# Theoretical Modeling and Experimental Study of Intramolecular Hydrogen-bond in Tetramethyl 3,7-dihydroxybicyclo[3.3.1]nona-2,6-diene-2,4,6,8-tetracarboxylate

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**Abstract:**

Theoretical study on *tetramethyl 3,7-dihydroxybicyclo[3.3.1]nona-2,6-diene-2,4,6,8-tetracarboxylate* is performed by using density functional theory (DFT) considering 6-31G basis sets. The results are compared with different experimental data obtained by using FT-IR spectroscopy in liquid state, using solvents of various polarities. Two hypothetical structures have been considered for the analysed compound: (i) one having intramolecular hydrogen bonding between OH enolic group and carbonylic oxygen from carboxylate group and (ii) the other with intramolecular hydrogen bonding between OH enolic group and methoxy oxygen from carboxylate group. The energy difference between these two possible forms is very low, suggesting a fast inter-conversion between each other. Our study was focused on the bands at 1600-1850 cm$^{-1}$, and 2900-3200 cm$^{-1}$ of spectrum. A reasonable agreement between theoretical and experimental data in liquid phase has been found.

Keywords : intramolecular hydrogen bond, energetics, conformations, IR spectroscopy, DFT.

## Introduction

Molecules have the tendency to develop the stongest interactions possible under the given conditions. The hydrogen bonds, especially the intramolecular one, as weak interactions, play an important role because they add up and thus generate very strong molecules conformations.

The secondary, tertiary and quaternary structure of proteins, the double helix of DNA, the membrane structures and complex intracellular particles like ribosomes are all maintained by weak interactions[1]. They give a deep insight into peptides and protein chemistry. Classically, a hydrogen bond is formed when the hydrogen atom attached to an electronegative atom (X) as a donor, interacts with a lone pair electron of another electronegativ atom (Y), as an acceptor, that is X-H...Y interactions[2,3]. One of the most suitable tool to investigate the nature of these hydrogen bonds is the FT-IR spectroscopy technique in liquide phase. The solvents play an

important role in the establisment of the spectra's shape, the increase of the solvent polarity could generate a considerable line enlargement and frequency shift[4-6]. The enolisable β-keto esters exhibit the phenomenon of conjugate chelation, through the intramolecular hydrogen bond, similar effects being observed in case of the corresponding diketone. As in them's case the frequency shifts of chelated esters have been used to measure double-bond character in a few series of compounds. The enolisable β-keto esters show absorption near 1718 cm$^{-1}$ and 1735 cm$^{-1}$ corresponding to the ketonic and ester carbonyl group, and also to others, at 1618 cm$^{-1}$ and 1656 cm$^{-1}$, which must arise from the chelate structure of enol form. The first band of these two bands is associated with the carbon double-bond absorption and the second with the chelated carbonyl absorption[7]. Presence of the intramolecular hydrogen bond and the solvent effects exhibit a significant influence on the normal mode vibration which involved C=O and C=C bonds in 1600 – 1850 cm$^{-1}$ spectral region.

The aim of our work is to give an accurate description of these intramolecular hydrogen bonds and solvent effects using theoretical molecular modeling and experimental IR spectroscopy study.

## Results and discussions

The experimental study consisted of the registration of the IR spectra in liquid state for *tetramethyl 3,7-dihydroxybicyclo[3.3.1]nona-2,6-diene-2,4,6,8-tetracarboxylate*[8]. It have been prepared several 20% concentrated solutions, using six solvents with different polarities (tetracarbon chloride, benzene, dichloromethane, ethylic ether, tetrahydrofurane, 1,4-dioxane). Infrared spectroscopic analyses were performed on a UR20 Carl Zeiss spectrophotometer, with a spectral resolution of 0.6 cm$^{-1}$, in 650-4000 cm$^{-1}$ spectral range. It have been used cells with CaF$_2$ windows and 0.1 mm thickness of the layer. The appropriate solvent for each investigated solution has been filled in the reference cell.

Theoretical calculations were carried out by DFT method at the B3LYP exchange-correlations functional, using 6-31G Pople's basis sets implemented in GAMESS[9] quantum chemical program package under Linux.

