

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

K. J. KOZIOL¹, **H. V. L. NGUYEN**^{1,2}, ¹*Univ Paris Est Créteil and Université Paris Cité, CNRS, LISA, 94010 Créteil, France*, ²*Institut Universitaire de France (IUF), 1 Rue Descartes, 75231 Paris, France*

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 derivatives 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 derivatives 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 ³⁴S and ¹³C isotopologues of 2MTP could be observed in natural abundances and the semi-experimental r_e^{SE} structure was determined. For 2Cl5MTP, the ³⁵Cl and ³⁷Cl 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.

¹[doi:10.3390/spectroscj1010005](https://doi.org/10.3390/spectroscj1010005), K. J. Koziol, H. El Hadki, A. Lüchow, N. Vogt, J. Demaison, H. V. L. Nguyen, *Spectrosc. J.* **1**, 49-64 (2023).

²[doi:10.1039/C5CP03513A](https://doi.org/10.1039/C5CP03513A), V. Van, W. Stahl, H. V. L. Nguyen, *Phys. Chem. Chem. Phys.* **17**, 32111-32114 (2015).

³[doi:10.1039/D2CP03897H](https://doi.org/10.1039/D2CP03897H), C. Dindic, H. V. L. Nguyen, *Phys. Chem. Chem. Phys.* **25**, 509-519 (2023).

⁴[doi:10.1016/j.jms.2012.06.005](https://doi.org/10.1016/j.jms.2012.06.005), I. A. Finneran, S. T. Shipman, S. L. W. Weaver, *J. Mol. Spectrosc.* **280**, 27-33 (2012).

⁵[doi:10.1016/j.jms.2017.11.007](https://doi.org/10.1016/j.jms.2017.11.007), V. Van, J. Bruikhuisen, W. Stahl, V. Illyushin, H. V. L. Nguyen, *J. Mol. Spectrosc.* **343**, 121-125 (2018).

⁶[doi:10.1002/cphc.201600757](https://doi.org/10.1002/cphc.201600757), V. Van, W. Stahl, H. V. L. Nguyen, *Chem. Phys. Chem.* **17**, 3223-3228 (2016).