



Gas-phase conformations of 2-methyl-1,3-dithiolane investigated by microwave spectroscopy

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ARTICLE INFO

Article history:

Received 21 August 2017

Received in revised form

19 November 2017

Accepted 20 November 2017

Available online 22 November 2017

Keywords:

Rotational spectroscopy

Conformational analysis

Dithiolane

Five-membered ring

Ab initio calculations

ABSTRACT

The conformational analysis of 2-methyl-1,3-dithiolane using quantum chemical calculations at some levels of theory yielded only one stable conformer with *envelope* geometry. However, other levels of theory indicated two *envelope* conformers. Analysis of the microwave spectrum recorded using two molecular jet Fourier transform microwave spectrometers covering the frequency range from 2 to 40 GHz confirms that only one conformer exists under jet conditions. The experimental spectrum was reproduced using a rigid-rotor model with centrifugal distortion correction within the measurement accuracy of 1.5 kHz, and molecular parameters were determined with very high accuracy. The gas phase structure of the title molecule is compared with the structures of other related molecules studied under the same experimental conditions.

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1. Introduction

Volatile sulfur-containing heterocyclic molecules are important flavor substances and raw materials for perfumes. It is known that sulfur-containing odorants of the chemical classes mercaptan (R-SH) and thioether (R-S-R') are intensely bad-smelling, especially in high concentrations, while the oxygen analogues, alcohol (R-OH) and ether (R-O-R'), have usually less perceptible smell or in many cases a much more pleasant odor. The reason for this phenomenon has not yet been completely understood. An explanation by Fischer that the sulfur-containing substances are recognized by human smelling receptors by the "lock and key" model [1] is not satisfactory, since almost no remarkable changes of the molecular structures could be found between the oxygen and the sulfur-containing analogs. Furthermore, the typical odors of sulfur-containing molecules cannot be imitated by sulfur-free substances which have similar molecular geometry and charge distribution. On the other hand, hydrogen bonds formed by sulfur-containing substances are much weaker than those by molecules with oxygen [2]. Therefore, we suppose that sulfur-containing substances form reversible bonds directly between the sulfur atom with sulfur-containing

amino acids in the proteins in the human receptors, which is not possible in the respective oxygen analogues. To understand and explain this phenomenon in more details, it is important to answer the questions how molecular shapes fit together. For this purpose, gas phase structures of sulfur-containing odorants are needed, since the sense of smell starts from gas phase molecules. A huge number of oxygen containing odorants were investigated in the gas phase, including the studies on linalool [3], a main component of lavender oil, on fruit esters such as isoamyl acetate (banana odor) [4] and ethyl valerate (green apple) [5] as well as on cassyrane (black currant) [6]. Considerably fewer gas phase investigations on sulfur-containing odorants have been carried out, though they are often the odor compounds found in nature. Some examples are cat ketone [7], dihydro-2-methyl-3-thiophenone [8], and methyl isopropyl sulfide [9].

In the present work, we report on the gas phase structure of 2-methyl-1,3-dithiolane (MDT, see Fig. 1), a volatile five-membered ring containing two sulfur atoms, obtained using a combination of quantum chemical calculations and Fourier transform microwave (FTWM) spectroscopy in a supersonic jet. This technique is ideally suited to determine the structures of sizeable molecules where different stable conformers exist whose energy differences are small and conformational distinction is not always possible by quantum chemical calculations alone. The results presented can be used for structure-activity correlation studies, as well as for

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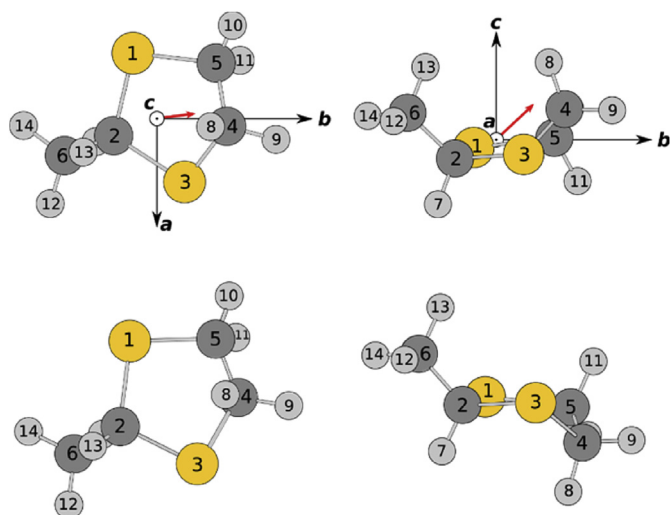


Fig. 1. Optimized geometries of 2-methyl-1,3-dithiolane. Upper trace: the most stable conformer obtained at all levels of theory in its principal axis system. Left hand side: view along the *c*-principal axis; right hand side: view along the *a*-principal axis. The circled dots indicate that the axis direction points out of the paper plane. The red arrows represent the dipole moment vector. Lower trace: the second conformer of 2-methyl-1,3-dithiolane obtained only at some levels of theory. The geometry calculated at the MP2/cc-pVTZ level is illustrated in complementary views to those in the upper trace. The energy is 0.89 kJ mol^{-1} higher than that of the first conformer. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

benchmarks to improve theoretical models, especially because there is still significant interest in characterizing the various conformers of organic molecules in terms of relative energies, structures, and dipole moments. Finally, the molecular geometry of MDT will be compared with the structures of other related five-membered rings.

