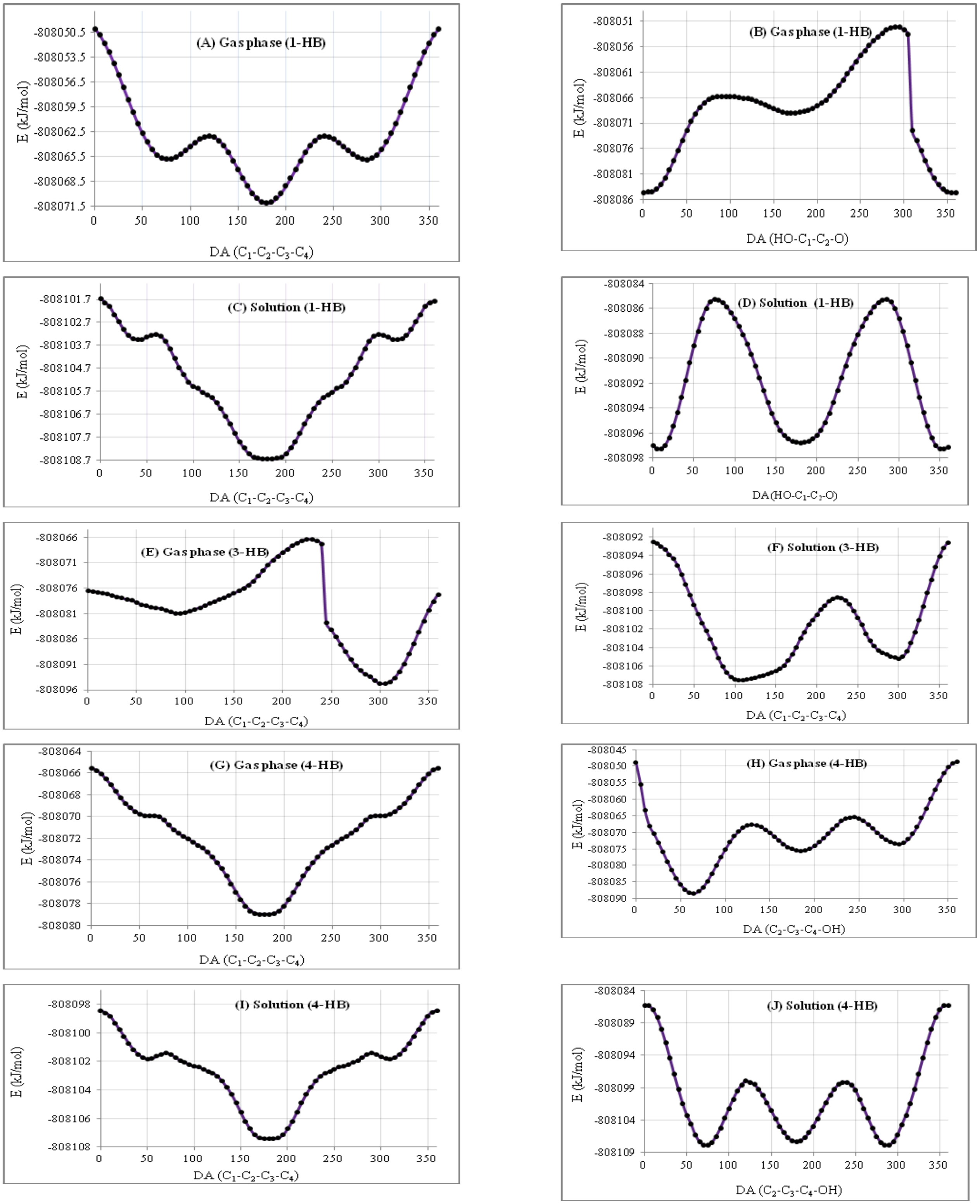
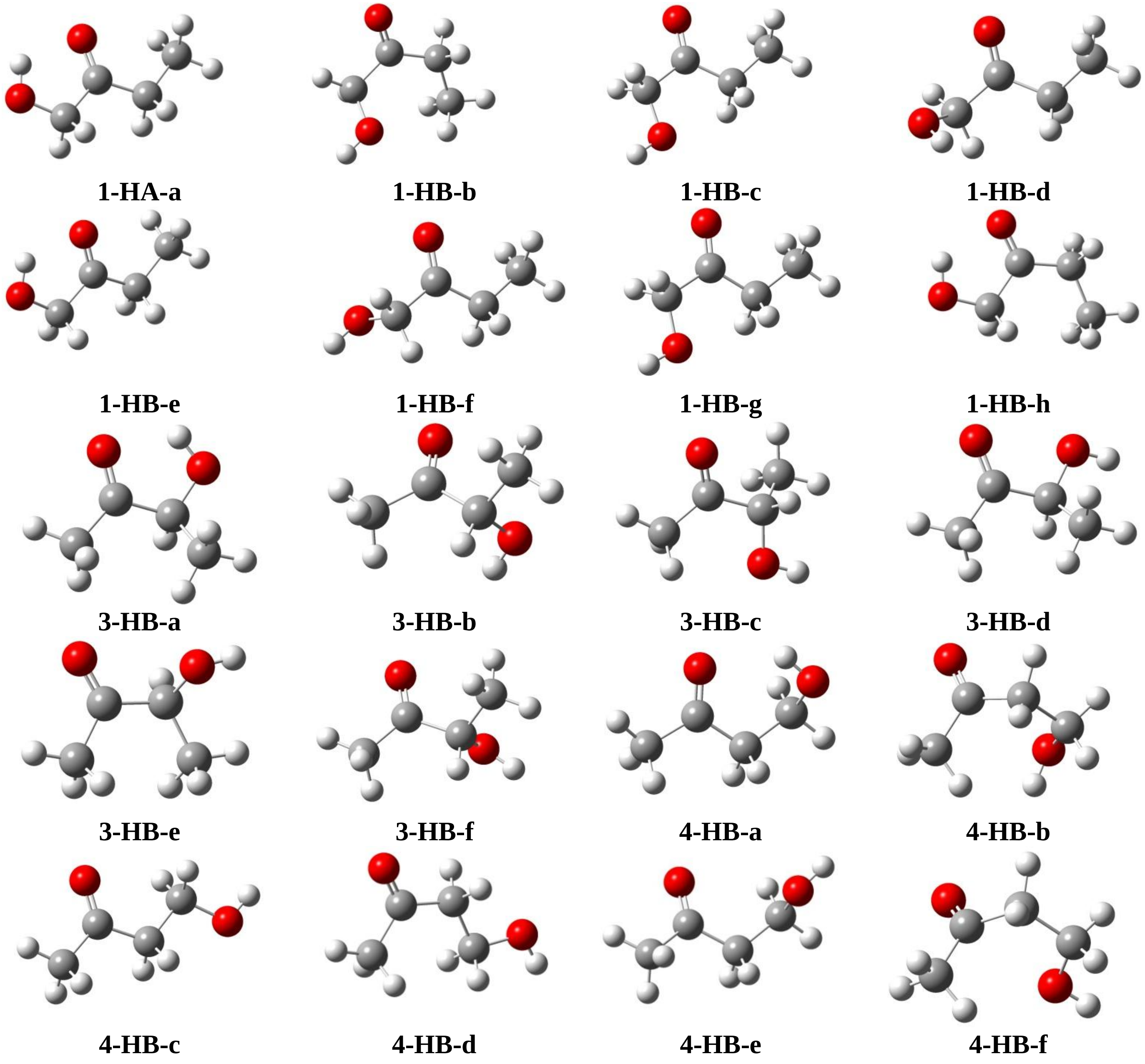


