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Original article

Studying the geometric parameters, stability of isomer and IR frequencies in Enaminone compounds with the DFT and HF methods: A theoretical study

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ABSTRACT

Enaminones are the large category of chemical compounds that their numerous applications caused to be interested by researchers and scientists in two important experimental and theoretical forms. Calculating chemistry as one of the vital field for the chemistry can help us to investigate of enaminone structures. Our three isomers of the compounds are enaminone. In this research, Sustainability and inter-molecular hydrogen bond strength of each isomer is investigated. Four methods HF, B3LYP, B3P86, B3PW91 and two basis set 6-311G**, 6-311++G** were used in order to making calculation. The results of calculations in geometry parameters indicated that in our parameters, B3P86 method and 6-311++G** basis set have considerable preference than other methods and basis sets. In regarding to this method and basis set, hydrogen bonding was investigated and the third isomer (III) showed the strongest hydrogen bond achieved. Finally theoretical vibrational frequencies, in B3P86/6-311++G** basis set was investigated.

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1. Introduction

Enaminones are chemical compounds consisting of an amino group linked through a C=C to a carbonyl group (see Figure. 1). Therefore, the term enaminone is used to indicate any compound containing the conjugated system N=C-C=O (Elias, 2010). Enaminones are typical push-pull systems in which the amine group pushes and carbonyl pulls electron density and have the ability to function both as nucleophile and as an electrophile (Michael et al., 1999; Almazroa et al., 2004; Ruffino et al., 2009). The C=O group, conjugated with the N=C moiety, gives this system enough stability to be easily prepared, isolated and stored under atmospheric conditions at room temperature (Shawali, 2010; Junior et al., 1999). With this description, these compounds are stable structural motifs which are prepared by inexpensive raw materials. Enaminone compounds are versatile readily obtainable reagents and their chemistry has received considerable attention in recent years (Elassar et al., 2003; Reidlinger et al., 1998; Cocco et al., 1997; Wiberg et al., 1998; Katritzky et al., 2000). In addition to it, Enaminones have shown synthetic utility in therapeutic and biological agents such as ciprofloxacin, ducarmycin, taxol, quinoline, anti-malarial, anti-convulsant, anti-inflammatory, anti-tumor, anti-fungal, and anti-bacterial (Mahmud et al., 2010; Edfioghho et al., 2009; Purnami et al., 2009; Moradi et al., 2008). A hydrogen bond is the electrostatic attraction between polar molecules that occurs when a hydrogen atom bound to a highly electronegative atom such as nitrogen, oxygen or fluorine. Hydrogen bonds constitute a very interesting class of molecular interactions which are of extreme importance in many fields of chemistry and molecular biology. Enaminones with their ability to form intrahydrogen bonded chelated rings represent one of the suitable compounds to study such concept. In enaminones of type 1° and 2° due to presence of N-H bond, it is possible to form hydrogen bonding in the form of O...H-N. This hydrogen bonding can cause to migrate hydrogen intramolecular and as a result various tautomers are generated. Tautomers are constitutional isomers of organic or inorganic compounds that readily interconvert by a chemical reaction called tautomerization. This reaction commonly results in the formal migration of a hydrogen atom or proton, accompanied by a switch of a single bond and adjacent double bond. The concept of tautomerizations is called tautomerism (Antonov, 2013; Smith et al., 2001; Katritzky et al., 1976). As we know, isomers are molecules with the same chemical formula but different chemical structures (Petrucci et al., 2002; Berzelius, 1830). Chemists have been some of the most active and innovative participants in this rapid expansion of computational science. Computational chemistry is simply the application of chemical, mathematical and computing skills to the solution of interesting chemical problems. It uses computers to generate information such as properties of molecules or simulated experimental results. In this research, sustainability and inter-molecular hydrogen bond strength of each isomer is investigated.

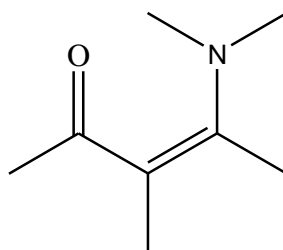


Fig. 1. The basic structure of enaminones.

2. Theoretical

2.1. Structure of enaminones

In figure .2, the desired enaminone and its isomers has been shown. All enaminone isomers were put and were calculate theoretically. Intramolecular hydrogen bonding as O...H-N lead to form important 6-member ring (see figure .3). Through forming this 6-member ring, the condition for resonance, hydrogen migration and tautomerism are provided. In figure .4, two tautomers of Ketamine (T1) and

Enolimine (T2) and transition state among them (TS) are observed. Hydrogen bonding in T1 form is as O...H-N and in T2 form is as O-H...N (Elias, 2010).

