



Vibrational and theoretical study of selected diacetylenes



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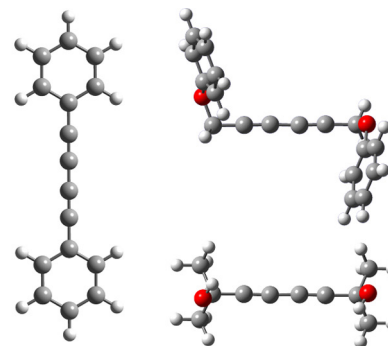
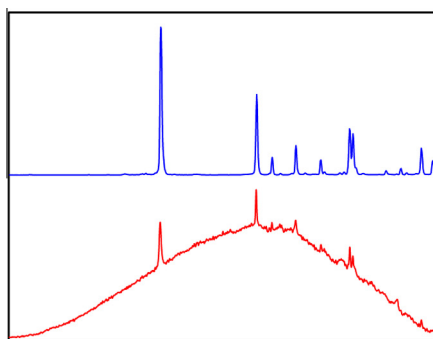
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HIGHLIGHTS

- The most stable conformers were found from theoretical calculations of diacetylenes.
- Band shifts and changes in bond lengths were observed when changing the substituent.
- FT-IR spectra measured by ATR technique and in transmission (KBr) were compared.
- Fermi Resonance (FR) in Raman and IR spectra was observed and explained.
- The orientation of diphenylbutadiyne on metal nanoparticles was predicted from SERS.

GRAPHICAL ABSTRACT



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ABSTRACT

Six commonly used disubstituted diacetylenes with short side-chains ($R-C\equiv C-C\equiv C-R$, where $R = CH_2-OH$, CH_2OPh , $C(CH_3)_2OH$, $C(CH_3)_3$, $Si(CH_3)_3$, and Ph) were analyzed using vibrational spectroscopy and quantum-chemical calculations to shed new light on structural and spectroscopic properties of these compounds. Prior to that the conformational analysis of diacetylenes was performed to search the Potential Energy Surface for low-energy minima. Theoretical investigations were followed by the potential energy distribution (PED) analysis to gain deeper insight into FT-Raman and FT-IR spectra that, in some cases, were recorded for the first time for the studied compounds. The analysis was focused mainly on spectral features of the diacetylene system sensitive to the substitution. Shifts of the characteristic bands and changes in bond lengths were observed when changing the substituent. Furthermore, Fermi resonance was observed in the vibrational spectra of some diacetylenes. FT-IR spectra were measured by using two methods, i.e. transmission (with KBr substrate) and Attenuated Total Reflection (ATR), showing the latter adequate and fast tool for IR measurements of diacetylenes. Additionally, Surface Enhanced Raman Spectroscopy (SERS) was applied for phenyl derivative for the first time to study its interaction with metallic nanoparticles that seems to be perpendicular.

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Introduction

Symmetrically disubstituted diacetylenes with two conjugated triple bonds ($R-C\equiv C-C\equiv C-R$), have been known for many years

as monomers for solid-state polymerization by 1,4-addition reaction with large yield obtaining nearly defect-free, single crystals or fully conjugated polymers [1–4]. Polymerization can result from thermal annealing or exposure to γ or UV irradiation, however, nature of the process depends upon the crystal structure of the diacetylene [4]. Many of diacetylene polymers possess attractive mechanical, electrical (high conductivity), and optical properties, making them potential candidates for reinforcement in polymer composites [5] and optoelectronic devices including waveguides,

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frequency doublers, light-emitting diodes, thin-film transistors, and gas sensors [6–8]. In particular, optical nonlinearity has been commonly reported for diacetylene polymers and they have been proven to possess one of the largest third-order nonlinear optical (NLO) properties [9–12]. In contrary to monomers, polymers are usually deeply colored, strongly dichroic, and often with a metallic luster [4,13], what suggests a highly conjugated molecular structure (linear polymer chain). High polymerization capability of diacetylenes comes from extensive π -electron delocalization that takes place along the backbone [9]. For instance, it has been reported that the excited triplet states are the key intermediate state in the photoinduced polymerization [14]. A great deal of interest for phenyl derivatives of diacetylenes has been observed among researchers mainly due to the ability to tune their electronic properties by changing functional groups and the geometry [15]. On the other hand, many reactions of transition metal carbonyl cluster complexes with conjugated diacetylenes have been studied deeply for over twenty years [16,17]. It has been shown that the cluster chemistry of diacetylenes is very rich and that it strongly depends on the nature of the metal cluster and the diacetylene used.

The first investigated diacetylene in our work is 2,4-hexadiyne-1,6-diol (**1**) (Fig. 1) that is diacetylene symmetrically disubstituted by $-\text{CH}_2\text{OH}$ group. **1** is an example of a slowly solid-state reactive monomer and upon high-dosage irradiation to obtain high monomer-to-polymer conversion, crystals of **1** become amorphous [4]. However, there are examples of poly-**1** application, for instance, as nanocomposites with carbon nanotubes [18]. **1** has been also used as a precursor for organic syntheses [19]. Additionally, some derivatives of **1** such as bis(*p*-toluene sulfonate) ester of **1** and 1,6-di(*N*-carbazolyl)-2,4 hexadiyne have been widely applied for polymerization and optical studies [4,8,9,20–22].

