

Supporting Information

The Activation Efficiency of Mechanophores Can Be Modulated by Adjacent Polymer Composition

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1 COMPUTATIONAL DETAILS

The External Force is Explicitly Included (EFEI)^[1-3] method was used to optimize the molecular geometries under a constant external stretching force. In the EFEI method, external mechanical forces are applied to a molecule during a quantum chemical geometry optimization by adding a constant to the nuclear gradient of a pair of atoms that drives these atoms apart. The geometry optimization converges when the external stretching force and the internal restoring force of the molecule cancel. Rupture forces were calculated iteratively. The CONstrained Geometries simulate External Forces (COGEF)^[4,5] method was used to constrain the bond angle β_1 to different values while simultaneously stretching the molecules apart with the EFEI method. In COGEF, geometrical constraints are applied during a geometry optimization, which is equivalent to the application of mechanical stress. Both EFEI and COGEF were carried out with the Q-Chem 5.2.1^[6] program package using Density Functional Theory (DFT)^[7,8] at the PBE^[9]/cc-pVDZ^[10] level of theory based on geometries optimized at zero force. The lack of imaginary frequencies at zero force confirmed that the obtained structures are indeed true minima. The Cartesian coordinates of all structures (the three investigated mechanophores with all tested linkers) are available online as part of the Supporting Information.

The analysis of strain distribution in the mechanically distorted molecules was achieved with the Judgement of Energy DIstribution (JEDI)^[11-13] analysis. Based on the harmonic approximation, the JEDI analysis quantifies the strain energies within each bond, bending and torsion of a mechanically deformed molecule. Color-coded structures of molecules under tensile stress were created with VMD 1.9.3,^[14] where the strain in each bond, bending and torsion was mapped onto the bonds.

To study the role of electron density at the bond critical points, topology analysis was carried out with the Quantum Theory of Atoms In Molecules (QTAIM)^[15] approach using the Multiwfn 3.7 program package.^[16] The wavefunctions required for these calculations were generated with Q-Chem.

2 DEPENDENCE OF RUPTURE FORCE ON THE LENGTH OF THE ALKYL CHAIN

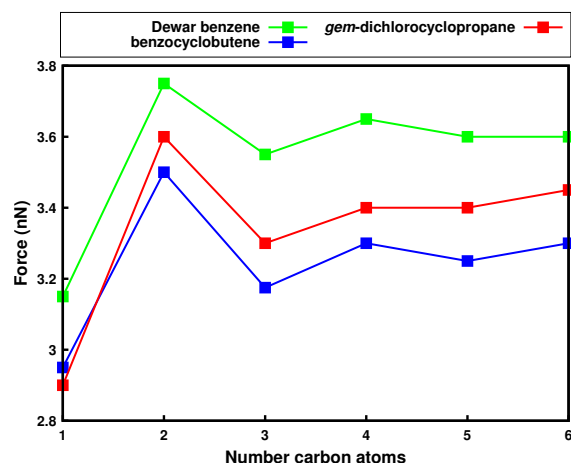


Figure S1: Amount of force required to activate the investigated mechanophores when changing the number of carbon atoms in the alkyl linker. Lines were included to guide the eye.

3 INFLUENCE OF THE LINKER ON THE RUPTURE FORCE

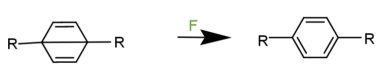
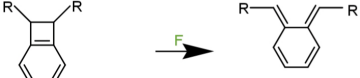
					
