



Contents lists available at ScienceDirect

Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy

journal homepage: www.elsevier.com/locate/saa

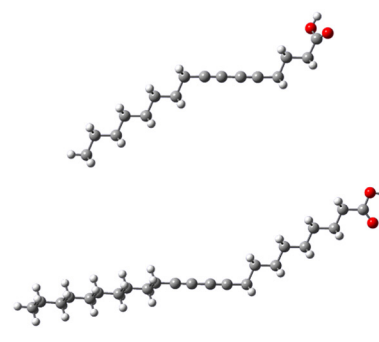
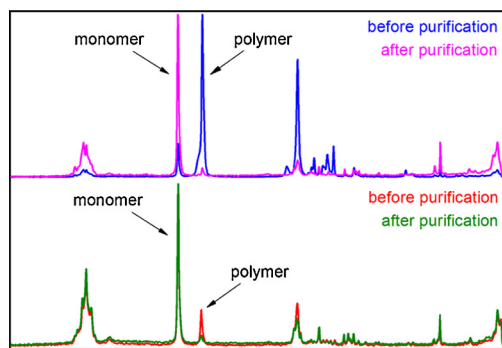
Vibrational and theoretical study of diacetylenic acids

Maciej Roman^a, Malgorzata Baranska^{a,b,*}^a Faculty of Chemistry, Jagiellonian University, Ingardena 3, 30-060 Krakow, Poland^b Jagiellonian Center for Experimental Therapeutics (JCET), Jagiellonian University, Bobrzynskiego 14, 30-348 Krakow, Poland

HIGHLIGHTS

- Conformers were found from theoretical calculations of diacetylenic acids.
- FT-IR spectra measured by ATR technique and in transmission (KBr) were compared.
- UV polymerization under various conditions was followed by Raman spectroscopy.
- Fermi Resonance (FR) in IR spectra was suggested.
- Calculations of dimers were applied for the interpretation of experimental spectra.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Received 24 February 2014

Received in revised form 1 April 2014

Accepted 24 August 2014

Available online 30 August 2014

Keywords:

Diacetylenic acids

Raman

Infrared

ATR

DFT

Polymerization

ABSTRACT

Three selected diacetylenic acids (DAs) with side-chains of various length ($\text{CH}_3-(\text{CH}_2)_m-\text{C}\equiv\text{C}-\text{C}\equiv\text{C}-(\text{CH}_2)_n-\text{COOH}$, where $m = 7, 9, 11$, and $n = 3, 8$) were analyzed using vibrational spectroscopy and quantum-chemical calculations. The conformational analysis was followed by potential energy distribution (PED) calculations to gain deeper insight into their FT-Raman and FT-IR spectra. The analysis was focused on spectral features of the diacetylene system sensitive to the substitution. In particular, the electron donor–acceptor properties of the substituent and the influence of side-chain length were studied. FT-IR spectra were measured by using two techniques, i.e. transmission (with KBr substrate) and Attenuated Total Reflection (ATR), and the latter seems to be less adequate for DAs measurements because the bands in the fingerprint region as well as the $\nu(\text{C}\equiv\text{C})_{\text{as}}$ mode are relatively of low intensity. Additionally, polymerization process of DAs was recognized using FT-Raman spectroscopy and strong and well-separated bands of diacetylenic polymers. Temperature and exposure to the sunlight are the factors of an important influence on the polymerization process of DAs. Since the investigated DAs are carboxylic acids, the interpretation of experimental spectra was performed on the basis of monomer and dimer calculations.

© 2014 Elsevier B.V. All rights reserved.

Introduction

Diacetylenic acids (DAs) are usually amphiphilic molecules constituting polar head and long alkyl tail (Fig. 1). Under suitable conditions, the DA monomers can assemble into organized structures

* Corresponding author at: Faculty of Chemistry, Jagiellonian University, Ingardena 3, 30-060 Krakow, Poland. Tel.: +48 12 6632253; fax: +48 12 6340515.

