



Vibrational spectroscopic characterization of cyclic and acyclic molecular rotors with 1,4-diethynylphenylene- d_4 rotators

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ABSTRACT

The synthesis and characterization of acyclic and cyclic molecular rotors with 1,4-diethynylphenylene- d_4 rotators are described. The ATR-FTIR and Raman spectra of acyclic rotor **3** and cyclic rotor **5E** were measured and interpreted. A feature of ATR-FTIR spectrum of rotor **5E** is a strong two-component band around 1730 cm^{-1} attributed to symmetric and asymmetric stretching vibration of the carbonyl group, while this is not observed in rotor **3**. Raman investigation in the wide temperature range of 350 - 10 K was carried out. The splitting of Raman bands in the region of stretching vibration of CC double and triple bonds at 170 and 260 K for rotor **5E** is observed. The splitting of bands is due to changes in molecular structure.

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1. Introduction

In recent years the subject of molecular machines has frequently been discussed by nanotechnologists resulting in a wide spectrum of different structures capable of performing controlled work in their environment being synthesized [1,2]. Some of those imitate a behavior of proteins that are responsible for all kinds of movement in biological cells [3]. A good example of this approach is an inorganic nanodevice, powered by a molecular motor, that can act as a nanopropeller [4]. Other machines are created in the image of macroscopic systems. Even creating a light-driven nanocar is a possibility [5]. Among those artificial machines, a group of molecular gyroscopes is especially promising. Molecular gyroscopes, analogous to their macroscopic counterparts known from mechanical systems, consist of a rotating element called rotator, an axle around which the rotator turns, and a stator, whose role is to act as a rigid frame and shield the rotator from a contact with adjacent molecules. That kind of structure makes molecular gyroscopes ideal candidates to produce ‘amphidynamic crystals’ – ordered solids that combine rigid lattice constraints and highly mobile components inside the lattice [6]. As a result, molecular gyroscopes can provide various functional materials that can find application in different fields of industry and science. One can envisage to create a new type of device to store rotational energy inside an amphidynamic crystal structure and

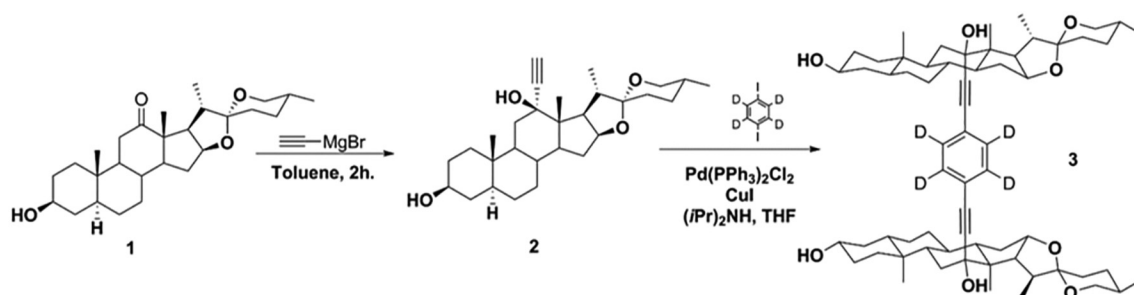
later release it. Similar structures that use molecular motors connected to long polymers were depicted by Weysser et al. [7]. Those rotors could store not only energy but also information [8]. Rotors that contain electric dipoles may provide amphidynamic crystals that can be used as tunable dielectrics [2,9]. Molecular rotors could also find applications as different kinds of sensors: photosensors in optoelectronics [10], thermosensors in metrology and microviscosity sensors [11] in medicine.

Numerous kinds of molecular gyroscopes have been synthesized until now and, in most of them, the 1,4-diethynylphenylene group acts as a rotator and an axis of rotation [8,12–14]. Stators are attached on either side of the 1,4-diethynylphenylene group and can be linked by additional bridging chains. As the main function of a stator is shielding the rotator its massiveness is one of its main requirements. By this, organic molecules are frequently employed and one of the approaches has been to use steroidal derivatives for the synthesis of molecular gyroscopes [8]. Such molecular rotors derived from 12-oxosapogenins has shown the capability of reaching rotary frequencies between the kilohertz and megahertz interval [12].

In this paper, we present the synthesis and vibrational spectroscopy characterization that can provide information on molecular dynamics and differences between the molecular structure of acyclic (rotor **3**) and cyclic (rotor **5E**) rotors. As the subject of the examination, we used newly synthesized molecular rotors with the 1,4-diethynylphenylene- d_4 group acting as a rotator and steroidal stators. In the cyclic molecular rotor, steroidal molecules of the stators were

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Scheme 1. Synthesis of rotor 3.

linked by an alkenylene diester bridge thus creating a more rigid framework. Stators of the acyclic molecular rotator were not additionally constrained. The vibrational spectra of two molecular rotors: one acyclic (**3**) and the other one cyclic (**5E**), were measured and interpreted.

