Supplementary Information

Contents

Computational details

All quantum chemical calculations reported in this paper were carried out with the Q-Chem 4.3 program package.[1] Ground state single point calculations, geometry optimizations and frequency calculations were performed with Density Functional Theory (DFT)[2,3] at the B3LYP[4,5]/cc-pVDZ[6] level of theory. Geometry optimizations in the electronically excited state were carried out with Time-Dependent Density Functional Theory (TDDFT)[7] at the same level of theory. Forces were applied with the EFEI (External Force is Explicitly Included) method.[8] In this approach, geometry optimizations under the influence of an external force are conducted. In the case of *trans*-3,4-dimethylcyclobutene, forces were applied to the carbon atoms of the methyl groups, driving them apart. The same atoms were used in the case of the macrocycle **1**. Forces needed for bond breaking were determined iteratively. The exciton density was calculated with the RI-ADC(2)-s method[9–12] using the VDZ basis and the RI-MP2-VDZ auxiliary basis set (see below).

Born-Oppenheimer Molecular Dynamics (BOMD) simulations under external forces were conducted by adding a constant equal to the external force to the nuclear gradient in every time step of the BOMD simulation in the desired direction. In *trans*-3,4-dimethylcyclobutene, the same atoms as in the EFEI calculations were used. The step size in the trajectory was 20 a.u., corresponding to 0.484 fs. The trajectories were run for a total of 2500 time steps, so that the total simulation time amounted to 1.2 ps. The initial velocities for the different temperatures were sampled from a Boltzmann distribution. We are well aware that, for the processes discussed here, longer simulation times would be beneficial. However, due to the large amount of temperature/force pairs and the plethora of trajectories needed for a thorough sampling, this is prohibitively expensive. The same is true for BOMD trajectories in the electronically excited state (S_1): Further insights into photo-mechanical and thermal effects would be gained if BOMD trajectories of the photochemical *cis→trans*-isomerization of isolated stiff-stilbene or the macrocycle **1** in the S_1 state were available, but these calculations are computationally not feasible.

The JEDI (Judgement of Energy DIstribution) analysis has been discussed in detail previously.[13–15] In the ground state JEDI analysis, the distribution of stress energy in a mechanically deformed molecule among its redundant internal modes is investigated.[13,14] In the harmonic approximation, an energy is calculated for each bond length, bond angle and dihedral angle. In the excited state JEDI analysis, in contrast, the energy released into each internal mode during relaxation on the excited state potential energy surface (PES) is calculated.[15] It is important to note that in the first case (ground state) a molecule is stretched actively, which means that energy is expended, whereas in the second case (excited state) energy is released by the motion along the excited state PES. Both variants of the JEDI analysis, however, require that the PESs can be approximated as harmonic. The color coded molecular structures were generated with VMD 1.9.1.[16] Details on the generation of these structures have been given previously.[14]

JEDI analysis of isolated *trans*-3,4-dimethylcyclobutene

To analyze the distribution of stress energy in *trans*-3,4-dimethylcyclobutene, we calculated an EFEI coordinate in which the force was applied to the carbon atoms of the methyl groups, driving them apart. We are well aware that in this setup the force vector is not parallel to the bond that ultimately breaks, thus decreasing the effective force by which this bond is stretched. This, however, is exactly the case in the macrocycle **1**. In each point of the EFEI coordinate, the distribution among all internal modes of the molecule is calculated via the ground state JEDI analysis. The modes shown in Figure S1A are of particular interest. The harmonic stress energies of these modes are shown in Figure S1B. In the beginning of the stretching coordinate, most energy is stored in the "vicinal bonds", which are the bonds adjacent to the bond that ultimately breaks. The bond angles between these two kinds of bonds and the dihedral angle involving both carbon atoms of the methyl groups also store significant amounts of stress energy. Only at large stretching forces the "critical bond", which is the one that ultimately breaks, stores most stress energy. However, it should be noted that at large forces the harmonic approximation becomes less and less reliable (Figure S1B), so that this might also be an artifact of the harmonic approximation.