2.2. Computational methods (Theoretical calculations)

Of the various methods in theoretical chemistry, two methods of HF and DFT and of DFT, three hybrid functions of B3LYP, B3P86 and B3PW91 are employed. Moreover, to obtain the optimal structure of isomers, two basis sets including 6-311G** and 6-311++G** was used according to molecular structure. Hence three methods and two basis sets, six route section were generated. In this way, the enaminone isomers were plotted through Gauss View software (version 5.0) (Figure .2). Then all enaminone structures in all route sections were calculated and optimized through Gaussian program (version 2009). All information related to molecular parameterse were drawn out from 24 output files (4 method × 2 basis set × 3 isomer = 24 output file).

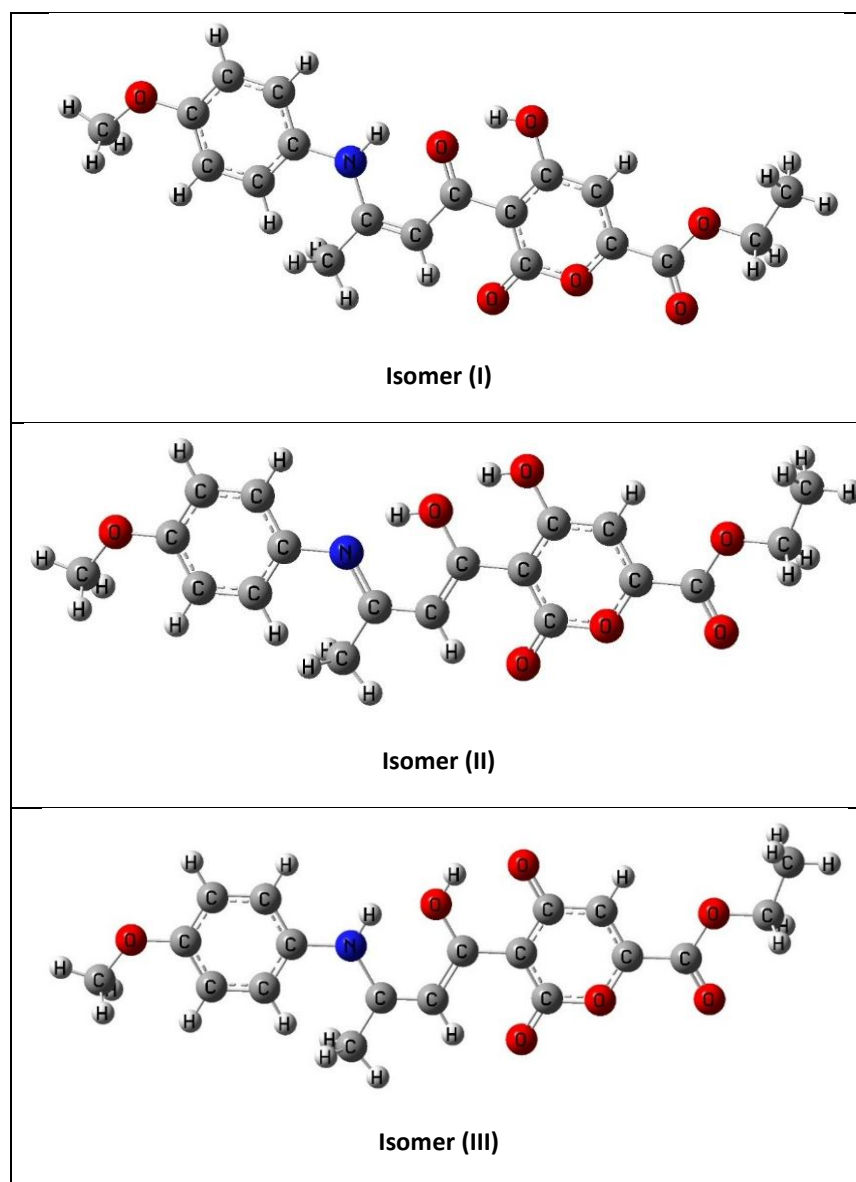


Fig. 2. Molecular structures of enaminone isomers.

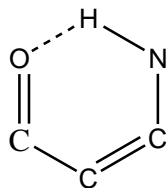


Fig. 3. Central 6-member ring of enaminones.

