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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

N. TOSA[1], A. BENDE[2], I. BRATU[2], I. GROSU[1]

[1] *Organic Chemistry Department, Babes-Bolyai University, 11 Arany Janos, RO 400028 Cluj-Napoca, Romania,*
[2] *National Institute for R&D of Isotopic and Molecular Technologies, 71-103 Donath, RO 400293 Cluj-Napoca, Romania*

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 ones, 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 electronegative atom (Y), as an acceptor, that is X-H...Y interactions[2,3]. One of the most suitable tools 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 spectra's shape establisment, 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 bonds, similar effects being observed in case of the corresponding diketones. The frequency shifts of chelated esters have been used to measure the 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 groups, respectively, and at 1618 cm^{-1} and 1656 cm^{-1}, which must arise from the chelate structure of enol form. The first 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 vibrational mode of C=O and C=C bonds in the spectral domain of 1600 – 1850 cm^{-1}.

The aim of our work is to give an accurate description of these intramolecular hydrogen bonds in tetramethyl 3,7-dihydroxybicyclo[3.3.1]nona-2,6-diene-2,4,6,8-tetracarboxylate, a potential macrocycles precursor, 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]. Several 20% concentrated solutions were prepared, using six solvents situated in 2.25 - 4.8 polarity values range (tetracarbon chloride, benzene, dichloromethane, ethylic ether, tetrahydrofurane, 1,4-dioxane). All these selected solvents are "transparent" on 1600 – 1850 cm^{-1} and 2800 – 3100 cm^{-1} spectral range and allow C=O and intramolecular hydrogen bonds study. 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 have been prepared. Cells with CaF_2 windows and 0.1 mm thickness of the layer, have been used. 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.

Two hypotetical structures for the investigated β-ketoester[10] were considered: the one with intramolecular hydrogen bonds being formed between the the enol hydrogen and the carbonyl oxygen atom (Fig. 1a), and respectively methoxy oxygen atom, both belonging to the methoxycarbonyl group (Fig. 1b). 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 within these two conformations. Both conformers exhibit an identical orientation of the molecular backbone. The C=O···H-O distance in conformer A is 1.6895 Å, while the H_3C-O···H-O distance in conformer B is 1.6788 Å, shorter than the other conformer (Table 1.).

Table 1

Conf_A		Conf_B	
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

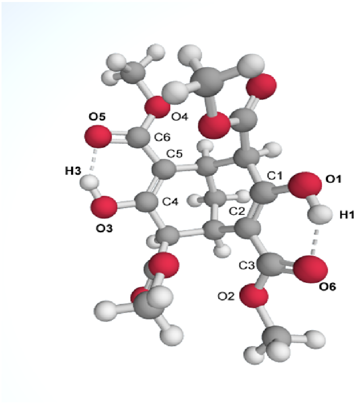


Figure 1. a) Conformation A

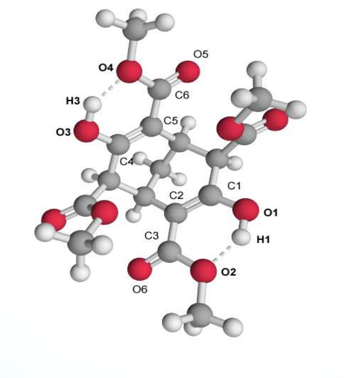


Figure 1. b) Conformation B

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

These two conformations were found to have an energetical barrier of only 0.2204 eV, that suggests a very fast interconversion between each other. Considering a transition state for this conformational equilibrium, the minima (the relative energies) calculated for the matching conformers were 3.047 eV for conf_A and 2.827 eV for conf_B (Fig. 2).

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 into account that the O-H stretching band depends on the solvent polarity and on eventual intramolecular hydrogen bonds, this band is situated around 2900 cm^{-1}.

It can be observed (Fig. 3 a.-f.) that, increasing the solvent polarity (from tetracarbon chloride to 1,4-dioxane), the origin of experimental absorption band is blue shifted and the band shape becomes larger.

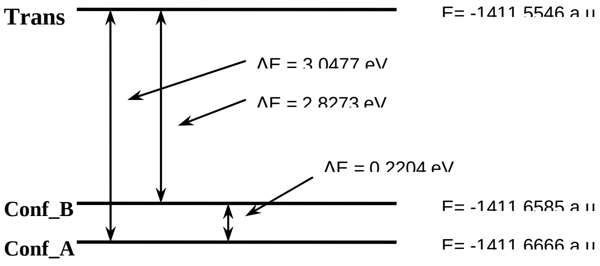
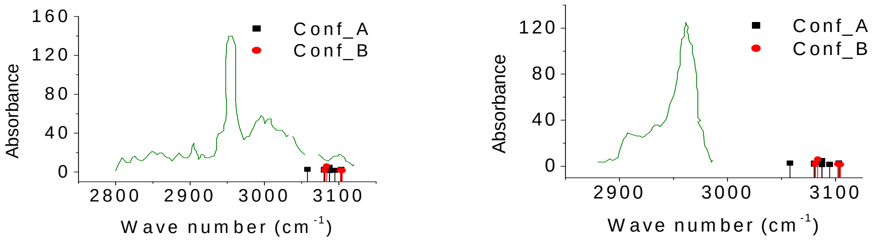
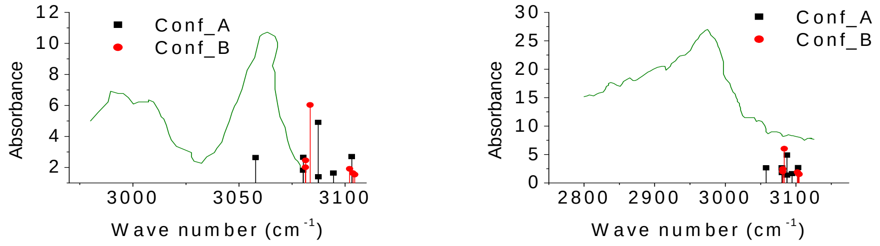


