A Spring-Loaded ROMPer

Significance: The [8]annulene 1, with one double bond in the trans configuration was synthesized in 20% yield on a 20 mmol scale. Compound 1 was shown to be kinetically stable but thermodynamically unstable, with the cis,cis isomer being thermodynamically favored. Compound 1 winds into a helical conformation in the solid state and both enantiomers of 1 are present within the unit cell of a crystal. The calculated strain energy for 1 is 18 kcal/mol, which allows it to participate in ring-opening metathesis polymerization (ROMP), unlike its cis,cis isomer. Compound 1 forms living polymers when mixed with Grubbs’ catalyst (1st gen.) and additional tricyclohexylphosphine ligand. In this fashion, regioregular poly(phenylene vinylene) (PPV) with all-ortho linkages was prepared and its hydrogenated derivate characterized by GPC and 1H and 13C NMR spectroscopy.

Comment: The authors reinvestigated chemistry pursued by Wittig et al. (Justus Liebigs Ann. Chem. 1955, S93, 127) and correctly identified a monomer that displays unique reactivity and yields interesting polymers. The regioselectivity of the ROMP imparts a well-defined secondary structure to P1 that can be exploited in sensing or molecular recognition schemes.