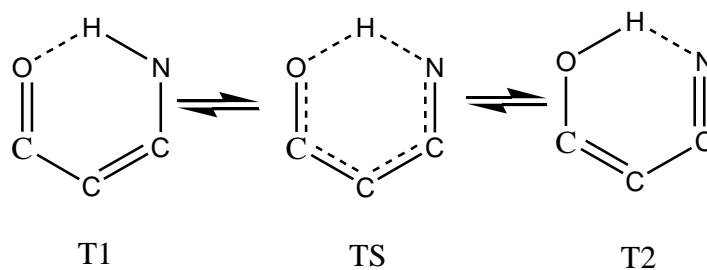


Fig. 4. Tautomers of enaminone.

3. Results and discussion

3.1. Selection of method

In order to select preferred method, we employed the length parameter of hydrogen bonding (O...H-N). In Table 1, the values to O...H length for all isomers in four method and two basis sets has been inserted. In each column that relates to special isomer, minimum figure has been marked. Because being low of figure is indicator of strength of O...H hydrogen bonding. Due to marked sections in Table 1, it will be revealed that the method of B3P86 has given the best values.

Table 1

Selection of preferred method using hydrogen bonding length.

	Isomer (I)		Isomer (II)		Isomer (III)	
	6-311G**	6-311++G**	6-311G**	6-311++G**	6-311G**	6-311++G**
HF	1.91796	1.91769	0.97119	0.97180	1.95742	1.95709
B3LYP	1.78934	1.79656	1.78955	1.79656	1.78973	1.79637
B3P86	1.74929	1.74887	1.74912	1.74908	1.74933	1.74885
B3PW91	1.76471	1.76815	1.76496	1.76804	1.76513	1.76808

3.2. Selection of basis set

We carry out the selection of preferred basis set in method of B3P86. Using four vital parameters (in the central 6-member ring of enaminones) of O...H length, N-H length, angle among O...H-N and distance between N and O, we select the preferred basis set. In Table 2, each isomer corresponds to special parameter the basis set were compared. In the H...O column, minimum value has been marked because O...H length reduction leads to increase hydrogen bonding strength. In the N-H column, maximum value has been marked because increase of H-N length lead to increase hydrogen bonding strength. In the O...H-N column, maximum value has been marked because increase of O...H-N angle lead to increase hydrogen bonding strength. In the N,O column, minimum value has been marked because N, O distance reduction leads to increase hydrogen bonding strength. Due to marked points in Table 2, it is revealed that the basis set of 6-311++G** has given better results. Therefore set of B3P86/6-311++G** will be selected.

Table 2

Selection of preferred basis set using four vital parameters in B3P86 method.

	Basis sets	O...H	H-N	O...H-N	N,O
Isomer (I)	6-311G**	1.75887	1.02495	138.32553	2.60895
	6-311++G**	1.74929	1.02572	138.52164	2.60743
Isomer (II)	6-311G**	1.74912	1.02698	138.32886	2.60884
	6-311++G**	1.74908	1.02748	138.50693	2.60747
Isomer (III)	6-311G**	1.74933	1.02695	138.22238	2.60896
	6-311++G**	1.74885	1.02753	138.42533	2.60735

3.3. Selection of the preferred isomer

Using preferred set of B3P86/6-311++G**, four vital parameters (in the central 6-member ring of enamines) of O...H length, N-H length, angle among O...H-N and distance between N and O, we design Table 3 in order to recognize the best isomer that generates strongest hydrogen bonding. Markings in Table 3 are based upon descriptions of part 3.2. (Selection of Basis set). Due to marks in Table 3, it is indicated that isomer (III) generate the strongest hydrogen bonding.

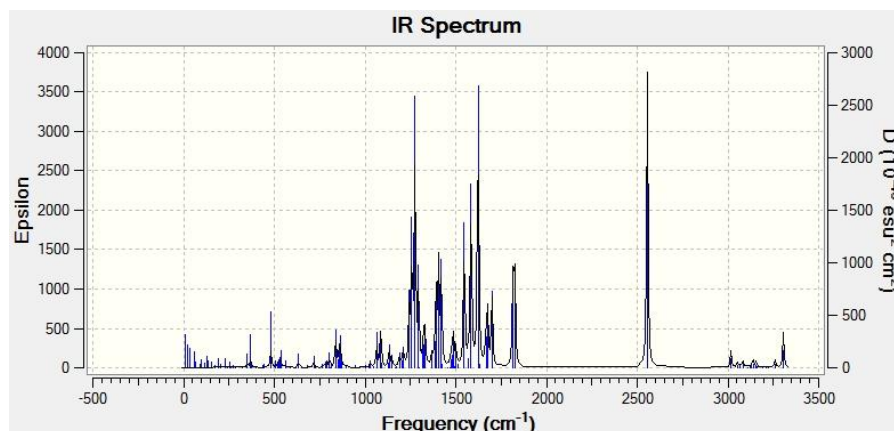
Table 3

Selection of preferred isomer using four vital parameters in B3P86/6-311++G**.