Figure 1: Potential energy surface (PES) scan of the calculated energies *vs.* dihedral angles using B3LYP/6-311++G** for compounds **1-HB**, **3-HB** and **4-HB** in both gas phase and aqueous solution.

For solution phase calculations on 3-Hydroxybutanone, the results indicated that there are a global minimum at α=110°, E= –808107.55 kJ/mol, a local minimum at α=300°, E= –808105.22 kJ/mol, a global maximum at α=0°, E= –808092.51 kJ/mol, and a local maximum at α=225°, E= –808098.55 kJ/mol, as shown in Figure 1.The corresponding conformations (**3-HB-c**, **3-HB-d**, **3-HB-e** and **3-HB-f**, respectively) are presented in figure 2. The structure of these conformations is indicated that inter-molecular hydrogen bonding between **3-HB** conformers and water molecules is favored relative to intra-molecular hydrogen bonding.


1-HA-a **1-HB-b** **1-HB-c** **1-HB-d**

1-HB-e **1-HB-f** **1-HB-g** **1-HB-h**

3-HB-a **3-HB-b** **3-HB-c** **3-HB-d**

3-HB-e **3-HB-f** **4-HB-a** **4-HB-b**

4-HB-c **4-HB-d** **4-HB-e** **4-HB-f**

Figure 2: The common conformations of Hydroxybutanones.