1,6-Diphenoxy-2,4-hexadiyne (**2**) (Fig. 1) is a derivative of **1** with a phenyl instead of proton in a hydroxyl group. None of two crystal forms of **2** undergo the polymerization reaction, however, they are useful as a room-temperature hydrogen fixers when combined with a palladium-alumina catalyst [23,24]. It has been also reported that **2** can be used as a ligand in cluster complexes with transition metals such as ruthenium [25–27].

Another member of a family of diacetylenic alcohols, 2,7-dimethyl-3,5-octadiyne-2,7-diol (**3**) (Fig. 1), is able to form crystalline inclusion complexes with a variety of guest molecules [28]. **3** has been shown to self associate *via* hydrogen bonds to form an extended tubular structure containing solvent molecules of crystallization. The solvent molecules are disordered and resemble water in zeolitic cavities [28].

Two other compounds, 2,2,7,7-tetramethyl-3,5-octadiyne (**4**) and 1,4-bis(trimethylsilyl)-1,3-butadiyne (**5**) (Fig. 1) are *t*-butyl derivative of diacetylene with quaternary carbon and Si atom, respectively. Both **4** and **5** have been widely studied as precursors of allenes that are of great importance in organic chemistry being very useful intermediates in syntheses of pharmaceuticals and flavors and fragrant compounds. In general, allenes can be synthe-

sized in high yields by metal catalyzed hydrosilylation of conjugated diacetylenes [29]. Moreover, **4** has been used for hydrophosphination reactions (metal-mediated addition of H–P bonds) to form alkyl- and vinyl-substituted phosphines that are useful building blocks in organic synthesis [30,31]. On the other hand, **5** is a precursor in synthesis routes of falcarinol-type polyacetylenes [32] that have shown anticancer, antibacterial, anti-inflammatory, and antiplatelet-aggregatory properties and can be found in many edible vegetables [33–35]; as well as in synthesis of bicyclic hetero-aromatic compounds [36] that are well known for their wide range of biological activity. It has been intensively applied for synthesis of other disubstituted diacetylenes with various side-chains (aryl, thiophene, alkyl, vinyl) [37]. **5** has been also studied as a ligand in complexes formation with transition metals such as titanium [38].

1,4-Diphenylbutadiyne (**6**) (Fig. 1) barely polymerizes in solid due to the steric hindrance even though aromatic rings should not interfere with its reactivity [4]. However, there are numerous examples of polymerization reactions applying **6** (some of them can be found in Ref. [13]). Moreover, **6** has been found to be worse molecular conductor than e.g. 1,2-diphenylacetylene [15]. On the other hand, **6** has been investigated successfully in complexes with transition metals such as cobalt [39], ruthenium [25–27,40,41], and nickel [42]. It has been also studied as a linker between porphyrin dyads that provides rapid and efficient energy transfer and can be applied for constructing light-harvesting elements and other molecular photonic devices [43]. Finally, **6** has been investigated in calcium-mediated hydroamination [44] and hydrophosphination [45] reactions leading to corresponding amines and phosphines.

There are several examples of experimental work on diacetylenic compounds carried out by vibrational spectroscopy. Diacetylene and its simple derivatives have been carefully analyzed and their vibrational spectra are well-known [46–48]. Furthermore, model compound of the most of molecules analyzed here, i.e. 2,4-hexadiyne ($\text{H}_3\text{C}-\text{C}\equiv\text{C}-\text{C}\equiv\text{C}-\text{CH}_3$), has been also investigated using IR and Raman spectroscopy [49]. Its characteristic bands of the diacetylenic system have been found at 2163 cm^{-1} for $\nu(\text{C}\equiv\text{C})_{\text{as}}$ band in IR spectrum and at 2265 cm^{-1} for $\nu(\text{C}\equiv\text{C})_{\text{s}}$ band in Raman spectrum. A few reports concerning vibrational spectra of compounds investigated in this paper can be found in literature as well [24,50,51]. More examples of vibrational studies on disubstituted diacetylenes have been mentioned in Ref. [52].

The aim of this work is to perform structural and spectroscopic studies on disubstituted diacetylenes in order to shed new light on the properties of $-\text{C}\equiv\text{C}-\text{C}\equiv\text{C}-$ moieties. For that, a series of similar diacetylenes was chosen, with aliphatic and aromatic substituents, as well as a derivative with Si atom instead of quaternary carbon in *t*-butyl group. The substituent effect on spectroscopic properties of symmetrically disubstituted diacetylenes has been already studied, but only theoretically, in our previous work [52]. Previously we have also performed spectroscopic analysis of

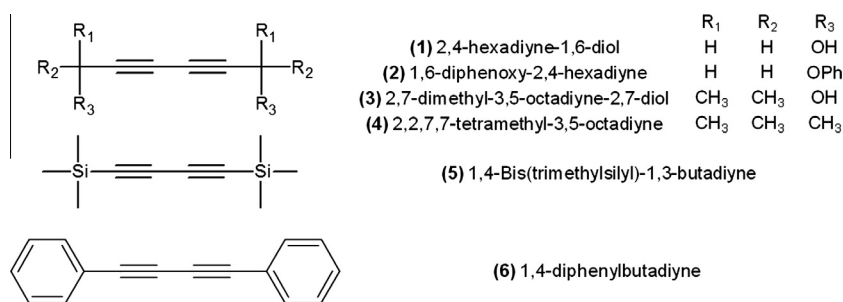


Fig. 1. Structures of the investigated diacetylenes.

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