Parameter	Isomer (I)	Isomer (II)	Isomer (III)
O...H	1.74929	1.74908	1.74885
H-N	1.02572	1.02748	1.02753
O...H-N	138.52164	138.50693	138.42533
N,O	2.60743	2.60747	2.60735

3.4. Investigation of theoretical IR spectra

Infrared spectroscopy (IR spectroscopy) is the spectroscopy that deals with the IR region of the electromagnetic spectrum that is light with a longer wavelength and lower frequency than visible light. It covers a range of techniques, mostly based on absorption spectroscopy. As with all spectroscopic techniques, it can be used to identify and study chemicals. In Figure .5 through Figure .7, the theoretical IR spectrums related to three enamine structures (isomers) are observable.

**Fig. 5.** Theoretical IR spectrum of isomer (I) in B3P86/6-311++G**.

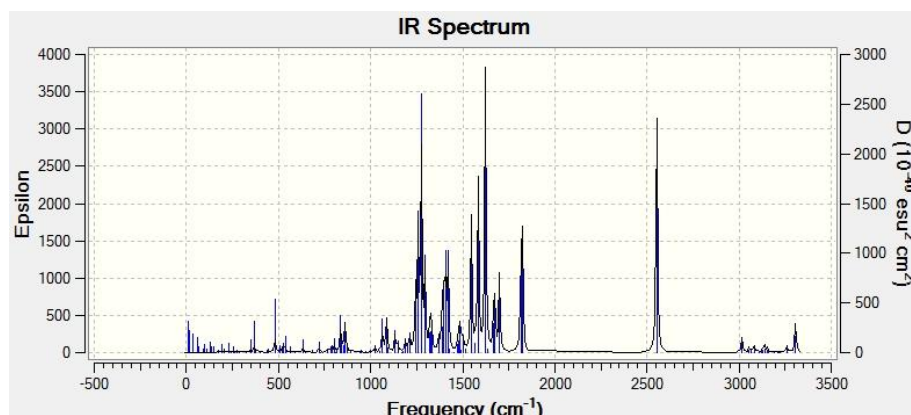


Fig. 6. Theoretical IR spectrum of isomer (II) in B3P86/6-311++G**.

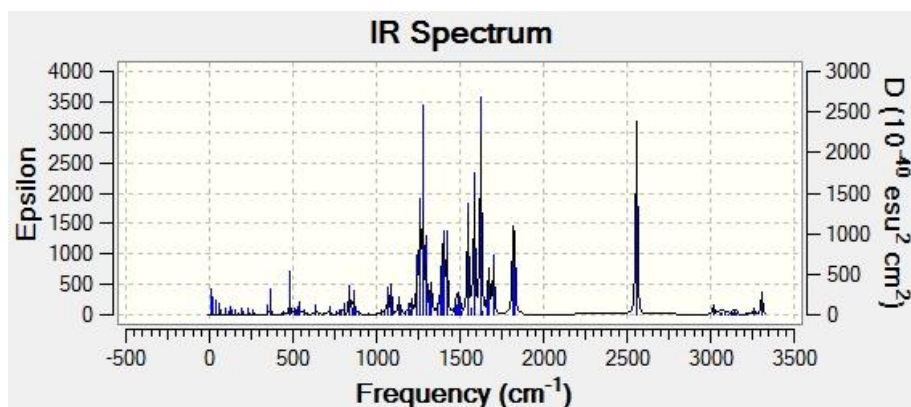


Fig. 7. Theoretical IR spectrum of isomer (III) in B3P86/6-311++G**.

5. Conclusion

In this project, the various enaminone structures (isomers) were investigated using theoretical methods of HF and DFT and two basis sets. After investigating geometric parameters revealed B3P86 method and 6-311++G** basis set are preferred. In preferred set of B3P86/6-311++G** the influence of isomers on hydrogen bonding was studied and results indicated that isomer (III) creates stronger hydrogen bonding in our enaminone structure. Indeed, in enaminone resulted from isomer (III), stability was studied and indicated that isomer (III) form is more stable than other forms. Finally the vibrational frequencies in B3P86/6-311++G** was investigated through IR spectrums.

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