Immediately before bond breaking, the "critical" bond stores only 31% of the stress energy (Figure S2), which can be considered an upper bound to the real value due to the unreliable harmonic approximation in this part of the stretching coordinate. As such, it is also an upper bound to the mechanochemical susceptibility of cyclobutene itself, since the mechanical energy it receives from stiff-stilbene is not fully passed on to the bond that ultimately breaks.
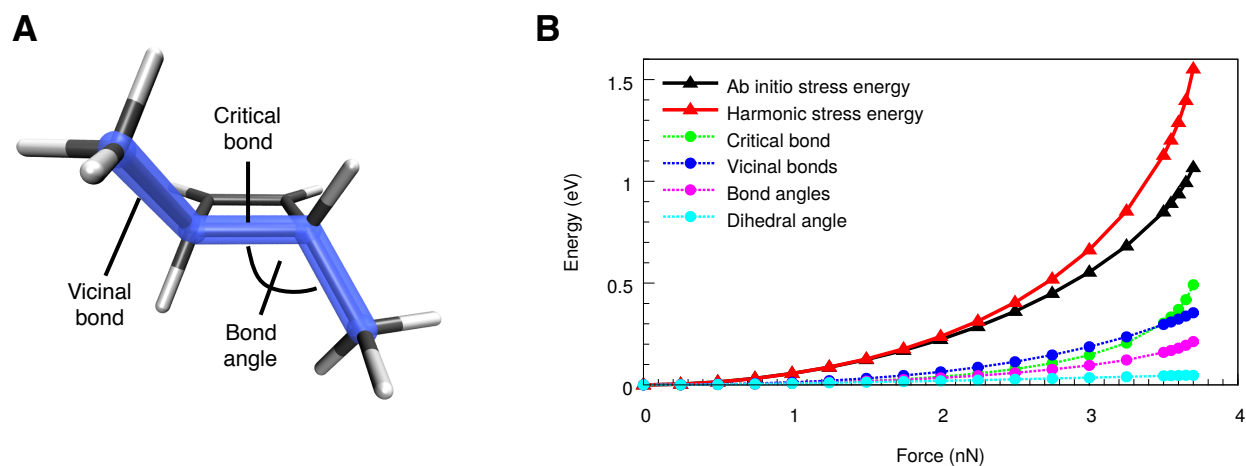
A

B

Figure S1: A: The JEDI analysis of *trans*-3,4-dimethylcyclobutene was conducted with special attention to those internal modes along the stretching coordinate. The "critical bond" is the bond that ultimately breaks, the "vicinal bonds" are the bonds connecting the methyl groups to the cyclobutene ring, the "bond angle" is the angle between these two kinds of bonds and the "dihedral angle" is shown in blue. B: The *ab initio* stress energy is the energy difference between the relaxed and the stretched molecule, calculated at the B3LYP/cc-pVDZ level of theory. The harmonic stress energy is the sum of the harmonic energies in every internal mode, calculated with the JEDI analysis. The distribution of stress energy among the internal modes depicted in A is given.
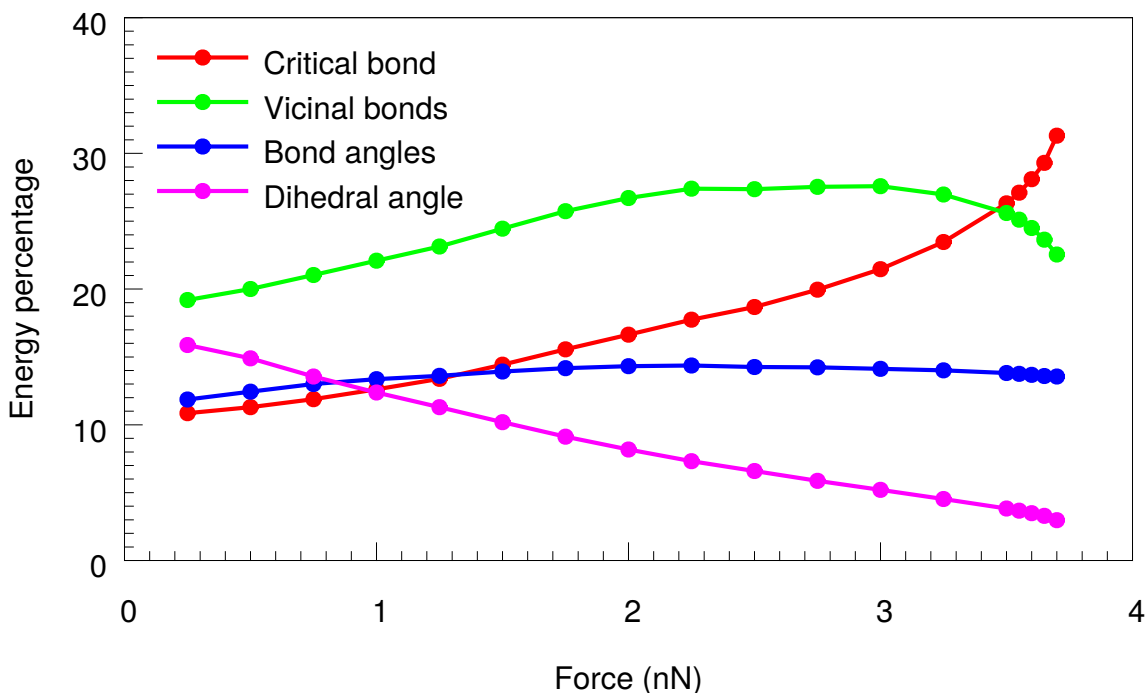
Figure S2: Distribution of stress energy among the most relevant internal modes of *trans*-3,4-dimethylcyclobutene. The percentages of stress energy stored in the modes shown in Figure S1A is plotted.