Substitution	Rupture force (nN)	Substitution	Rupture force (nN)	Substitution	Rupture force (nN)
$-\text{C}\equiv\text{C}-\text{CH}_3$	1.59	$-\text{C}\equiv\text{C}-\text{CH}_3$	1.80	$-\text{NH}-\text{CO}-\text{CH}_3$	1.35
$-\text{NH}-\text{CO}-\text{CH}_3$	1.61	$-\text{NH}-\text{CO}-\text{CH}_3$	1.91	$-\text{C}\equiv\text{C}-\text{CH}_3$	1.64
$-\text{C}=\text{C}-\text{CH}_3$	2.10	$-\text{O}-\text{CH}_2-\text{CH}_3$	1.96	$-\text{O}-\text{CO}-\text{CH}_3$	2.05
$-\text{O}-\text{CO}-\text{CH}_3$	2.22	$-\text{O}-\text{CO}-\text{CH}_3$	2.33	$-\text{C}=\text{C}-\text{CH}_3$	2.15
$-\text{NH}-\text{CH}_2-\text{CH}_3$	2.42	$-\text{NH}-\text{CH}_2-\text{CH}_3$	2.49	$-\text{NH}-\text{CH}_2-\text{CH}_3$	2.46
$-\text{O}-\text{CH}_2-\text{CH}_3$	2.64	$-\text{C}=\text{C}-\text{CH}_3$	2.59	$-\text{CO}-\text{NH}-\text{CH}_3$	2.59
$-\text{C}=\text{N}-\text{CH}_3$	2.94	$-\text{C}=\text{N}-\text{CH}_3$	3.04	$-\text{O}-\text{CH}_2-\text{CH}_3$	2.63
$-\text{CO}-\text{NH}-\text{CH}_3$	2.96	$-\text{CH}_2-\text{CH}_2-\text{CH}_3$	3.18	$-\text{C}=\text{N}-\text{CH}_3$	2.66
$-\text{CH}_2-\text{CH}_2-\text{CH}_3$	3.52	$-\text{N}=\text{N}-\text{CH}_3$	3.24	$-\text{N}=\text{N}-\text{CH}_3$	2.79
$-\text{N}=\text{N}-\text{CH}_3$	3.70	$-\text{CO}-\text{NH}-\text{CH}_3$	3.40	$-\text{CH}_2-\text{CH}_2-\text{CH}_3$	3.27
$-\text{CO}-\text{O}-\text{CH}_3$	4.27	$-\text{CO}-\text{O}-\text{CH}_3$	3.56	$-\text{CO}-\text{O}-\text{CH}_3$	3.87

Table S1: Rupture forces for the mechanical activation of Dewar Benzene, benzocyclobutene and *gem*-dichlorocyclopropane using different linkers that connect the mechanophores to the rest of the polymer backbone.

4 RUPTURE FORCES USING COMBINATIONS OF DIFFERENT LINKERS

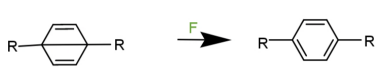
					
Substitution (Linker1, Linker2)	Rupture force (nN)	Substitution (Linker1, Linker2)	Rupture force (nN)	Substitution (Linker1, Linker2)	Rupture force (nN)
–C≡C–CH ₃ , –O–CH ₂ –CH ₃	2.05	–C≡C–CH ₃ –C=C–CH ₃	2.15	–NH–CO–CH ₃ –CO–NH–CH ₃	1.6
–C≡C–CH ₃ –CO–O–CH ₃	2.65	–C≡C–CH ₃ –CO–O–CH ₃	2.65	–NH–CO–CH ₃ –CO–O–CH ₃	1.9
–CO–O–CH ₃ –O–CH ₂ –CH ₃	3.3	–O–CH ₂ –CH ₃ –C=C–CH ₃	3.15	–CO–NH–CH ₃ –CO–O–CH ₃	3.0

Table S2: Rupture forces for the mechanical activation of Dewar Benzene, benzocyclobutene and *gem*-dichlorocyclopropane using combinations of different linkers.

5 JEDI ANALYSIS

5.1 DEWAR BENZENE

Substitution	Strain percentage			Absolute energy (a.u.)
	Bond lengths	Bond angles	Dihedral angles	
–NH–CO–CH ₃	27.55	18.03	54.42	0.0134181807
–C=C–CH ₃	24.09	22.55	53.36	0.0109785290
–CO–O–CH ₃	39.17	20.34	40.49	0.033472350

Table S3: Percentage of total strain stored in the bond lengths, bond angles and dihedral angles of Dewar benzene with different linkers as well as strain energy in the scissile C–C bond at a stretching force that is 0.01 nN lower than the rupture force.