According to C_1–C_2–C_3–C_4 (α) and HO-C_4-C_3-C_2 (γ) dihedral angles, internal rotation of C_2–C_3 and C_3–C_4 bonds of **4-HB** in gas phase yielded global minimum at γ= 65°, E= –808088.52 kJ/mol and global maximum at γ= 0°, E= –808048.82 kJ/mol (Figure 1), which respectively correspond to the **4-HB-a** and **4-HB-b** structures in Figure 2. It is clear that **4-HB-a** conformer is eclipsed relative to carbonyl group and due to suitable orientation of hydroxyl and carbonyl group, the formation of hydrogen bonding is possible. By attention to the Figure 1it is clear that there are a local minimum at α=180°, E= –808078.96 kJ/mol, and a local maximum at α=0°, E= –808065.54 kJ/mol which respectively corresponds to the **4-HB-c** and **4-HB-d** conformers in Figure 2. The relative stability of **4-HB-c** can be attributed to the C_1–H and C_3–C_4 bonds eclipsed to the carbonyl group and also n-butane analogue staggered conformation, whereas the relative instability of **4-HB-d** conformer can be explained due to its n-butane like eclipsed form.

By performing the procedure of the torsional scan for C_2–C_3 and C_3–C_4 bonds of **4-HB** in solution phase, we found two same global minimum at γ=75°, and γ=285° with E= –808107.92 kJ/mol and a global maximum at γ=0° with E= –808086.31 kJ/mol as shown in Figure 1. Figure 2 shows the structure of related most stable conformation **4-HB-e** (owing to the C_1–H and C_3–C_4 bonds eclipsed relative to the carbonyl group), and most unstable conformation **4-HB-f** (because of eclipsed form of C_2–C_3 and C_4–OH bonds and also steric repulsion of hydroxyl group and C_1 methyl group which are 2.69 Å far from each other). According to the Figure 1, there is a conformation at α=180, E= –808107.40 kJ/mol which energetically is very similar to the **4-HB-e** conformer with E= –808107.92 kJ/mol. Moreover a local maximum is observed at α=0°, E= –808098.44 kJ/mol. The structure of two recent conformations are completely similar to the **4-HB-c** and **4-HB-d** conformers respectively, but in lower energy relative to the gas phase.

Table **1** shows the maximum and minimum points of potential energy surface, and rotational barrier for Hydroxybutanones in both gas phase and aqueous solution.

Table 1: The maximum and minimum points of potential energy surface, and rotational barrier for Hydroxybutanones obtained by B3LYP/6-311++G** method in gas phase and aqueous solution.[a]

Compound	Calculation phase	Torsion angle and Energy	Maximum point	Minimum point	Rotational barrier
1-HB	Gas phase	α E	0 –808050.08	180 –808071.14	21.06
		β E	290 –808052.08	0 –808084.58	32.50
	Aqueous solution	α E	0 –808101.65	180 –808108.66	7.01
		β E	75 –808085.26	5 –808097.29	12.03
3-HB	Gas phase	α E	225 –808066.44	305 –808094.79	28.35
	Aqueous solution	α E	0 –808092.51	110 –808107.55	15.04
4-HB	Gas phase	α E	0 –808065.55	180 –808078.96	13.41
		γ E	0 –808048.82	65 –808088.52	39.70
	Aqueous solution	α E	0 –808098.44	180 –808107.40	8.96
		γ E	0 –808086.31	75 –808107.92	21.61

[a] All energies are in kJ/mol.

A comparison of results presented in Table 1 indicated that:

1) For a particular molecule the location of maximum and minimum points are different in some cases for gas phase and aqueous solution, which indicates that the environment of the molecule is affected the conformations.

2) In all cases the rotational barriers in aqueous solution are less than relative to its value for gas phase, which probably can be attributed to the reduction of participation of intra-molecular hydrogen bonding in aqueous solution.

Electronic and thermodynamic parameters:

The relation of the hardness with the HOMO–LUMO gap is physically clear. It is obvious that the more stable structure has the largest HOMO–LUMO energy gap [14–16]. Due to the Maximum Hardness Principle (MHP), an electronic system with a larger HOMO–LUMO gap should be less reactive and more stable than one having a smaller gap [14,17,18].