BOMD simulations of *trans*-3,4-dimethylcyclobutene at different temperatures

In our BOMD calculations of *trans*-3,4-dimethylcyclobutene, we find that the force needed to rupture the labile bond decreases with increasing temperature, or, equivalently, the time until bond rupture at a given force decreases with increasing temperature. For example, in the case of 0 K and a force of 2.5 nN that drives the methyl groups apart, bond rupture is not observed at all on the time scale of the simulation (1.2 ps). At 505 K, rupture occurs after 505 fs, while at 900 K this time decreases to 41 fs. The observation that higher temperatures lead to lower rupture forces is consistent with the existing literature.[17–20]

Which modes are displaced first?

Within the harmonic approximation, the energy E is connected to the displacement Δx via

$$E = \frac{1}{2}k(\Delta x)^2 . \tag{1}$$

The stretching force F is connected to the displacement via

$$F = k\Delta x . \tag{2}$$

Hence, for a constant stretching force, we can write

$$\Delta x \sim \frac{1}{k} . \tag{3}$$

Inserting Eq. 3 in Eq. 1 establishes a link between the energy stored in a mechanically stretched mode and its displacement:

$$E \sim \frac{1}{k} \tag{4}$$

Hence, the higher the force constant, the less energy is stored in it. Although it is not possible to rigorously define force constants for every redundant internal mode in a molecule, the concept shown here illustrates the observation that "soft" modes (dihedral angles, bond angles) are displaced more easily than "hard" modes (single, double, triple bonds) by the same stretching force.

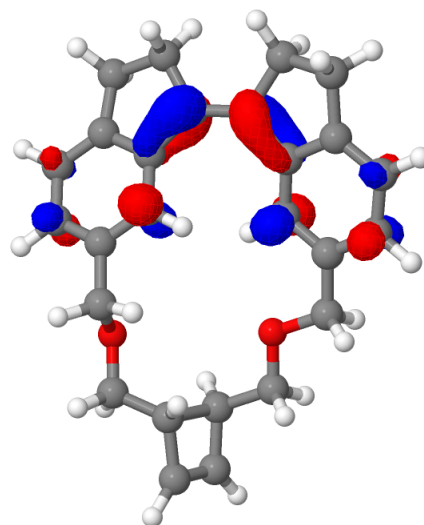## Exciton analysis at the RI-ADC(2)-s level of theory

Exciton analysis at the RI-ADC(2)-s level of theory revealed that the first electronically excited state has 85.1% single excitation character. The exciton is completely localized on the stiff-stilbene moiety (Figure S3).
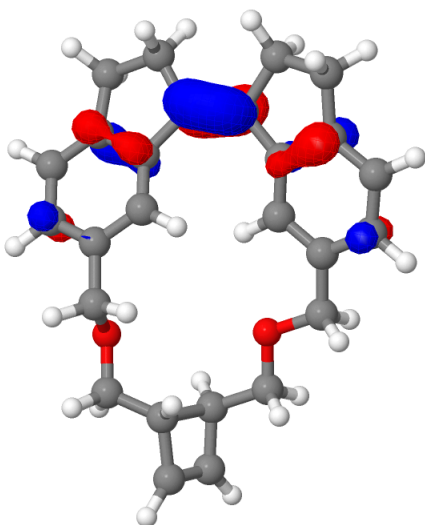
Figure S3: Natural Transition Orbitals (NTOs) of the macrocycle 1, accounting for 78.5% of the excitation into the first electronically excited state of the molecule. The exciton is located solely on the stiff-stilbene moiety. Pictures were generated using JMol.[21]

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