5.2 BENZOCYCLOBUTENE

Substitution	Strain percentage			Absolute energy (a.u.)
	Bond lengths	Bond angles	Dihedral angles	
–NH–CO–CH ₃	12.41	19.14	68.45	0.02943622
–C=C–CH ₃	35.09	27.78	37.13	0.0288327
–CO–O–CH ₃	21.11	20.24	58.66	0.0295591

Table S4: Percentage of total strain stored in the bond lengths, bond angles and dihedral angles of benzocyclobutene with different linkers as well as strain energy in the scissile C–C bond at a stretching force that is 0.01 nN lower than the rupture force.

5.3 *gem*-DICHLOROCYCLOPROPANE

Substitution	Strain percentage			Absolute energy (a.u.)
	Bond lengths	Bond angles	Dihedral angles	
–NH–CO–CH ₃	4.13	2.63	93.24	0.0050843
–C=C–CH ₃	22.05	25.90	52.05	0.008019
–CO–O–CH ₃	26.09	19.39	54.51	0.0277913

Table S5: Percentage of total strain stored in the bond lengths, bond angles and dihedral angles of *gem*-dichlorocyclopropane with different linkers as well as strain energy in the scissile C–C bond at a stretching force that is 0.01 nN lower than the rupture force.

6 ELECTRON DENSITY AT THE BOND CRITICAL POINTS

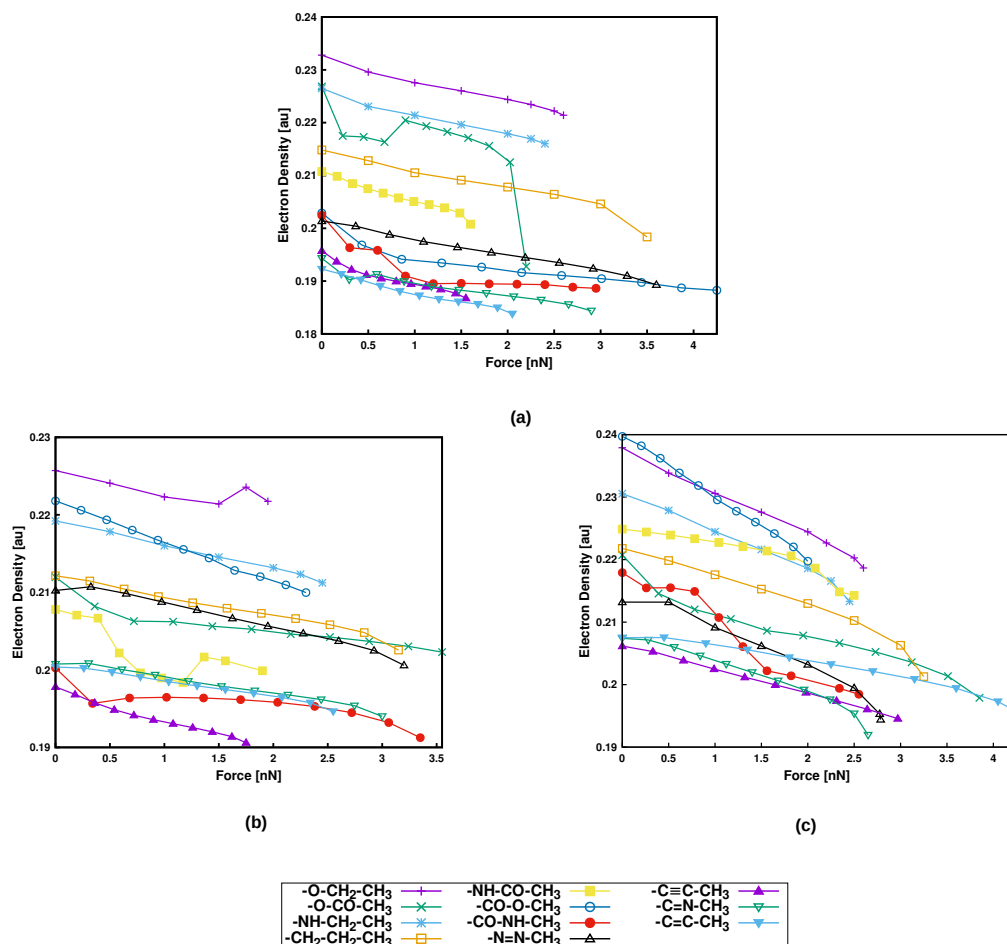


Figure S2: Electron densities in the scissile C–C bonds in Dewar benzene (a), benzocyclobutene (b) and *gem*-dichlorocyclopropane (c) using different linkers, as a function of external stretching force.