There were considered two hypotetical structures for the investigated β-ketoester[10], the intramolecular hydrogen bonds being formed between the the enol hydrogen and the carbonyl oxygen atom (Fig 1a), respectively methoxy oxygen atom, both belonging to the methoxycarbonyl group (Fig1b). The strength of the hydrogen bond shows a steady increase of the stability of β-ketoester chelate, which through such of intramolecular weak interactions closes a stable six-membered ring.

The strength of the hydrogen bond is a little bit different among these two conformations. Despite the different nature of these two interactions, both conformers exhibit an identical orientation of the

molecular backbone. The C=O⋯H-O distance in conformer A is 1.6895 Å, and the H₃C-O⋯H-O distance in conformer B is 1.6788 Å, shorter than in the other conformer (Table 1.).



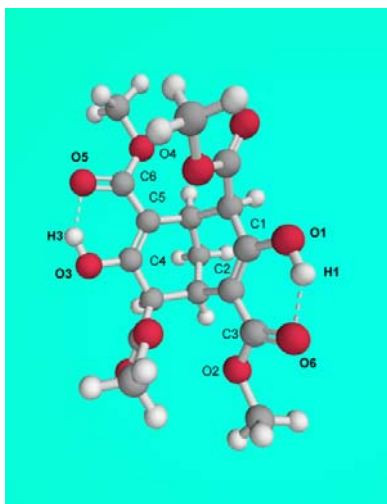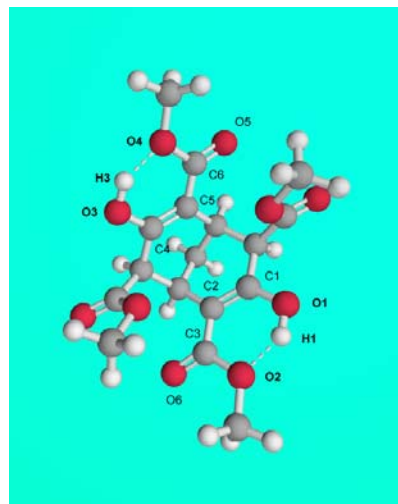**Figure 1a** Conformation A



**Figure 1b** Conformation B

**Table 1**

The selected molecular parameters of confA and confB calculated by DFT method using B3LYP exchange-correlation function with 6-31G basis set.

| ConfA | | ConfB | |
|---|---|---|---|
| Coord. | Values | Coord. | Values |
| Bond lenghts (Å) | | | |
| O3-H3 | 1.0060 | O3-H3 | 0.9949 |
| H3⋯O5 | 1.6895 | H3⋯O4 | 1.6788 |
| O5-C6 | 1.2649 | O4-C6 | 1.4107 |
| C6-O4 | 1.3683 | C6-O5 | 1.2399 |
| C6-C5 | 1.4492 | C5-C6 | 1.4554 |
| C5-C4 | 1.3717 | C5-C4 | 1.3686 |
| C4-O3 | 1.3567 | C4-O3 | 1.3606 |
| Angles (Deg.) | | | |
| H3⋯O5-C6 | 100.794 | H3⋯O4-C6 | 106.278 |
| O5-C6-O4 | 120.675 | O4-C6-O5 | 119.636 |
| O5-C6-C5 | 125.097 | O4-C6-C5 | 114.151 |
| C6-C5-C4 | 117.839 | C6-C5-C4 | 123.124 |
| C5-C4-O3 | 123.603 | C5-C4-O3 | 124.904 |
| C4-O3-H3 | 109.562 | C4-O3-H3 | 110.091 |

This two conformations were found to have an energetical barrier of only 0.2204 eV for the conversion of confA into confB, that suggesting a very fast interconversion between each other. Considering a transition state

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for this conformational equilibrium, these minima (the relative energies) calculated of the matching conformers being 3.047 eV for confA and 2.827 eV for confB (figure 2).
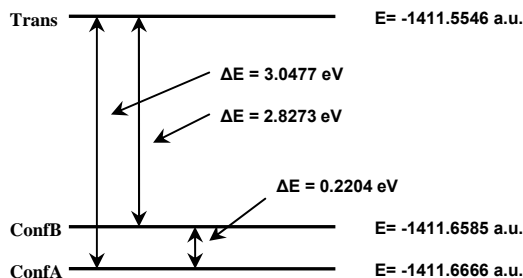


