Pushing vs Pulling: The Unique Geometry of Mechanophore Activation in a Rotaxane Force Actuator

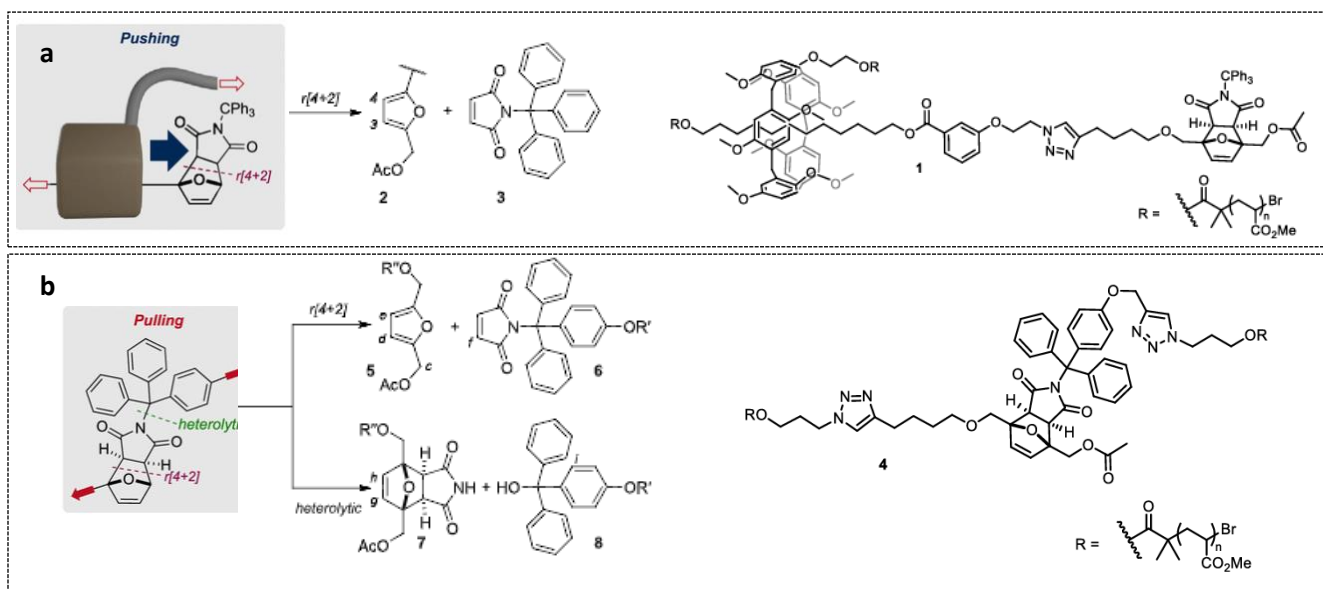L. Chem, G. D. Bo *J. Am. Chem. Soc.* **2024**, *146, 24*, 16381–16384

Fig 1: Pushing vs pulling actuation for the activation of a Diels–Alder mechanophore. (a) Pushing actuation leads to the release of N-triphenylmethyl maleimide 3 *via* a retro-[4 + 2] cycloaddition in rotaxane **1**. (b) Pulling actuation gives rise to two competing dissociations in mechanophore 4: r[4 + 2] or heterolytic scission at the C–N bond.

## Who are the corresponding authors and what are their research areas?

Guillaume De Bo – *Professor of Organic Chemistry at the University of Manchester, UK*
His research is centered on the use of mechanical force in innovative synthetic processes and the development of new molecular actuators.

What is the main claim of the article?

The work presents a strategy to control the selectivity and efficiency of mechanophore activation or deformation in the chain-centered rotaxane actuator. This is possible due to the unique rotaxane architecture, which allows for two possible activation paths of the Diels-Alder mechanophore (pushing and pulling).

How is it demonstrated?
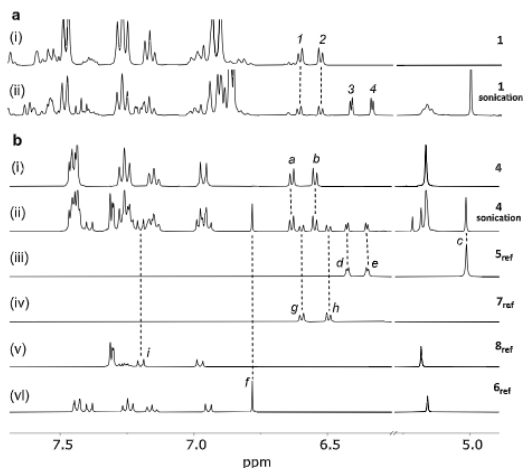
Author have shown ^{1}H NMR analysis results (Fig.2) to confirm two different outcomes from the two different activation pathways: *pushing* (a) and *pulling* (b), ^{1}H NMR of synthesized reference compounds were shown to support and assign ^{1}H NMR analysis of the deformation of the mechanophore in both cases.