7 BOND ANGLES IN THE LINKERS

7.1 DEWAR BENZENE

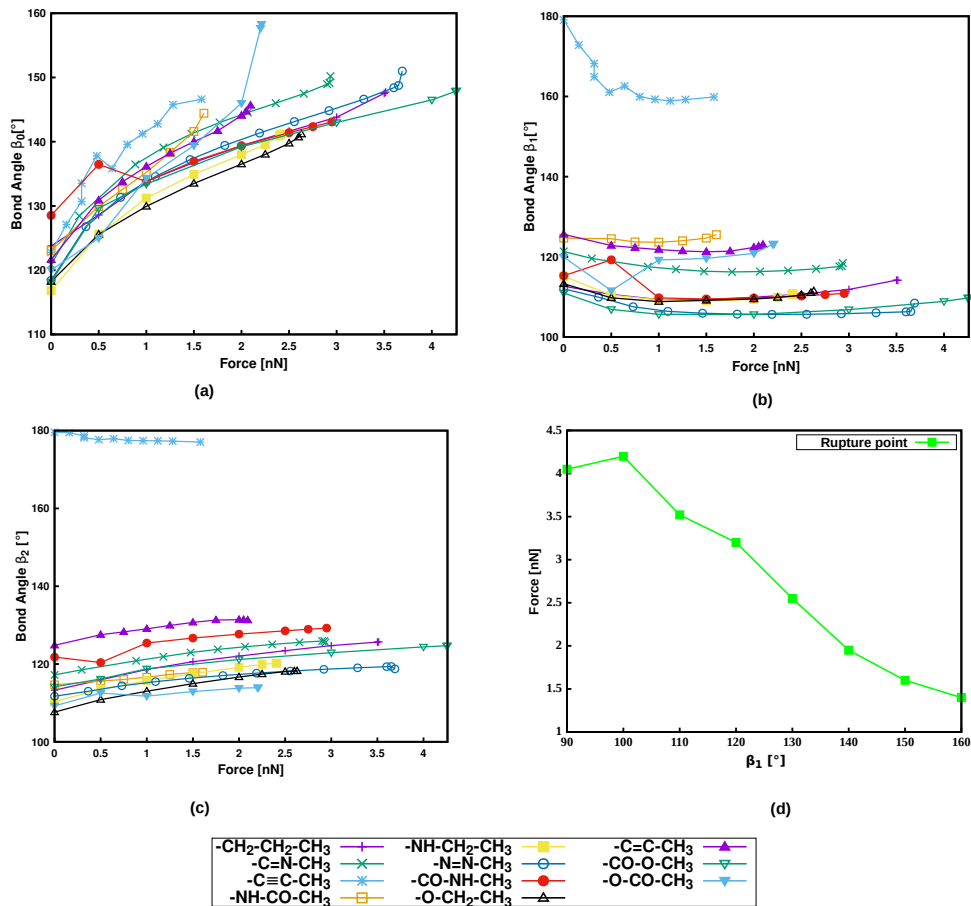


Figure S3: Bond angles β_0 (a), β_1 (b) and β_2 (c) as a function of external stretching force applied to the terminal methyl groups in Dewar benzene with different linkers. (d) Rupture forces as a function of the constrained angle β_1 .

