TUNING THE METHYL TORSION IN 2-METHYLTHIOPHENE DERIVATIVES BY RING SUBSTITUTION

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2-methylthiophene (2MTP) features a methyl group at the 2-position of the thiophene ring that undergoes internal rotation hindered by a V_3 barrier of 197.6 cm^{-1}.[1] Adding another substituent at the 5-position has a major impact on the barrier height, which appeared to be of electronic origin due to the absence of sterical hindrance. If a chlorine atom is present at the 5-position, as in 2-chloro-5-methylthiophene (2Cl5MTP), the V_3 barrier increases to 246.2 cm^{-1}. Being separated by the sulfur atom, the apparent influence of chlorine on the methyl internal rotation can only be explained by electronic properties transferred through the π-conjugated system. While it is surprising that replacing the chlorine atom that has a strong $-$I and $+$M effect with a second methyl group, as in 2,5-dimethylthiophene, leads to a minor change in the V_3 barrier (248.0 cm^{-1}),[2] replacing it with an acetyl group as in *syn*-2-acetyl-5-methylthiophene greatly reduced the barrier to 157.3 cm^{-1}.[3] Comparison of the barriers to those of the corresponding furan derivates shows a large impact of the hetero atom with an increase to 412.9 cm^{-1} for 2-methylfuran,[4] 439.1 cm^{-1} for 2,5-dimethylfuran,[5] and 356.5 cm^{-1} for *syn*-2-acetyl-5-methylfuran.[6] The methyl torsional barrier of 2-methylfuran derivates is tuned by the same manner as it is for the thiophene analogues. For 2MTP and 2Cl5MTP, we used a state-of-the-art pulsed molecular jet Fourier transform spectrometer to measure the microwave spectra in the frequency range of 2-26.5 GHz. The spectra of the ^{34}S and ^{13}C isotopologues of 2MTP could be observed in natural abundances and the semi-experimental r_e^{SE} structure was determined. for 2Cl5MTP, the ^{35}Cl and ^{37}Cl nuclei give rise to a nuclear quadrupole hyperfine structure in the spectrum in addition to the A-E torsional splittings of the methyl internal rotation.

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