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Stability Order of the Conformations and Relative Intramolecular Hydrogen Bond Studies of 4-Hydroxy-3-(1-hydroxyvinyl)-pent-3-ene-2-one

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B3LYP method was applied for a complete study of 4-hydroxy-3-(1-hydroxyvinyl)-pent-3-ene-2-one and gaining the stability order of the conformations and relative intramolecular hydrogen bond strengths among 13 different possible conformers of this system.

Key Words: Conformations, Relative intramolecular hydrogen bond, 4-Hydroxy-3-(1-hydroxyvinyl)-pent-3-ene-2-one.

INTRODUCTION

It is clearly evident that the behaviour of biomolecules *i.e.* DNA and proteins originates from hydrogen bonding or more precisely, hydrogen interactions between different parts of such macromolecules. In present work, the 4-hydroxy-3-(1-hydroxyvinyl)-pent-3-ene-2-one (HHEP) was chosen for the study of intramolecular hydrogen bonding in a specific environment[1]. The molecule 4-hydroxy-3-(1-hydroxyvinyl)-pent-3-ene-2-one was selected for the following reasons: (i) the molecule has many different conformers despite of its simple structure, (ii) having three enol/keto groups in the molecule provides more opportunity to examine the interaction of these groups in a molecule, (iii) some conformers of this molecule have intramolecular hydrogen bonds and the system has not been studied yet.

EXPERIMENTAL

Possible structures for 4-hydroxy-3-(1-hydroxyvinyl)-pent-3-ene-2-one (HHEP) are shown in Fig. 1. These structures were optimized at B3LYP/6-31G* level using Gaussian 98 package[1]. Using the previous studies done on β-diketones it is acceptable that the addition of sp layers ($\alpha = 0.036$) and p ($\beta = 1.1$) on the proton involved in hydrogen bonding, would result in a geometry that is in good accordance with experiment[2]. Thus, these layers are added to the hydrogen bonding and other protons (other than methyl hydrogens) to simplify the comparison between different conformers of HHEP.

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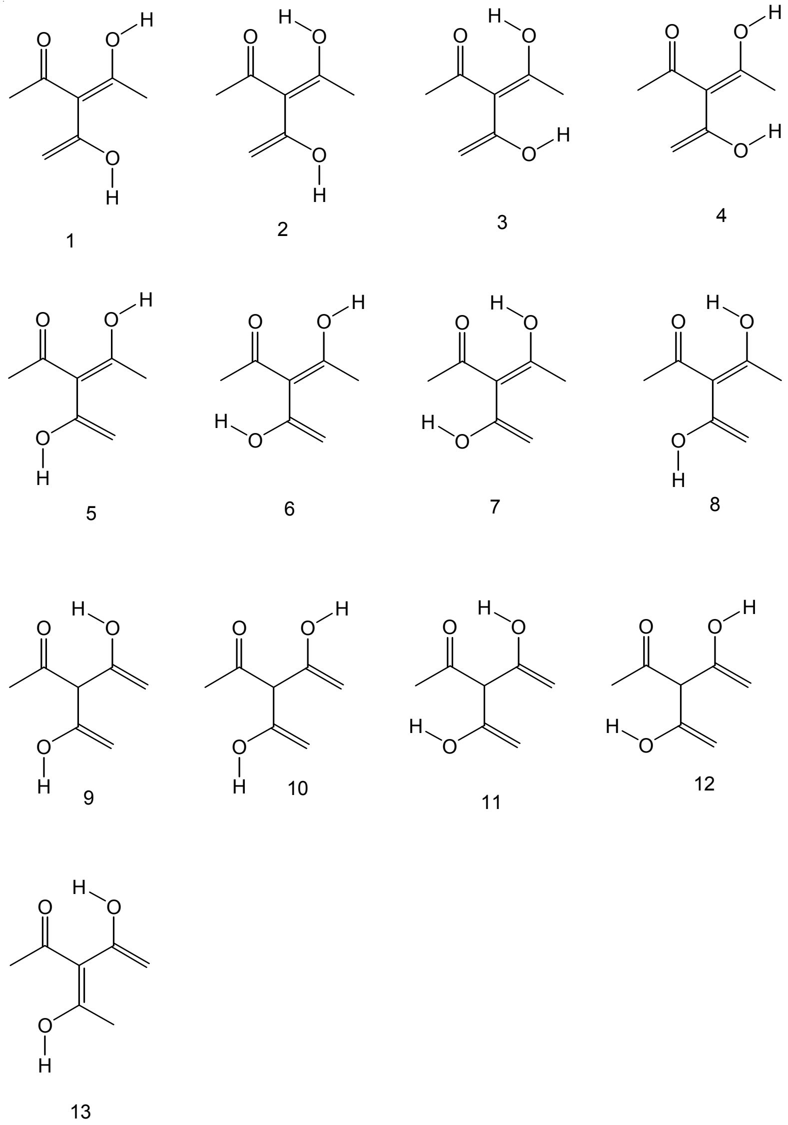