Substitution	β_0 (initial)	β_0 (final)
$-\text{C}\equiv\text{C}-\text{CH}_3$	122.78	146.61
$-\text{NH}-\text{CO}-\text{CH}_3$	123.05	144.43
$-\text{C}=\text{C}-\text{CH}_3$	121.63	145.65
$-\text{O}-\text{CO}-\text{CH}_3$	120.03	158.29
$-\text{NH}-\text{CH}_2-\text{CH}_3$	116.81	141.15
$-\text{O}-\text{CH}_2-\text{CH}_3$	118.22	141.17
$-\text{C}=\text{N}-\text{CH}_3$	120.86	150.19
$-\text{CO}-\text{NH}-\text{CH}_3$	128.53	143.09
$-\text{CH}_2-\text{CH}_2-\text{CH}_3$	123.76	147.72
$-\text{N}=\text{N}-\text{CH}_3$	118.43	150.99
$-\text{CO}-\text{O}-\text{CH}_3$	118.18	147.93

Table S6: Initial ($F = 0$) and final (0.01 nN before bond rupture) values of the bond angle β_0 in Dewar benzene.

Substitution	β_1 (initial)	β_2 (initial)	β_1 (final)	β_2 (final)
$-\text{C}\equiv\text{C}-\text{CH}_3$	179.08	179.64	159.86	177.05
$-\text{NH}-\text{CO}-\text{CH}_3$	124.67	114.65	125.53	117.87
$-\text{C}=\text{C}-\text{CH}_3$	125.61	124.81	123.05	131.26
$-\text{O}-\text{CO}-\text{CH}_3$	119.94	109.22	123.24	113.95
$-\text{NH}-\text{CH}_2-\text{CH}_3$	115.12	110.32	110.83	120.20
$-\text{O}-\text{CH}_2-\text{CH}_3$	113.29	107.64	111.44	118.20
$-\text{C}=\text{N}-\text{CH}_3$	121.34	117.22	118.44	125.51
$-\text{CO}-\text{NH}-\text{CH}_3$	115.54	122.68	110.92	129.95
$-\text{CH}_2-\text{CH}_2-\text{CH}_3$	112.67	113.27	114.15	125.69
$-\text{N}=\text{N}-\text{CH}_3$	112.03	111.72	108.46	118.75
$-\text{CO}-\text{O}-\text{CH}_3$	110.98	114.14	109.80	124.70

Table S7: Initial ($F = 0$) and final (0.01 nN before bond rupture) values of the bond angles β_1 and β_2 in Dewar benzene.

