THE 2,4-CHALLENGE IN THE MICROWAVE SPECTRA OF 2,4-DIMETHYLTHIAZOLE AND 2,4-DIMETHYLFLUOROBENZENE: STRATEGY TO ASSIGN VERY LOW BARRIER METHYL INTERNAL ROTATION

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The analysis and modeling of internal rotations with extremely low barriers is a challenging task in microwave spectroscopy. An almost free internal rotation hindered by a barrier less than 20 cm^{-1} causes large torsional splittings in the spectrum. For molecules with two inequivalent methyl groups, the methyl rotations couple with each other, especially in aromatic molecules through π conjugation, and all rotational lines split into quintets, making spectral assignment and modeling very difficult. The spectral analysis becomes even more complicated if additional effects are present such as the ^{14}N nuclear quadrupole coupling, which causes quadrupole hyperfine splittings in addition to the torsional splittings.[1] Probably for these reasons, a very limited number of studies on aromatic systems undergoing nearly barrier-free internal rotations have been reported.[2]

We will present here the challenges for two such molecules, 2,4-dimethylthiazole (24DMTA) and 2,4-dimethylfluorobenzene (24DMFB). The microwave spectra were recorded using a pulsed molecular jet Fourier transform microwave spectrometer operating in the frequency range from 2.0 to 26.5 GHz.[3] The experimental work was supported by quantum chemical calculations. For both molecules, the *XIAM*$_{mod}$ program[4,5] was used at the beginning to fit the first assigned lines, but it fails to predict new lines at higher *J* and *K* values, as well as to achieve the measurement accuracy of 2 kHz for the final data set.[6] To assign more lines, fitting each torsional species separately using odd power order parameters to get reliable predictions using the *WS18* code[7] and the *SFLAMS* code,[4] as well as checking the assigned frequencies by

[1] doi.org/10.1515/psr-2020-0037, H.V.L. Nguyen, I. Kleiner, *Phys. Sci. Rev.* **7**, 679−726 (2020).

[2] doi.org/10.3390/molecules27123948, H.V.L. Nguyen, W. Caminati, J.-U. Grabow, *Molecules*. **27**, 3948 (2022).

[3] doi.org/10.1063/1.1147553, J.-U. Grabow, W. Stahl, H. Dreizler, *Rev. Sci. Instrum.* **67**, 4072−4084(1996).

[4] doi.org/10.1063/1.5142401, S. Herbers, S.M. Fritz, P. Mishra, H.V.L. Nguyen, T.S. Zwier, *J. Chem. Phys.* **152**, 074301 (2020).

[5] doi.org/10.1016/j.jms.2020.111289, S. Herbers, H.V.L. Nguyen, *J. Mol. Spectrosc.* **370**, 111289 (2020).

[6] doi.org/10.1515/zna-1990-0817, J.-U. Grabow, W. Stahl, *Z. Naturforsch.* **45a**, 1043−1044 (1990).

[7] doi.org/10.1063/5.0049418, T. Nguyen, W. Stahl, H.V.L. Nguyen, I. Kleiner, *J. Chem. Phys.* **154**, 204304 (2021).

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combination difference loops (Ritz cycles)[8] is the key to success. Finally, the *BELGI-C_s-2Tops-hyperfine*[9] and *BELGI-C_s-2Tops*[10] programs were used for 24DMTA and 24DMFB, respectively, to decrease the standard deviation to measurement accuracy in a global fit. For 24DMTA, the barriers to internal rotation of the 2- and 4-methyl groups were determined to be 19.070(58) cm^{-1} and 396.707(25) cm^{-1}, respectively. They are 3.23(40) cm^{-1} and 227.039(51) cm^{-1} for 24DMFB.

[8] doi.org/10.1016/j.jms.2015.10.005, Y. Zhao, H.V.L. Nguyen, W. Stahl, J.T. Hougen, *J. Mol. Spectrosc.* **318**, 91−100 (2015).

[9] doi.org/10.1063/5.0049418, V. Van, T. Nguyen, W. Stahl, H.V.L. Nguyen, I. Kleiner, *J. Mol. Struct.* **1207**, 127787 (2020).

[10] doi.org/10.1016/j.jms.2011.07.005, M. Tudorie, I. Kleiner, J.T. Hougen, S. Melandri, L.W. Sutikdja, W. Stahl, *J. Mol. Spectrosc.* **269**, 211−225 (2011).

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