Sulfur-containing Flavors: Gas Phase Structures of Dihydro-2-methyl-3-thiophenone

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We report on the different gas-phase structures of dihydro-2-methyl-3-thiophenone. The investigation was performed using a combination of quantum chemical calculations and molecular beam Fourier transform microwave spectroscopy [1].
The substance is present in coffee, roasted peanuts, and whiskey [2]. It is formed during food preparation such as roasting peanuts and contributes to the savory flavor composition. Furthermore, it is produced as an important metabolite by microorganisms such as yeasts and bacteria. The biosynthetic pathway of dihydro-2-methyl-3-thiophenone in the bacterium Chitinophaga Fx7914 was recently discovered and shows the general interest in this small molecule [3]. The microwave spectrum was recorded under molecular beam conditions in the frequency range from 9 to 14 GHz. For the two main conformers of dihydro-2-methyl-3-thiophenone, highly accurate rotational constants and centrifugal distortion constants were obtained. No splittings due to internal rotation of the methyl group could be observed in the microwave spectrum. This is in agreement with the theoretical predictions of the barrier heights, which have been determined to be more than 1000 cm^{-1} at the MP2/6 311++G(d,p) level of theory. In addition to the most abundant ^{32}S isotopologue of the main conformer, also the ^{34}S-isotopologue was assigned, which occurs with a natural abundance of about 4%. Using the experimental rotational constants, different quantum chemical calculations were validated for the two observed conformers. To complete the theoretical investigation of dihydro-2-methyl-3-thiophenone, different transition states were optimized to understand the intramolecular conversion between the two conformers at the MP2/6-311++G(d,p) level. The transition states were optimized using the Berny algorithm.
As in general, sulfur compounds were not studied as intensively as their oxygen analogues by high resolution rotational spectroscopy, this work might serve as a benchmark for further studies.

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