7.2 BENZOCYCLOBUTENE

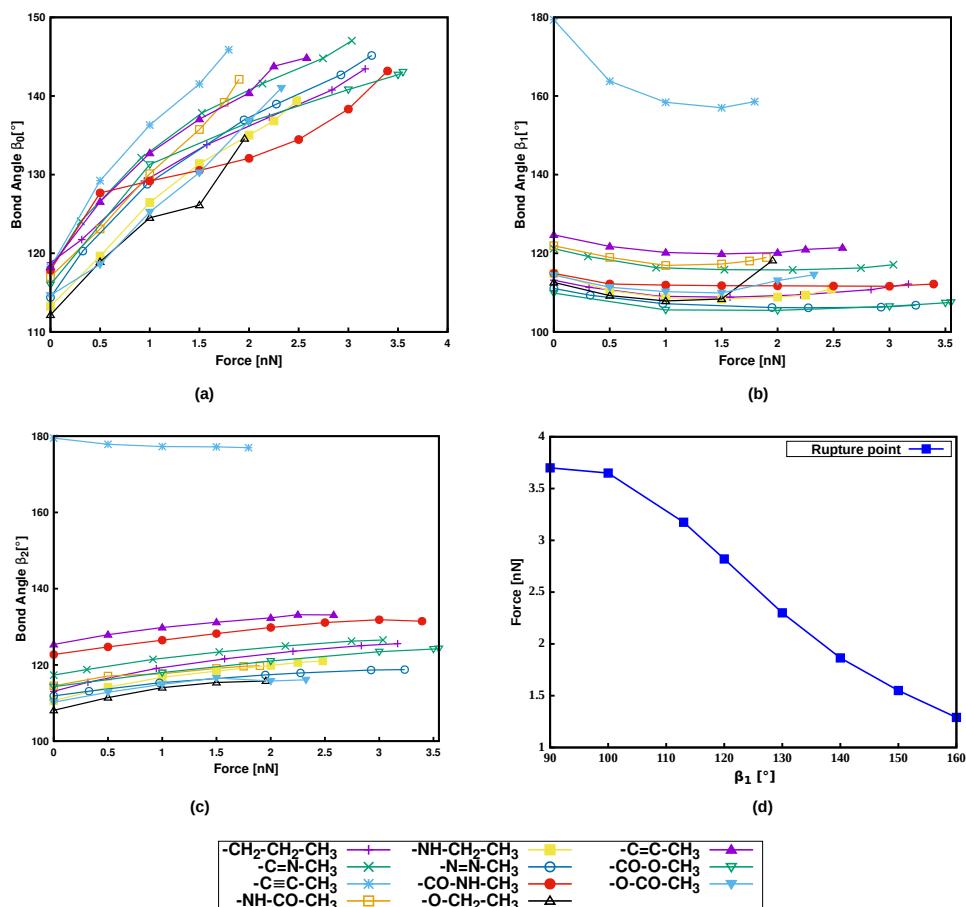


Figure S4: Bond angles β_0 (a), β_1 (b) and β_2 (c) as a function of external stretching force applied to the terminal methyl groups in benzocyclobutene with different linkers. (d) Rupture forces as a function of the constrained angle β_1 .

Substitution	β_0 (initial)	β_0 (final)
$-\text{C}\equiv\text{C}-\text{CH}_3$	118.171	145.894
$-\text{NH}-\text{CO}-\text{CH}_3$	120.048	140.658
$-\text{O}-\text{CH}_2-\text{CH}_3$	112.153	134.608
$-\text{O}-\text{CO}-\text{CH}_3$	113.25	141.284
$-\text{NH}-\text{CH}_2-\text{CH}_3$	111.734	138.678
$-\text{C}=\text{C}-\text{CH}_3$	118.263	144.854
$-\text{C}=\text{N}-\text{CH}_3$	117.916	147.029
$-\text{CH}_2-\text{CH}_2-\text{CH}_3$	118.802	143.453
$-\text{N}=\text{N}-\text{CH}_3$	114.382	145.159
$-\text{CO}-\text{NH}-\text{CH}_3$	117.876	143.183
$-\text{CO}-\text{O}-\text{CH}_3$	119.926	142.93

Table S8: Initial ($F = 0$) and final (0.01 nN before bond rupture) values of the bond angle β_0 in benzocyclobutene.

Substitution	β_1 (initial)	β_2 (initial)	β_1 (final)	β_2 (final)
$-\text{C}\equiv\text{C}-\text{CH}_3$	179.49	179.31	158.53	176.95
$-\text{NH}-\text{CO}-\text{CH}_3$	125.71	115.08	126.032	118.005
$-\text{O}-\text{CH}_2-\text{CH}_3$	112.59	108.08	118.19	115.79
$-\text{O}-\text{CO}-\text{CH}_3$	115.81	109.73	114.55	115.99
$-\text{NH}-\text{CH}_2-\text{CH}_3$	113.85	110.82	109.04	120.93
$-\text{C}=\text{C}-\text{CH}_3$	124.68	125.36	121.42	133.12
$-\text{C}=\text{N}-\text{CH}_3$	121.175	117.33	117.089	126.53
$-\text{CH}_2-\text{CH}_2-\text{CH}_3$	113.14	113.07	112.17	125.57
$-\text{N}=\text{N}-\text{CH}_3$	111.05	111.87	106.79	118.77
$-\text{CO}-\text{NH}-\text{CH}_3$	114.89	122.72	112.17	131.47
$-\text{CO}-\text{O}-\text{CH}_3$	109.87	114.30	107.51	124.29

Table S9: Initial ($F = 0$) and final (0.01 nN before bond rupture) values of the bond angles β_1 and β_2 in benzocyclobutene.