E-mail address: baranska@chemia.uj.edu.pl (M. Baranska).

such as vesicles and lamellae in solution or solid state [1]. For single-chain amphiphiles, the spacer group between the rigid segment and the head-group is necessary to form vesicles. Therefore, most of studies on the utility of polymerized diacetylenic acid (PDA) vesicles were focused on the system, where the position of diacetylenic group is located in the middle of the molecules like in **1**, **2**, and **3** (Fig. 1) [2].

Polymerization of the assembled DA monomers can be initiated by UV light irradiation (effective polymerization is obtained for

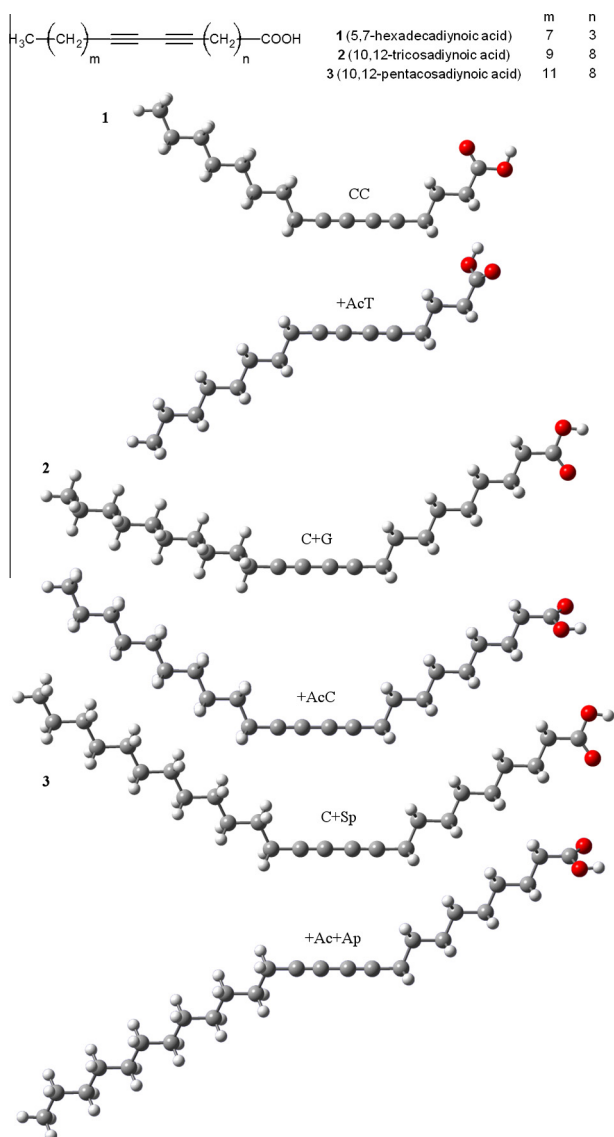


Fig. 1. Structures and selected low-energy conformers of all investigated diacetylenic acids.

$\lambda < 300$ nm). DA monomers, depending on preliminary conformation, undergo polymerization in the bulk, in two-dimensional monolayers, and along one-dimensional lines [3]. The well-organized and conjugated ene-yne backbone (alternating double and triple bonds with highly delocalized, one-dimensional π -electron system) of PDAs, first reported by Wegner in 1969 [4], has two spectroscopically distinct phases absorbing at ca. 640 and 540 nm, blue and red, respectively [5]. In general, the unperturbed PDA vesicles possess long conjugation length and exhibit a deep blue color [6].