Figure 2. Partial ^{1}H NMR (400 MHz, acetone-d6, 298 K) spectra of:(a) pushed mechanophore 1 before (i) and after (ii) sonication, and(b) pulled mechanophore 4 before (i) and after (ii) sonication, along with reference compounds 5ref (iii) and 7ref (iv), 8ref (v), and 6ref (vi)

A computational investigation of the *pushing* and *pulling* actuation was conducted. Authur rationally focused on three indicative parameters (the elongation of C−C and C−N scissile bonds a and b (Figure 3a,b), their related bond angles α and β (Figure 3a,c), and dihedral angle ω (Figure 3a,d)

In the pushing activation, elongation of bond a, opening of bond angle α, twisting of dihedral angle were observed, while the top part of the mechanophore (bond b and bond angle β) remained almost unaffected in. This suggests that most of the deformation develops at the contact between the macrocycle and the mechanophore leading to retro-[4+2] cycloaddition. In the case of *pulling*, mechanophore experiences a more acute deformation that propagates along the backbone connecting the two pulling Anchors. Both bonds a and b, and both angles α and β increase substantially during elongation suggesting two competitive deformations (retro-[4+2] cycloaddition and heterolytic cleavage of C-N bond).
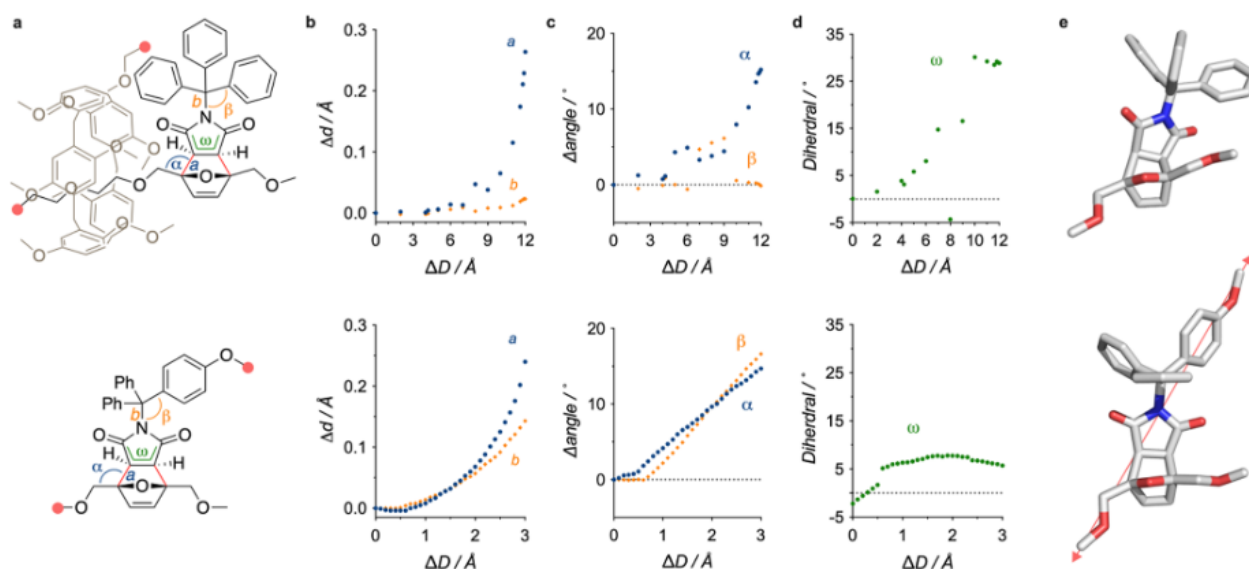

Figure 3. Computational investigation of the pushing and pulling actuations (CoGEF, DFT entry B3LYP/6-31G*, gas). (a) Models in the computation indicating key structural parameters. Predicted scissile bond are shown in red. Anchor atoms are indicated by the pink disks. Evolution of bond a and b (b), angles α and β (c), and dihedral ω (d) upon simulated elongation of rotaxane (top) and linear (bottom) models. (e)Equilibrium geometries at the E_{max} of the Diels–Alder mechanophore upon pushing (top) or pulling (bottom).

What are the typical experimental conditions?

Mechanical activation: High-intensity ultrasound (20 kHz, 13.0 W/cm^2, 1s ON/1s OFF in THF/H$_2$O: 75/1 at 5-10°C, 90 min)
DFT calculation: Con-strained Geometries Simulate External Force (CoGEF) calculations (B3LYP/6-31G*, gas)

Which are the key related papers?

1. R. Stevenson, G. D. Bo, *J. Am. Chem. Soc.* **2017**, *139, 46*, 16768–16771
2. M. Zhang, G. D. Bo*, J. Am. Chem. Soc.* **2018**, *140, 40*, 12724–12727