

Structure and Vibrational Spectra of Tetramethyl 3,7-Dihydroxybicyclo[3.3.1]nona-2,6-diene-2,4,6,8-tetracarboxylate and Bicyclo[3.3.1]nonane-3,7-dione

N. Tosa¹, A. Bende², S. Cîntă Pînzaru³, I. Grosu¹, E. Surducan²

¹Organic Chemistry Department, Babes-Bolyai University, 11 Arany Janos, RO 400028 Cluj-Napoca, Romania

²National Institute for R&D of Isotopic and Molecular Technologies, 71-103 Donath, RO 400293 Cluj-Napoca, Romania

³Molecular Spectroscopy Department, Babes-Bolyai University, Mihail Kogalniceanu 1, RO 400084 Cluj-Napoca, Romania

ABSTRACT. The conversion of *tetramethyl 3,7-dihydroxybicyclo[3.3.1]nona-2,6-diene-2,4,6,8-tetracarboxylate* into *bicyclo[3.3.1]nonane-3,7-dione* was achieved by using a conventional method and under microwave irradiation. The IR and Raman spectra were obtained and vibrational assignments could be made. The Density Functional Theory (DFT) was applied to calculate the structure and spectra and good agreement with experimental data was obtained.

Introduction

Supramolecular chemistry offers the potential to construct synthetic macromolecules with control at molecular level, a goal which has only truly been realised in natural bio-macromolecular systems. The performances of synthesised materials are critically dependent on the spatial arrangement of the constituents at molecular level. An additional development direction is to apply the synthesised material to molecular engines or for nanofilms¹ obtaining. The investigated compounds are potential macrocycles precursors, the major application of the method developed here being the films growing in situ, under similar reaction conditions on a surface or interface².

The aim of our work was to elucidate the structure of the *tetramethyl 3,7 - dihydroxybicyclo[3.3.1]nona-2,6-diene - 2,4,6,8-tetracarboxylate* (**1**) and *bicyclo[3.3.1]nonane-3,7-dione* (**2**) using vibrational spectroscopy, in conjunction with DFT calculation. The straightforward conversion of the tetramethyl 3,7 – dihydroxybicyclo [3.3.1]nona - 2,6 - diene - 2,4,6,8 – tetracarboxylate into bicyclo[3.3.1] nonane-3,7-dione by the one step conventional and microwave irradiation was proposed in our earlier work³. Our spectroscopic study reveals that these such of molecules participate into a keto-enol tautomeric equilibrium⁴. The compound **1** mainly exist as a dienol whereas the compound **2** exists as a diketone at ambient temperature⁵. Theoretical calculations were used in

order to gain a deeper understanding of the vibrational experimental spectra and structure of these complex molecules.

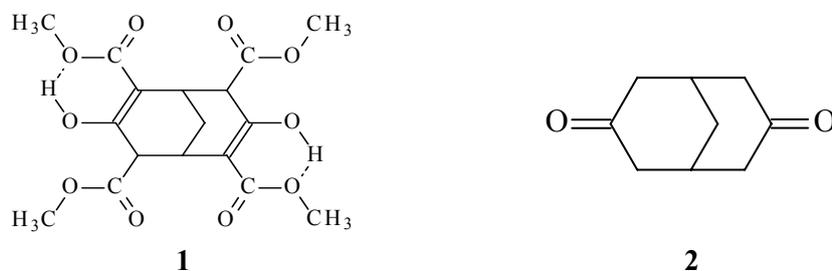


Fig. 1. Theoretical structures for compound **1** and compound **2**.

In particular, we used DFT as it is known that this method is a performant computational alternative to the conventional quantum chemical methods, since it is less computationally demanding and take account of the effects of the electron correlation.

Results and Discussion

The theoretical study has been done at DFT method with the B3LYP exchange-correlations functional, using 6-31G** Pople's basis sets implemented in GAMESS⁶ quantum chemical program package. The geometry structures were optimized at B3LYP with analytical gradient method, while the harmonic vibrational frequency values of theoretical IR and Raman spectra were obtained considering 6-31G** basis set.

Tetramethyl 3,7-dihydroxybicyclo[3.3.1]nona-2,6-diene-2,4,6,8-tetracarboxylate. The large number of harmonic vibrational frequency makes very difficult to identify and to assign the normal modes of different molecular fragment with the different frequency values. Since a lot of vibrational frequencies have small intensity only that values can be picked out from the spectra which have a significant intensity and which could have implication in our investigation. In the spectral segment of 800 – 820 cm⁻¹ several theoretical frequency lines were found, corresponding only to the $\rho(\text{C-O-H})$ fragment vibrations, where three different IR active and a single Raman frequency can be observed with a significant magnitude of intensity. In the 980 – 1060 cm⁻¹ spectral region of the IR spectra, for the different theoretical spectra can be found a number of five-six IR active and two Raman active modes with significant intensity. Their vibrations are more difficult to locate because of the complexity of vibrational motion. Even so, for most of case in the collective motion of atoms can be observed a characteristic vibration of the -C-C-C- bridge situated in the molecular