2. Material and Methods

2.1. Synthesis of the Materials

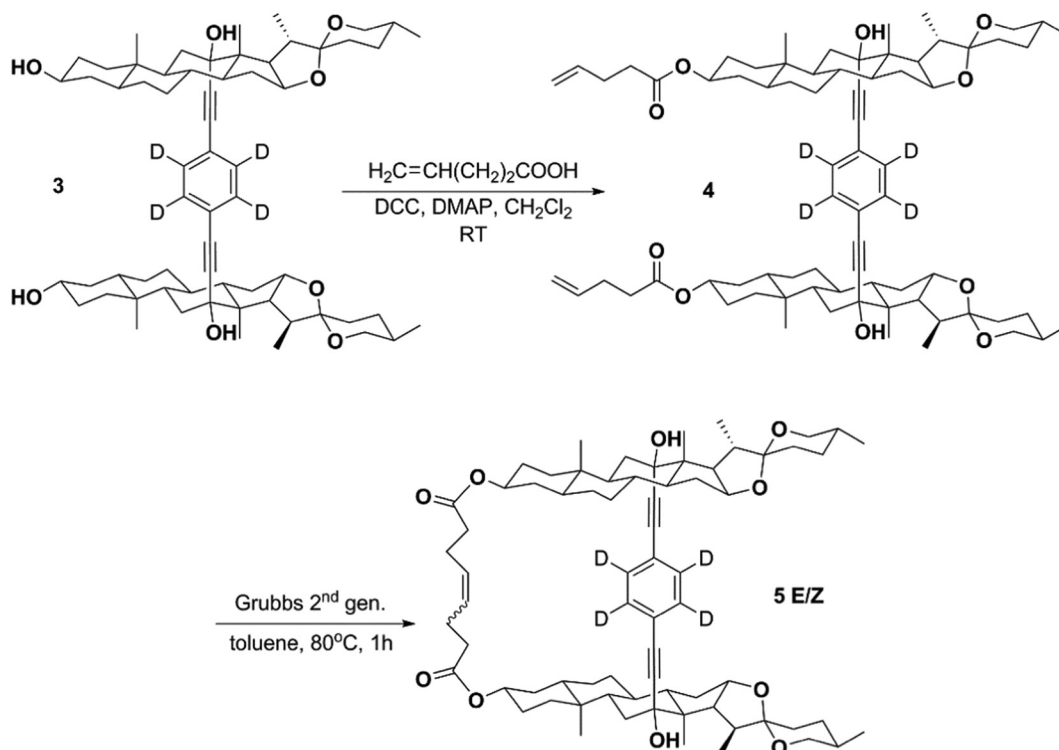
2.1.1. General Methods

Reagent-grade chemicals were purchased and used as received. Solvents were freshly distilled. Flash column chromatography and dry flash chromatography were performed with silica gel, pore size 40A (70–230 mesh) unless otherwise stated. All reactions were monitored by Thin Layer Chromatograph (TLC) on silica gel plates 60 F₂₅₄. ¹H (400 MHz) and ¹³C NMR (100 MHz) spectra for all compounds were recorded at ambient temperature and were referenced to Tetramethylsilane (TMS) (0.0 ppm) and CDCl₃ (77.0 ppm), respectively, unless otherwise stated. NMR resonance multiplicities were reported using the following abbreviations: b = broad, s = singlet, d = doublet, t = triplet, q = quartet, and m = multiplet; coupling constants *J* were reported in Hz. IR spectra were measured in a CHCl₃ solution or for powder sample

with a FTIR spectrometer, and data are reported in cm⁻¹. Melting points were determined by a Kofler bench (Boetius type) apparatus and are uncorrected.

2.1.2. Synthesis of 12 α -ethynyl-25R-5 α -spirostane-3 β ,12 β -diol (**2**)

A solution of hecogenin acetate **1** (2.00 g, 4.2 mmol), 1.0 eq) in toluene (120 mL) was cooled to 0 °C followed by addition of ethynylmagnesium bromide solution (42.0 mL, 21.2 mmol, 5.0 eq, 0.5 M in THF - Tetrahydrofuran). The mixture was heated to reflux for 2 h. The reaction mixture was cooled to room temperature and the solvent was removed in vacuo, the residue was diluted with CH₂Cl₂ (100 mL), quenched with a saturated solution NH₄Cl (2 × 50 mL) and dried over Na₂SO₄. Purification on column chromatography using silica gel and CH₂Cl₂/acetone (95:5) as eluent, afforded the desired compounds. Product **2** was isolated as a white solid (0.95 g, 49%). Melting point: 247–248 °C. FTIR (ν , cm⁻¹): 3381, 2926, 1701, 1456, 1372, 1055, 978, 897, 641. MS (EI) *m/z* (%): 456 (M⁺, 10), 397 (20), 384 (40), 342 (30), 147 (20), 139 (100), 126 (20), 55 (35). ¹H NMR [400 MHz, CDCl₃] (δ , ppm): 4.40 (1H, dd, *J*_{16 α -17 α} = 8.4 Hz, *J*_{16 α -15 α} = 7.6 Hz, H-16 α), 3.58 (1H, m, H-3 α), 3.47 (1H, m, H-26_{eq}), 3.37 (1H, dd, *J*_{gem} = 11.2 Hz *J*_{26 α x-25 α x} = 10.8 Hz, H-26_{ax}), 2.47 (1H, s, H-29), 2.39 (1H, dd, *J*_{17 α -16 α} = 8.4 Hz, *J*_{17 α -20} = 6.4 Hz, H-17 α), 2.04 (1H,



Scheme 2. Synthesis of rotors 5.

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