# SULFUR HYDROGEN BONDING: A COMPARISON OF THE DIMERS AND MONOHYDRATES OF THENYL AND FURFURYL ALCOHOLS AND MERCAPTANS

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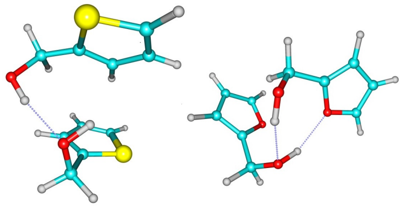

The dimers of thenyl alcohol ($TA_2$) and furfuryl alcohol ($FA_2$), and the monohydrates of both alcohols ($TA\cdots H_2O$, $FA\cdots H_2O$) and their corresponding mercaptans ($TM\cdots H_2O$, $FM\cdots H_2O$) were generated in a supersonic jet expansion and probed using both chirped-pulse and cavity Fourier transform microwave spectroscopy. The experimental results, supported by ab initio molecular orbital calculations, allow comparing the conformational preferences and the role of the sulfur and oxygen atoms in the O-H$\cdots$O/O-H$\cdots$S/S-H$\cdots$O hydrogen bonds (HBs) stabilizing the dimers. In the furfuryl monohydrates ($FA\cdots H_2O$, $FM\cdots H_2O$) water behaves as a proton donor to the ring oxygen, in competence with a second HB to the alcohol or thiol side chain[a]. Different behavior was observed when the ring oxygen is replaced by sulfur atom in the thenyl monohydrates ($TA\cdots H_2O$ and $TM\cdots H_2O$) as the water molecule is binding to the side chain and the $\pi$ electronic cloud of the ring. The water motion in both thenyl dimers is detected by tunneling splittings of the rotational transitions, denoting a weaker binding compared to the furfuryl compounds. The alcohol dimers $(TA)_2$ and $(FA)_2$ again reveal the different HB strengths in the furfuryl and thenyl groups. The alcohol dimer forms a network of two consecutive O-H$\cdots$O hydrogen bonds involving the oxygen ring, while in the thenyl dimer the alcohol group prefers binding to the $\pi$ cloud than to the sulfur atom in the ring. Spectroscopic, structural and computational data will be reported.

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[a] M. Juanes, A. Lesarri, R. Pinacho, E. Charro, J. E. Rubio, L. Enriquez, M. Jaraiz, *Chem. Eur. J.*, **2018**, 24, 1–9, in press