Figure 2. The optimised energetical diagram for the transition state, respectively for both conformations of the *tetramethyl 3,7-dihydroxybicyclo[3.3.1]nona-2,6-diene-2,4,6,8-tetracarboxylate*



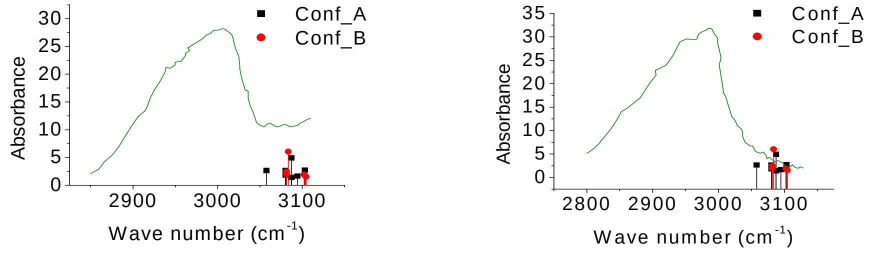
a. tetracarbon chloride

b. benzene



c. dichloromethane

d. ethylic ether

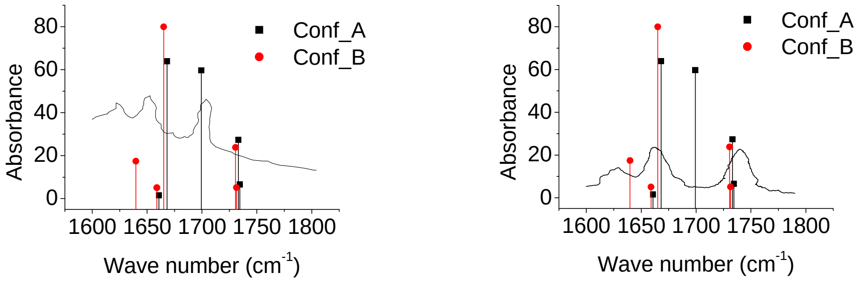


e. tetrahydrofurane

f. 1,4-dioxane

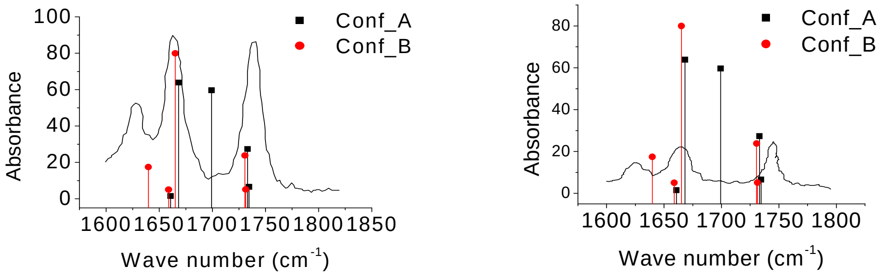
Figure 3. Theoretical and experimental IR spectra (2800 – 3200 cm-1) in the C-H and O-H stretching region, using solvents with various polarities.

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



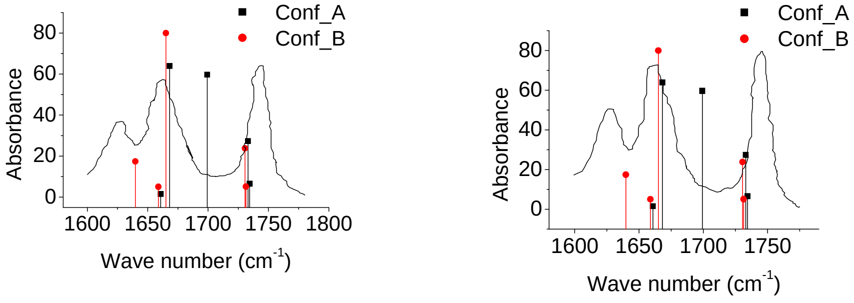
a. tetracarbon chloride

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.

CONCLUSIONS

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 have been modeled. The energy difference between the 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 bonds in the 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 conf_A has no correspondence in the experimental spectra. As a consequence of the increase of the solvent polarity, a considerable line enlargement and frequency shift of the C-H, and the associated O-H enol stretching bands, has been observed. Summarizing the results, it can be concluded that the geometry of the conf_B structure is in better agreement with the experimental data than that of the conf_A structure.

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