**Figure 2** The optimised energetical diagram for the transition state, respectively for both conformations of the *tetramethyl 3,7-dihydroxybicyclo[3.3.1]nona-2,6-diene-2,4,6,8-tetracarboxylate*
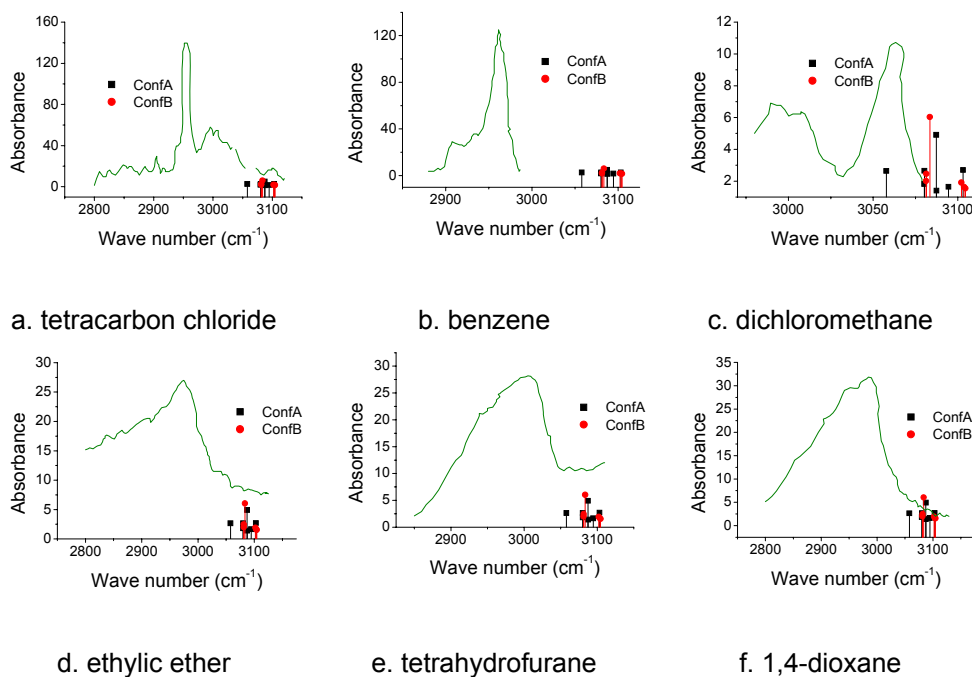


a. tetracarbon chloride        b. benzene        c. dichloromethane



d. ethylic ether        e. tetrahydrofurane        f. 1,4-dioxane

**Figure 3**. Theoretical and experimental IR spectra (2800 – 3200 cm-1) in the C-H and O-H stretching region, using solvents with various polarities.

The IR spectra in the O-H region, C=O and C=C stretching vibrations, respectively have been studied in a wide range of solvents solutions of 20% concentration. Taking account that the O-H stretching band depends on the solvent polarity, it has been shown that, due to the

intramolecular hydrogen bond, this band is situated in this case around 2900 cm^{-1}.

