Mechanochemistry
The curious case of cyclopropane

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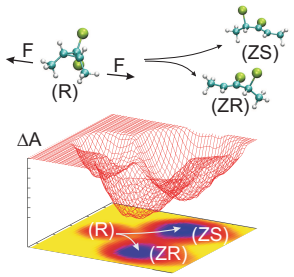
The stereochemistry of mechanochemical ring-opening reactions in cyclopropane derivatives has provided several enigmatic experimental results. [1] This issue is addressed here with advanced *ab initio* simulations - Car–Parrinello Molecular Dynamics [2, 3, 4] - of *cis*– and *trans*-1,1-dichloro-2,3-dimethylcyclopropane.

In particular, force-transformed free energy landscapes are computed via metadynamics, [5, 6] which accesses the thermodynamics of mechanochemical reactivity. Dynamical effects are probed through extensive trajectory shooting simulations. [7] It is demonstrated that forces of approximately 2 nN induce barrierless ring-opening of both cis and trans isomers, which rationalizes the lack of selectivity observed experimentally.



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