skeleton. The segment situated at the $1140 - 1290 \text{ cm}^{-1}$ interval of absorption spectra is the largest compact band region and the most densely loaded with frequency lines. Similarly to the previous region the vibrations of this spectral region are also complex being involved simultaneously the motion of the tetracarboxyl groups, the $-\text{C}-\text{O}-\text{H}$ groups, and the molecular skeleton. Some frequency values could be found also in the Bicyclo[3.3.1]nonane-3,7-dione IR spectra, such as ν_{86} . The few frequency lines are present in the $1320 - 1400 \text{ cm}^{-1}$ spectral region, that are characteristic to the bridge of molecular skeleton and to the $-\text{C}-\text{O}-\text{H}$ fragment. The region $1620-1780 \text{ cm}^{-1}$ is characteristic of double bond vibrations of $>\text{C}=\text{O}$ situated into the methoxycarbonyl groups and the $-\text{C}=\text{C}-$ into the molecular skeleton, having the highest intensity in the whole spectra. The frequency intensities of these normal mode vibrations are some of the most intense lines in the whole IR and Raman spectra, supporting the explanation of the local character of fragment's vibrations. The experimental spectra reveal also very strong IR bands at 1661 , 1734 and 1743 cm^{-1} , and 1627 (very strong), 1729 and 1740 cm^{-1} as weak-medium bands in the FT-Raman spectrum (Fig. 2).

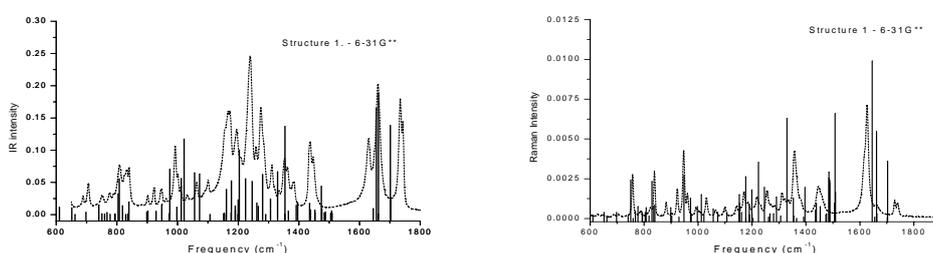


Fig. 2. The experimental and theoretical FT-IR and FT-Raman spectra of **1**.

Bicyclo[3.3.1]nonane-3,7-dione (2). Due to the molecular symmetry a considerable number of frequency lines are missing both from the IR and Raman spectra, while the other lines have very small intensity. However, both absorption spectra are more simple than in the case of structure (**1**). The frequency line at 708 cm^{-1} is characteristic of the carbon rings motion and due to the molecular symmetry the Raman shape is more intense than the analogous IR line intensity. An excellent confirmation was experimentally observed in the FT-Raman spectrum (Fig. 14), where this is the most intense band.

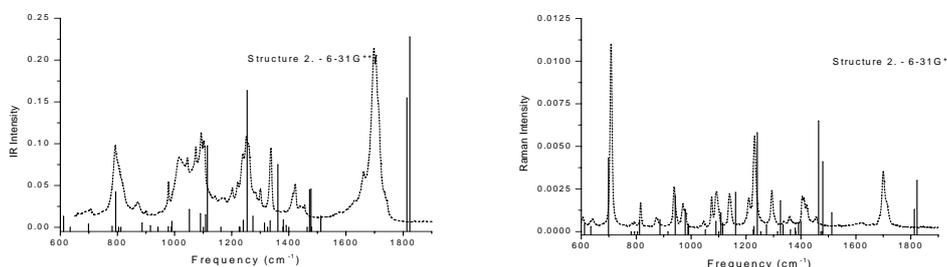


Fig. 3. The experimental and theoretical FT-IR and FT-Raman spectra of **2**.

In 1000-1400 cm^{-1} spectral region can be found the bulk of the lines in both vibrational spectra. The vibrational motion of these normal modes are very complex and could not be localized to the single bond distance or bond angle. Besides of the C-C-C bridge and C-C-C ring vibrations, different C-H vibrations (bending, rocking, and twisting) could be observed. The 1600-1750 cm^{-1} spectral region is characteristic to the $>\text{C}=\text{O}$ stretching vibrations, which are both IR and Raman active. The experimental spectra reveal very intense bands at 1698 and 1705 cm^{-1} (FT-IR) and a strong band at 1700 cm^{-1} with a shoulder at 1710 cm^{-1} (FT-Raman).

Conclusions

The investigations of the molecular structure of the compounds **1** and (**2**), in solid state, using FT-IR and FT-Raman spectroscopy in conjunction with the DFT calculations, revealed both tautomers of **1** (major enolic form) and exclusively ketonic form for the compound **2**. The intramolecular O...H bonds from the molecule of **1** are established between the H of the $\rho(\text{C}-\text{O}-\text{H})$ fragment and O of $\text{C}-\text{O}-\text{CH}_3$ fragment of the methoxycarbonyl group, both connected in the $\text{C}=\text{C}$ moiety.

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