Upon exposure to various external stimuli such as solvents, temperature, mechanical stress, pH, ions, ligand–receptor interaction, biomolecules, and other chemicals, the PDAs and the PDA-based materials change their color to red, orange or purple by conformational perturbation of the structure, thus enabling the polymer backbone rearrangement required to affect the conjugation length [1,5–11]. This unique property renders PDAs to be utilized as an active material in various applications such as chemosensors, biosensors, immunosensor, ion sensors, temperature sensors, and molecular switches [6,12–18]. Linear DAs play an important role in film forming [19]. PDAs as biosensors can be applied in many branches of science, medicine, and biology [17,18,20–24].

1, 2, and 3 have also been used for preparing PDA-based materials made by incorporating metal oxide or metal nanoparticles into the system [1]. As a result, a simple method for controlling the reversible-thermochromic behaviors of such nanocomposites was suggested [1]. Moreover, it was shown that the Langmuir–Blodgett technique is a successful tool for studies of chiral PDA films [7,25], third-order nonlinear optical effects and electric conduction properties of PDAs [26,27], and thermal polymerization of PDAs that proceeds at an appreciably enhanced rate on surface enhanced Raman scattering (SERS) active substrates under the irradiation [28,29].

Acetylenic and diacetylenic fatty acids have been known to be fungitoxic [30,31]. The fungal activity of these compounds depends on their chain length and pH of the medium. For instance, 2-hexadecynoic acid has received the most attention for its antifungal, antimicrobial, and cytotoxic properties. Antifungal activity of this compound and other acetylenic fatty acids come from a mechanism of fatty acid biosynthesis inhibition [30]. On the other hand, among all studied diynoic compounds 2,6-hexadecadiynoic acid displayed the best overall antifungal activity and was more effective than monoacetylenic acids [30,31].

Additionally, 5,9-hexadecadiynoic acid has been checked as a possible inhibitor of Human Topoisomerase I. However, the results were not satisfactory and this compound showed less usefulness than corresponding diene [32]. On the other hand, some DAs such as **3** are of interest of nanotechnology and nanoscience due to their potential in fabricating novel molecular nanoelectronic devices comprised of conjugated polymer nanowires [33].

Long-chain diacetylenic compounds are well-known secondary metabolites of plants with potential health benefits [34,35]. The most common natural compounds of this type are faltarinol and faltarindiol, which have been proven to be cytotoxic against numerous cancer lines [36] and can be found in various plants from Apiaceae family such as wild carrot, celeriac, parsnip, and parsley [37,38]. Thus, DAs selected here can be considered as a model compounds of the natural ones to study experimentally and theoretically, their structural and spectroscopic properties. Theoretical calculations using model compounds with various substituents have been already shown to be a supportive tool for the interpretation of experimental data [39].

Vibrational spectroscopy were successfully applied for DAs investigations, however, most studies performed on polymerization process in Langmuir films, liposomes, and nanocomposites. IR and Raman spectroscopy were used as fast and reliable techniques for purity control of polymerization products [1,40]. However, the majority of work reported in literature is related to the polymerization process in monolayers of Langmuir–Blodgett films studied by IR, Raman (especially resonance Raman), and SERS (or SERRS) [29,41,42]. Furthermore, a few studies based on vibrational spectroscopy methods have been also reported in the field of polymerization kinetics or thermochromism [28,43]. However, there is no research focused on structural properties of the diacetylenic system in DAs that may have a crucial influence on polymerization process. Thus, the aim of this work is to perform structural and spectroscopic studies on three commonly used DAs (Fig. 1) in order to shed new light on the properties of $-C\equiv C-C\equiv C-$ moieties. Due to different number of methylene groups in the chain of the investigated compounds, the influence of aliphatic chain length on properties of the diacetylene system is carefully examined.

Experimental and theoretical methods

Vibrational spectroscopy

Raman spectra were recorded using a Bruker MultiRAM FT-Raman spectrometer equipped with a Nd:YAG laser, emitting

Download English Version:

<https://daneshyari.com/en/article/1229288>

Download Persian Version:

<https://daneshyari.com/article/1229288>

[Daneshyari.com](https://daneshyari.com)