2-PROPIONYLTHIOPHENE: PLANAR, OR NOT PLANAR, THAT IS THE QUESTION

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The molecular planarity of molecules that contain an alkyl group attached to a system with conjugated double bonds has posed a great challenge for both experiments and theory for a long time. This also holds true for the case of 2-propionylthiophene [1] where a propionyl group is attached at the second position of the planar, aromatic thiophene ring. Quantum chemical calculations performed at different levels of theory yield contradicting results on whether the ethyl group of the propionyl moiety is lying in-plane with the thiophene ring or slightly tilted out-of-plane.

In the microwave spectrum both *syn*-2PT and *anti*-2PT were assigned. For the energetically more favourable *syn*-conformer it was possible to observe several ^{13}C-isotopologues. This allowed the determination of a partial experimental heavy atom skeleton structure which revealed a tiny, but non-zero tilt angle of the ethyl group out of the thiophene plane, thereby convincingly confirming the non-planarity of 2-propionylthiophene. The results were further supported by inertial defects of both conformers calculated from the experimental rotational constants.

Aditionally, splittings arising from the internal rotation of the terminal methyl group were analysed, yielding torsional barriers of 806.94(54) cm^{-1} and 864.5(88) cm^{-1} for the two observed conformers, respectively.

[1] C. Dindić, W. Stahl, H.V.L. Nguyen, *Phys. Chem. Chem. Phys.*, 2020, **22**, 19704-19712.

[a]Posthumous Abstract