

TWO EQUIVALENT METHYL INTERNAL ROTATIONS IN 2,5-DIMETHYLTHIOPHENE INVESTIGATED BY MICROWAVE SPECTROSCOPY

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The microwave spectrum of 2,5-dimethylthiophene, a sulfur-containing five-membered heterocyclic molecule with two conjugated double bonds, was recorded using two molecular beam Fourier transform microwave spectrometers operating in the frequency range from 2 to 40 GHz. Highly accurate molecular parameters were determined. The rotational constants obtained by geometry optimizations at different levels of theory are in good agreement with the experimental values. A C_{2v} equilibrium structure was calculated, where one hydrogen atom of each methyl group is antiperiplanar to the sulfur atom, and the two methyl groups are thus equivalent.

Transition states were optimized at different levels of theory using the Berny algorithm to calculate the barrier height of the two equivalent methyl rotors. The fitted experimental torsional barrier of $247.95594(30) \text{ cm}^{-1}$ is in reasonable agreement with the calculated barriers. Similar barriers to internal rotation were found for the monomethyl derivatives 2-methylthiophene (194.1 cm^{-1}) and 3-methylthiophene (258.8 cm^{-1}). A labeling scheme for the group G_{36} written as the semi-direct product $(C_3^I \times C_3^I) (\times C_{2v})$ was introduced.