7.3 *gem*-DICHLOROCYCLOPROPANE

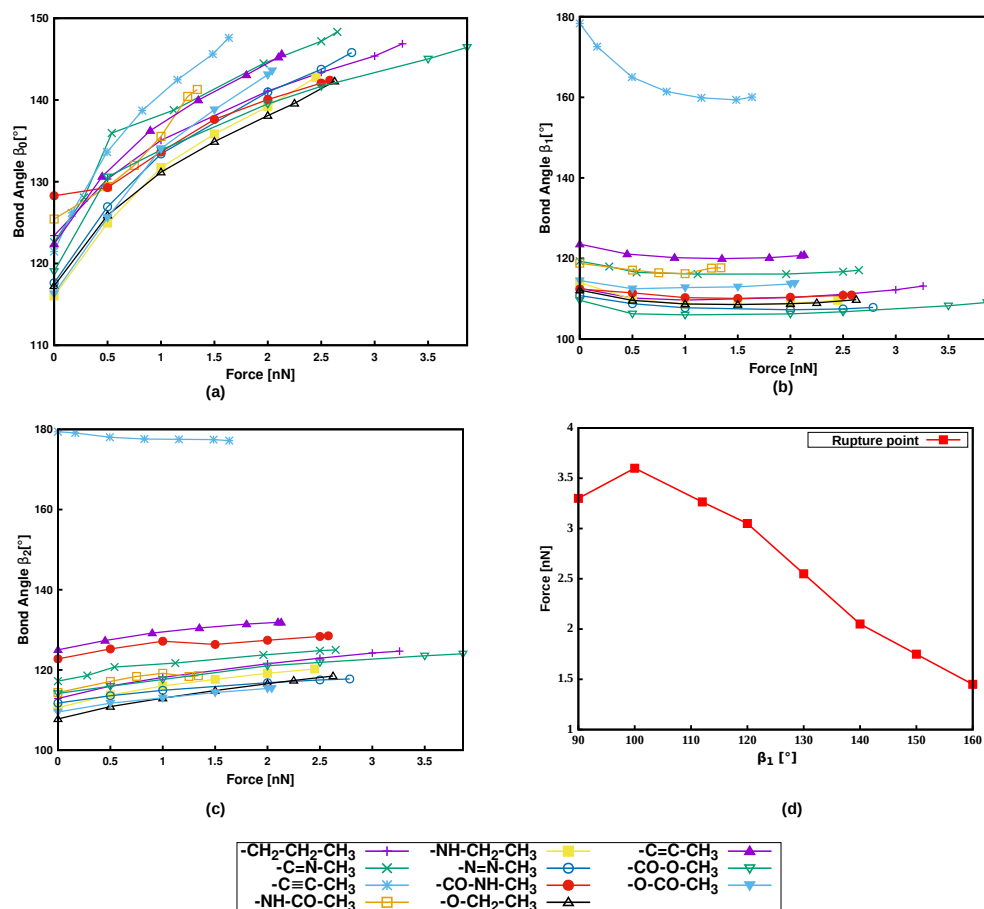


Figure S5: Bond angles β_0 (a), β_1 (b) and β_2 (c) as a function of external stretching force applied to the terminal methyl groups in *gem*-dichlorocyclopropane with different linkers. (d) Rupture forces as a function of the constrained angle β_1 .

Substitution	β_0 (initial)	β_0 (final)
–NH–CO–CH ₃	129.373	141.233
–C≡C–CH ₃	121.469	147.619
–O–CO–CH ₃	116.307	143.588
–C=C–CH ₃	122.318	145.621
–NH–CH ₂ –CH ₃	116.030	142.323
–CO–NH–CH ₃	128.291	142.284
–O–CH ₂ –CH ₃	117.126	142.300
–C=N–CH ₃	122.61	148.311
–N=N–CH ₃	117.639	141.101
–CH ₂ –CH ₂ –CH ₃	123.419	146.877
–CO–O–CH ₃	119.029	146.292

Table S10: Initial ($F = 0$) and final (0.01 nN before bond rupture) values of the bond angle β_0 in *gem*-dichlorocyclopropane.

Substitution	β_1 (initial)	β_2 (initial)	β_1 (final)	β_2 (final)
–NH–CO–CH ₃	118.82	114.37	117.70	118.56
–C≡C–CH ₃	178.33	179.39	164.78	178.10
–O–CO–CH ₃	114.53	109.81	113.84	115.41
–C=C–CH ₃	123.63	124.91	120.89	131.85
–NH–CH ₂ –CH ₃	114.45	110.29	111.79	120.37
–CO–NH–CH ₃	116.98	121.20	110.97	128.45
–O–CH ₂ –CH ