

# Influence of axle length on the rate and mechanism of shuttling in rigid H-shaped [2]rotaxanes

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A series of [2]rotaxane molecular shuttles was prepared containing a dibenzo[24]crown-8 (DB24C8) wheel and a rigid H-shaped axle with varying track lengths between recognition sites; from 7.4 to 20.3 Å as defined by 1-4 phenyl rings or a naphthyl group. The rate of shuttling was measured by variable temperature  $^1\text{H}$  NMR spectroscopy for neutral compounds and EXSY experiments for dicationic species. The rates were found to be independent of the length of the axle, except when the distance between the two recognition sites might be short enough ( $n = 1$ ) to allow the crown ether to simultaneously interact with both recognition sites providing a short-cut mechanism which could lower the energy barrier. This notion is supported by DFT calculations and solid-state characterization of model compounds that mimic possible transition states. © 2017 The Royal Society of Chemistry.