2. Quantum chemical calculations

MDT is a five-membered heterocyclic molecule with two sulfur atoms at the 1 and 3 positions of the ring and a methyl group attached to the carbon at the 2 position. Several starting geometries based on the structures of the two conformers of cyclopentane [10] were created and optimized at the MP2/6–311++G (d,p) level of theory using the GAUSSIAN09 package [11] to search for stable conformers. Quantum chemistry is a powerful tool to understand microwave spectra. The optimized geometries and molecular parameters of stable conformers give reasonable estimations to start the spectral assignment. Conversely, experimental parameters obtained with high accuracy by microwave spectroscopy can be used for benchmark calculations. For example, in the study of Grimme et al. [12] the experimental data of isoamyl acetate [4], diisopropyl ketone [13], and triethyl amine [14] were used to validate the quantum chemical results.

The MP2/6–311++G (d,p) level of theory was chosen, because it yields rotational constants which are in close agreement with the experimental values for other five-membered rings [15,16]. Anharmonic frequency calculations were carried out at the same level to decide, whether the optimized geometries are true minima or saddle points, and to obtain centrifugal distortion constants.

We found only one conformer which has an *envelope* structure as shown in the upper trace of Fig. 1. The calculated rotational constants $A = 2.780$, $B = 2.724$, and $C = 1.605$ GHz indicate that MDT is a near oblate top with a Ray's asymmetry parameter $\kappa = 0.903$. The Cartesian coordinates are given in Table S-1 in the

Electronic Supporting Information (ESI). This is in contrary to many previous investigations on other related five-membered rings where structure optimizations delivered two conformers (see Section 5 which follows). Therefore, we repeated the calculations at different levels of theory using various combinations of the HF, DFT, MP2, and CCSD methods and different basis sets including correlation consistent and Pople basis sets [17] to check for convergence. Surprisingly, some levels of theory, for example the MP2/cc-pVTZ level, yielded two conformers (see Table S-2 in the ESI). The geometry of the second conformer depends on the level of theory in use, but in most cases it features a structure which is a mixture of *twist* and *envelope*. Harmonic frequency calculations were performed for all optimized structures, and confirmed that in most cases all of them are stable minima, except for two levels using the M06–2X method where the second conformer shows one imaginary frequency, meaning that it is a saddle point and not a stable conformer. If not else stated, all values given from now on will refer to the MP2/6–311++G (d,p) level of theory.

MDT features a methyl group which, in general, exhibits internal rotation and causes A-E splittings of all rotational lines in the microwave spectrum [18]. We calculated the barrier to internal rotation and obtained a value of 1650 cm^{-1} . Sample one-top calculations using the program XIAM [19] show that torsional splittings are small and cannot be resolved with our spectrometers. This is not surprising, because in many other molecules where *n*-alkyl methyl groups are present [20–22], the A-E splittings were not observable under the same measurement conditions.

3. Microwave spectroscopy

3.1. Measurements

The rotational spectra were recorded with two molecular jet FTMW spectrometers operating in the frequency range from 2 to 40 GHz. The spectrometer located in Aachen, Germany, operates from 2 to 26.5 GHz [23] and the other one in Paris, France, subsequently from 26.5 to 40 GHz [24]. Details of the spectrometers are given in the literature and will not be repeated here. MDT was purchased from Alfa Aesar GmbH & Co. KG, Karlsruhe, Germany. The stated purity was 99% and we used the sample without further purification. A piece of a pipe cleaner as sample carrier was soaked with the liquid substance, then placed in front of the nozzle of the spectrometers. For the measurements, a helium stream at a pressure of approximately 200 kPa was used. The helium-MDT mixture was expanded through the pulsed nozzle into the cavity. Helium was chosen as carrier gas instead of argon or neon since the molecular beam is warmer and higher energy levels are still populated. This is important for obtaining accurate centrifugal distortion constants.

A broadband scan was recorded in the frequency range from 9 to 14 GHz, where overlapping spectra were automatically taken with a step size of 0.25 MHz. Afterwards, all lines were remeasured at higher resolution, where they appeared as doublets due to the Doppler effect. The mean value of the line widths is approximately 15 kHz. The measurement accuracy of isolated lines is estimated to be 1.5 kHz. A portion of the scan as well as a typical high resolution spectrum is illustrated in Fig. 2.

3.2. Spectral assignment

The microwave spectrum of the only conformer of MDT obtained at the MP2/6–311++G (d,p) level of theory was predicted with the program XIAM in its rigid-rotor mode using the rotational constants given in Section 2. The dipole moment components $|\mu_a| = 0.12 \text{ D}$, $|\mu_b| = 0.80 \text{ D}$, and $|\mu_c| = 0.80 \text{ D}$ suggest a spectrum

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