

Structure determination of myrtenal by microwave spectroscopy and quantum chemical calculations



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ABSTRACT

The rotational spectrum of myrtenal has been investigated using a Fourier transform microwave spectrometer coupled to a supersonic expansion in the 2–20 GHz frequency range. Of the two possible conformers expected in the gas phase, only the *s-trans* conformer which was calculated 12 kJ mol⁻¹ lower in energy than the *s-cis* conformer was observed. The spectra of the ten ¹³C and ¹⁸O isotopic species of *s-trans*-myrtenal were observed in natural abundance. The ground state rotational constants are $A = 1666.269706(55)$ MHz, $B = 962.344291(40)$ MHz and $C = 836.903508(43)$ MHz. A partial r_s structure was calculated using Kraitchman's equations. A r_0 structure was also derived using additional data from a B3LYP/6-311++G(d,p) calculation. The structural parameters of the –C=C–C=O pattern of myrtenal ($r_0(\text{C}=\text{C}) = 1.341(16)$ Å, $r_0(\text{C}–\text{C}) = 1.479(98)$ Å, $r_0(\text{C}=\text{O}) = 1.220(13)$ Å, $\angle(\text{OCC}) = 124.4(13)^\circ$ and $\angle(\text{CCC}) = 119.3(11)^\circ$) are very close to those in *trans*-acrolein and in *trans-trans*-cinnamaldehyde.

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1. Introduction

The total emissions of biogenic organic compounds in the troposphere are estimated to be 1100 Tg yr⁻¹ [1]. They are dominated by isoprene (535 Tg yr⁻¹) followed by α - and β -pinenes (respectively 66 Tg yr⁻¹ and 205 Tg yr⁻¹) and limonene (115 Tg yr⁻¹). In the troposphere, they are oxidized by the OH radical or by ozone O₃, in the presence of NO_x and H₂O, leading to a wide variety of terpenoids: ketones, aldehydes and carboxylic acids [2,3]. These compounds have a lower vapor pressure than the terpenes and may participate in the formation of secondary organic aerosols (SOA). The formation of SOA from the precursors α - and β -pinenes has been the subject of numerous studies [4–11].

The mechanisms of oxidation of terpenes in the atmosphere are complex and far from being completely elucidated. In particular, the products of oxidation are not all known or they are sometimes not taken into account in the models. This is the case of myrtenal (C₁₀H₁₄O-6,6-dimethylbicyclo[3.1.1]hept-2-en-2-carboxaldehyde, see Fig. 1) which is a bicyclic aldehyde of the monoterpene family. Myrtenal could be a first-oxidation product of α - or β -pinene in the atmosphere. Indeed Vereecken and Peeters [6] proposed a mechanism of formation of myrtenal from β -pinene, which consists in a first H-atom abstraction by the OH radical, followed by an O₂ addition, subsequent reaction with NO (and elimination of

NO₂) and a final reaction with O₂ (and elimination of HO₂). Very recently, Mutzel et al. investigated the role of the OH-oxidation of α -pinene in the formation of SOA [7]. They found that the contribution of myrtenal to α -pinene SOA formation could be as high as 23%, the SOA marker compounds formed by the oxidation of myrtenal being terebic acid, pinic acid and diaterpenylic acid acetate. Finally Amelynck et al. recently studied the reactions of H₃O⁺·(H₂O)_n ($n = 0, 1, 2$), NO⁺ and O₂⁺ with myrtenal along with citral and citronellal by the FA-SIFT technique [11].

Apart from being produced by the degradation of terpenes in the atmosphere, myrtenal is also a natural molecule which is found in many medicinal plants. The main source of myrtenal are *Asterataea* plants. Their leaf essential oils contains up to 26% of myrtenal [12]. Myrtenal may have various medicinal applications. For instance, it is a novel chemotherapeutic agent against hepatocellular carcinoma [13], or it can inhibit acetylcholinesterase which is a known Alzheimer target [14]. Thanks to its endocyclic unsaturation and to its chirality, myrtenal is a very useful precursor in chemistry to synthesize chiral ligands [15].

The structure of myrtenal is based on that of α -pinene with a formyl group in place of the methyl group. In myrtenal, the carbon-oxygen double bond of the aldehyde moiety is conjugated with the endocyclic C=C double bond of the bicyclic hydrocarbon structure. Two conformers (referred as *s-cis* and *s-trans*) are then expected, differing by the orientation of the carbonyl moiety with respect to the carbon-carbon single bond (see Fig. 2). Myrtenal is a chiral molecule with two asymmetric carbon atoms (atoms

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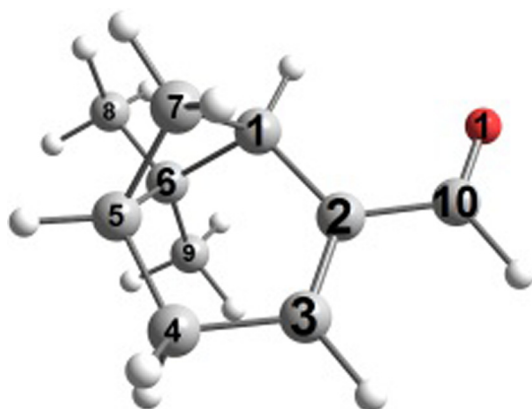


Fig. 1. Numbering scheme of the carbon (labeled 1–10) and oxygen (in red, labeled 1) atoms of myrtenal used in this work. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

number 1 and 5, see Fig. 1). The absolute configuration of (–)-myrtenal was recently established using vibrational circular dichroism [16]. Kaplan et al. studied the ^1H NMR spectrum of myrtenal in order to get insight into its structure [17].