Fig. 1. Different structures for 4-hydroxy-3-(1-hydroxyvinyl)-pent-3-ene-2-one (HHEP)

RESULTS AND DISCUSSION

Different conformers of 4-hydroxy-3-(1-hydroxyvinyl)-pent-3-ene-2-one (HHEP) and their energies relative to the most stable one (8) are given in Fig. 1. The energies and selected bond lengths are given in Table-1. Some of these systems possess hydrogen bonding (2, 3, 7, 8, 9, 11, 13) each of which has a counterpart to be compared from the stability viewpoint (compare 2 and 1 or 4 and 3 for example). This stability relative to non hydrogen bonded counterpart is in some case about 70 kJ mol^{-1} (compare 2 and 1 or 4 and 3). This stabilization is assigned to a π conjugation which is occurred in enol-keto skeleton. This value is much more than 21 kJ mol^{-1} which is assigned to a conjugation effect in acetylacetone in the absence of hydrogen bonding[3].

TABLE-1
ENERGIES RELATIVE TO THE MOST STABLE STRUCTURE (8), SOME BOND LENGTHS ARE ALSO GIVEN FOR COMPARISON

Structure	Energy (kJ mol^{-1})	Bond length (Å)					
		O···H	O–H	C=O		C=C	C–O
1	78.820	-	0.967	1.222	1	1.364	1.352
2	3.920	1.485	1.032	1.258	2	1.392	1.315
3	5.196	1.793	0.972	1.208	3	1.337	1.355
4	79.340	-	0.967	1.222	4	1.366	1.351
5	78.820	-	0.967	1.222	5	1.364	1.352
6	51.730	-	0.966	1.236	6	1.363	1.365
7	2.687	1.524	1.021	1.253	7	1.390	1.319
8	0	1.516	1.022	1.253	8	1.388	1.320
9	95.840	1.759	0.979	1.223	9	1.337	1.362
10	100.800	-	0.967	1.213	10	1.334	1.372
11	109.300	1.843	0.976	1.222	11	1.335	1.367
12	105.100	-	0.967	1.212	12	1.338	1.368
13	51.720	1.750	0.982	1.236	13	1.344	1.360

On the other hand, stability relative to the counterpart lacking hydrogen bond is sometimes as little as 5 kJ mol^{-1} (compare 9 to 10). Structure 9 is not much more stable than 10 despite of its hydrogen bond and this is another evidence that the extra stability is due to π conjugation in the enol-keto skeleton because unlike the other structures having hydrogen bonds, this one lacks of a planar structure which is necessary for π conjugation. Even more, a comparison of the two structures 11 and 12 surprisingly reveals that the one with hydrogen bond (11) is of less stability. This energy difference is important because it shows more stability of keto over enol form[2].

The most similar structure to 8 is 7 with the exception that the second O-H which is not involved in intramolecular hydrogen bonding is oriented into the molecule. This minor difference is responsible for its less stability relative to structure 8 for 2.687 kJ mol^{-1} and therefore the intramolecular hydrogen bond length is rather more than in structure 8 (Table-1) since the closer is the second O-H group to the this group the looser becomes the intramolecular hydrogen bond.