It can be observed (Figure 3 a.-f.) that increasing the solvent polarity (from tetracarbon chloride to 1,4-dioxane) the origin of experimental absorption band has blue shifted and the band shape becomes larger.
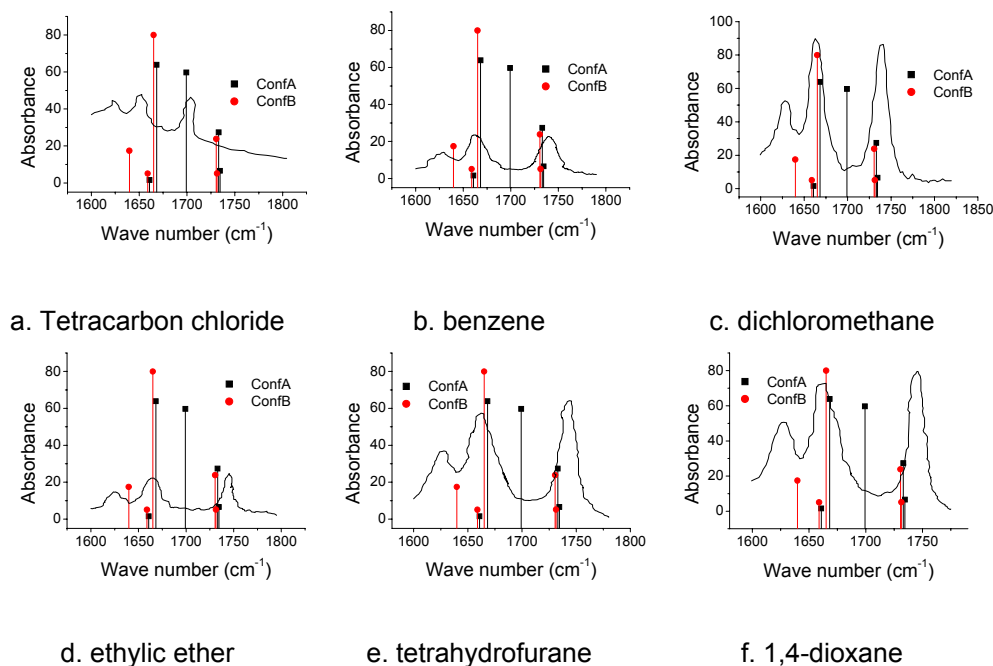
a. Tetracarbon chloride     b. benzene     c. dichloromethane

d. ethylic ether     e. tetrahydrofurane     f. 1,4-dioxane

**Figure 4**. Theoretical and experimental IR spectra (1600 – 1800 cm-1) in the C=O and C=C stretching region, using solvents with various polarities.

A good agreement between the theoretical frequency values and the experimental results has been found in 1600-1850 cm^{-1} spectral region, especial for the lines belonging to confB structure (Figure 4 a.-f.). In these normal modes are involved two characteristic bond stretching (C=C and C=O) and C-O-H angle bending. The corresponding frequencies of C=O are belonging to carbonyl group involved in intramolecular hydrogen bond formation (1639.1 cm^{-1} for confA, and 1699.3 cm^{-1} for confB) and to carbonyl included in ester group, which exists as a nonbonded group (1730.6 cm^{-1} and 1731.4 cm^{-1} for confA, 1733.1 cm^{-1} and 1734.5 cm^{-1} for confB ). The corresponding frequencies for C=C bond stretching are 1665.1 cm^{-1} and 1658.9 cm^{-1}for confA, 1660.8 cm^{-1} and 1668.2 cm^{-1} for confB. The C-O-H angle bending are coupled with bonded C=O in case of confA and with C=C in case of confB, having 50 cm^{-1} frecuency shift between them. This frequency shift suggests that confB spectral shape is closer to the experimental spectra and its geometry structure is more realistic than confA one.

## Conclusions

It have been modelated a two possible conformations of the *tetramethyl 3,7-dihydroxybicyclo[3.3.1]nona-2,6-diene-2,4,6,8-tetracarboxylate*, both of them involving the formation of intramolecular hydrogen bond. The energy difference between these two forms is very low ΔE=0.2204 eV, suggesting a fast inter-conversion between each other, passing through a transition state. The IR spectroscopy study in liquid phase, in conjunction with DFT revealed the existence of intramolecular hydrogen bond in analysed compound. The calculated and experimental IR spectra are in good agreement, especially in the 1600 – 1850 cm$^{-1}$ spectral region, meanwhile in the 2800 – 3100 cm$^{-1}$ spectral region it has been registered blue shift of the calculated frequency due to the solvents polarity and the chelatization *via* intramolecular hydrogen bond effects. The characteristic line for *bonded* C=O at 1700 cm$^{-1}$ of the theoretical spectrum of confA has no correspondence in the experimental spectra. As a consequence of the increase of the solvent polarity it has been observed a considerable line enlargement and frequency shift of the C-H, and the associated O-H enol stretching bands. Summarizing the results it can be concluded that the confB geometry structure is in the better agreement with the experimental data than confA structure.

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