Lowering the Torsional Barriers by Sterical Hindrance: Microwave Spectrum of the Three-top Molecule 2,6-Dimethylanisole

The title molecule 2,6-dimethylanisole (26DMA, $C_5H_3(CH_3)_2OCH_3$) is one of the six isomers of dimethylanisole systematically studied by microwave spectroscopy. The spectrum of 26DMA was recorded using a pulsed molecular jet Fourier transform spectrometer. The experimental part was supported by quantum chemical calculations carried out at the B3LYP/6-311++G(d,p) level of theory.

As calculated and experimentally proven for the three mono-methylanisoles (*o*-, *m*-, and *p*-methylanisole [1], [2], [3]) and three dimethylanisoles (2,3-dimethylanisole [4], 3,4-dimethylanisole [5], and 2,4-dimethylanisole [6]), the barrier to internal rotation of the methoxy methyl rotor surpasses 1000 cm^{-1}, causing unresolvable torsional splittings in the microwave spectrum.

With both *ortho* positions substituted by a methyl group in 26DMA, the methoxy part is highly sterically hindered. It is thus forced to tilt out of the plane spanned by the heavy atoms of the phenyl ring by an angle of 90°. Many experimental studies have shown that sterical hindrance often increases the barrier to internal rotation. Surprisingly, in the case of 26DMA, the torsional barrier decreases dramatically to about 460 cm^{-1}, leading to observable fine splittings in the microwave spectrum. Thus, 26DMA represents a three-top molecule, featuring two equivalent aryl methyl rotors and one methoxy methyl rotor.

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