Hydrogen bond strength depends on the nature of the system with which the cyclic enol is measured. Similar to the most common definition for hydrogen bonding strength in β-diketones, which is the energy required to rotate the bridging hydrogen atom by 180°, the hydrogen bonding strength in 2 relative to 1 is calculated to be about 74.9 kJ mol^{-1}. In the same manner, the hydrogen bonding strength in 3 relative to 4 is calculated to be about 74.1 kJ mol^{-1}.

The hydrogen bonding strength in 7 relative to 6 is calculated to be about 49 kJ mol^{-1}. Hydrogen bond strength in 8 is calculated to be 78.8 kJ mol^{-1} in relation to 5. Also hydrogen bond strength in 10 is calculated to be 5 kJ mol^{-1} in relation to 9 and finally as noted before, amongst the two structures 11 and 12, the one with hydrogen bonding (11) is surprisingly less stable by 4.2 kJ mol^{-1}. This parameter in 8 has the most value which is attributed to π-conjugation and resonance. Resonance contribution in hydrogen bonding in systems 2, 3, 7, 8, 9 and 11 is obtained by subtracting the estimated 21 kJ mol^{-1} value for π-conjugation. The extra stability due to resonance thus obtained is outlined in Table-2. Hydrogen bonding lengths corresponding to these resonance contributions are also given in Table-2 for comparison[4].

TABLE-2
RESONANCE CONTRIBUTION IN STABILITY

Structure	Resonance contribution (kJ mol^{-1})	Bond length (Å)	Bond strength (kJ mol^{-1})
(2)	53.9	1.485	74.9
(3)	53.1	1.793	74.1
(7)	28.0	1.021	49.0
(8)	57.8	1.022	78.8
(9)	-16.0	0.979	5.0
(11)	-25.2	1.843	-4.2

If the two structures 3 and 7 or 2 and 8 are compared, it is seen that 7 is rather more stable than 3 and the same is true for 2 and 8.

This observation that 8, despite of having a weaker hydrogen bond, is more stable than 2 is accounted for considering this fact that the planes spanning the groups CH_2 and OH will become perpendicular to the molecule plane after optimization and therefore 8 will be preferred over 2.

Nevertheless, hydrogen bonding strengths in 3 is about 25 kJ mol^{-1} more than that of 7 which could be attributed to a better resonance in 7. The same reasoning is hold for other couples 8 and 2 and others.

The inconsistency between calculated bond lengths and strengths on one hand and the resonance contribution on the other hand, it can be concluded that the definition of hydrogen bonding strength in β-diketones, which is equal to the energy required to rotate bridging hydrogen atom by 180°, does not lead to a good result. Therefore, bond lengths are used for comparison[3].

Comparisons of C-O bond lengths in structures 2, 3, 7, 8, 9 and 11 with corresponding C-O bond lengths in the counterpart structures without intramolecular hydrogen bonds give us interesting results. In those structures in which resonance causes more stability, C-O bond length in the one with intramolecular hydrogen bond is shorter. C=O bond lengths in the systems with hydrogen bonding is more than usual values which is due to its involvement in π-conjugation[2,4].

The O-H bond lengths in the systems with hydrogen bonding are more than usual which is due to a sort of trade off between the hydrogen bond length and the O-H bond length. In other words, the more is the strength of hydrogen bond, the more is the O-H bond length and the less is its strength.

Conclusion

The present study shows that structure 8 is more stable than its nearest counterpart (2) by 3.9 kJ mol^{-1} while it is much more stable (78.8 kJ mol^{-1}) than its counterpart without an intramolecular hydrogen bonding. Stability of 8 over 2 despite of a great similarity between these two systems was traced to the spatial differences between these two structures. The calculations carried out also show that the energy of π-conjugation is more than what predicted for acetyl acetone[4-8].

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