Another property is the electric dipole polarizability which is inversely proportional to the hardness. The Minimum Polarizability Principle (MPP) has been also postulated [19], which is due to natural direction of systems to the lowest polarizability. Thus the systems with higher hardness and lower polarizability are more stable than one having lower hardness and higher polarizability, in other words, hardness correlates with the stability and polarizability correlates with the reactivity [20].

Table **2** shows the electronic and thermodynamic parameters of Hydroxybutanones for most stable and unstable optimized conformers in both gas phase and aqueous solution obtained by B3LYP method with 6-311++G** basis set. These parameters are included zero point energy (E_0), HOMO energy (E_{HOMO}), LUMO energy (E_{LUMO}), chemical hardness (η), chemical potential (μ), polarizability ($<\alpha>$), dipole moment (μ'), heats of formation (ΔH_f) and free energies of formation (ΔG_f).

Table 2: Calculated energies, chemical hardness, chemical potential, polarizabilities and dipole moment for most stable and unstable optimized conformers of Hydroxybutanones in both gas phase and aqueous solution by B3LYP method and 6-311++G** basis set.

Conformer	E_0 (*ev*)	E_{HOMO} (*ev*)	E_{LUMO} (*ev*)	η	μ	$<\alpha>$	μ' (Debye)	ΔH_f (kJ.mol^{-1})	ΔG_f (kJ.mol^{-1})
1-HB-a	–8372.08	–7.69	–1.17	3.26	–4.43	55.81	3.39	–775.33	–666.58
1-HB-b	–8371.88	–7.07	–1.25	2.91	–4.16	56.11	2.92	–753.38	–651.63
1-HB-e	–8372.34	–7.72	–1.10	3.31	–4.41	70.14	4.44	–800.17	–691.86
1-HB-f	–8372.22	–7.34	–1.30	3.02	–4.32	70.52	6.05	–786.02	–683.90
3-HB-a	–8372.20	–7.58	–1.24	3.17	–4.41	56.49	3.40	–784.17	–678.98
3-HB-b	–8372.06	–6.97	–1.21	2.88	–4.09	56.28	1.85	–770.55	–668.37
3-HB-c	–8372.35	–7.32	–1.07	3.13	–4.19	71.50	3.71	–798.05	–696.62
3-HB-e	–8372.32	–7.31	–1.29	3.01	–4.30	71.61	6.25	–795.21	–691.89
4-HB-a	–8372.11	–7.34	–1.13	3.10	–4.24	56.39	3.85	–775.98	–671.76
4-HB-b	–8371.96	–7.00	–0.91	3.04	–3.95	56.56	4.01	–761.29	–660.49
4-HB-e	–8372.33	–7.25	–0.89	3.18	–4.07	70.88	3.80	–796.78	–694.82
4-HB-f	–8371.35	–7.16	–0.94	3.11	–4.05	70.91	3.89	–790.28	–690.37

According to the data presented in Table 2 it is clear that approximately in all cases, the more stable conformers have 1) lower zero point energy, 2) lower chemical potential, 3) lower polarizability and 4) higher hardness relative to the less stable one. For example, **1-HB-a** has less zero point energy than **1-HB-b** and therefore it must be more stable which is consistent with PES analysis. **1-HB-a** conformer has also more hardness, less polarizability and less chemical potential and therefore according to the MHP and MPP, it must be more stable than **1-HB-b** conformer. Thermodynamic data (ΔH_f and ΔG_f) are also can be applied for comparison of the stability of conformations. In all cases the most stable conformers have more negative values of heats of formation (ΔH_f) and free energies of formation (ΔG_f).

In hydroxybutanones the molecular dipole moment (as μ' presented in Table 2) is a function of orientation of two electronegative oxygen atoms and geometry of the molecule.

Conclusion

We applied DFT method for conformational analysis of Hydroxybutanones in both gas phase and aqueous solution at B3LYP/6-311++G** level. The potential energies surfaces (PES) were calculated as a function of one or two torsional angle, and most stable and unstable conformations was determined. The electronic and thermodynamic parameters were also calculated for most stable and unstable conformers and the results were consistent with PES analysis, so that the Maximum Hardness Priciples and Minimum Polarizability Principles and thermodynamic data supported the stability of conformations.

Computational details

All calculations were carried out using the Gaussian 09 suites of programs employing the standard 6–311++G** basis set as implemented therein [21]. Density functional theories have been used to carry out calculations of energies and geometry optimizations for the Hydroxybutanones. The B3LYP was used to calculate the potential energy surfaces as a function of dihedral angles.

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