Microwave spectroscopy of molecules cooled in a supersonic expansion is particularly well adapted to the study of heavy rotors like terpenes and terpenoids. Camphor [18], fenchone [19], citronellal [20], thymol and carvacrol [21], perillaldehyde [22], carvone and limonene [23], camphene [24] and the hydrates of camphor [25] were investigated by this technique. The rotational spectrum of myrtenal is still unknown. We first present in this article our study of the microwave spectrum of myrtenal and of its ten ^{13}C and ^{18}O isotopic species. The experimental data were then used to calculate a partial substitution structure r_s and an effective r_0 structure with the help of quantum chemical calculations.

2. Quantum chemical calculations

The quantum calculations described below were performed using the Gaussian 09 software [26] implemented in the High-

Performance Computing Linux cluster of the laboratory. The B3LYP [27] and M06-2X [28] density functionals as well as the MP2 [29] methods combined with Pople split-valence triple-zeta basis set augmented with diffuse and polarization functions (6-311++G(d,p) and 6-311++G(3df,2pd)) and the Dunning's correlation consistent basis set aug-cc-PVTZ were used in the frozen-core approximation.

Myrtenal is a molecule which presents two possible conformers differing by the orientation *s-cis* or *s-trans* of the aldehyde moiety with respect to the $\text{C}_2\text{—C}_{10}$ single bond. A relaxed scan was performed at the MP2/6-311++G(d,p) level in order to obtain the difference of energy between the two conformers of myrtenal and the barrier of rotation of the aldehyde moiety around the $\text{C}_{10}\text{—C}_2$ bond. The calculated potential energy curve is shown Fig. 2. The *s-trans* conformer lies higher in energy than the *s-cis* conformer by 12.2 kJ mol^{-1} (including the ZPE correction), with a barrier of isomerization of 26 kJ mol^{-1} . These values are in agreement with previous calculated values in *trans*-cinnamaldehyde [30] (difference of energy of 9 kJ mol^{-1} , barrier of isomerization of 33 kJ mol^{-1}). This huge difference of energy should prevent the *s-cis* conformer to be observed in the supersonic expansion. Indeed, at 363 K, which was the highest temperature of myrtenal used in this work, the abundance of the *s-cis* conformer of myrtenal is 1.6%. In the following, the conformation of myrtenal is not specified any more since only the *s-trans* conformer was observed. We have also calculated the barrier of internal rotation of the two methyl groups by performing a non-relaxed scan at the MP2/6-311++G(d,p) level, allowing the methyl groups to rotate around the $\text{C}_6\text{—C}_8$ and $\text{C}_6\text{—C}_9$ bonds with a step of 10° while all the parameters were fixed at the MP2/6-311++G(d,p) equilibrium structure. The internal barriers of rotation of the methyl groups were calculated to be 1077 cm^{-1} around the $\text{C}_6\text{—C}_8$ bond and 1053 cm^{-1} around the $\text{C}_6\text{—C}_9$ bond. These high barriers of rotation should prevent torsional structure due to methyl internal rotation tunneling effect to be observed.

Geometry optimizations, calculations of the components of the dipole moment along the three axis of inertia and the quartic centrifugal distortion constants (in the harmonic approximation) of myrtenal were performed using the methods and basis listed

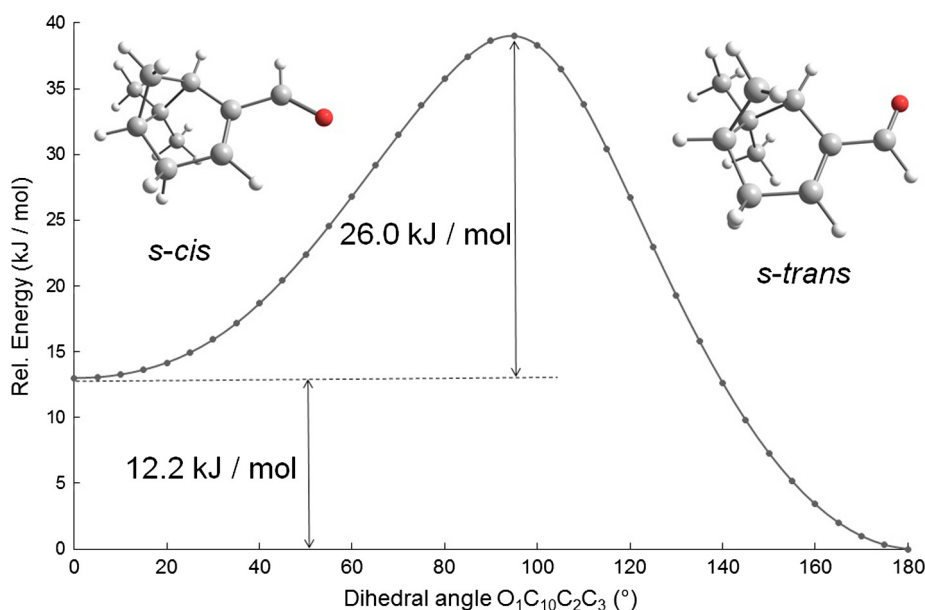


Fig. 2. Relaxed scan of the potential energy surface of myrtenal at the MP2/6-311++G(d,p) level of theory along the $\tau(\text{O}_1\text{C}_{10}\text{C}_2\text{C}_3)$ dihedral angle. Atoms labels are shown in Fig. 1.

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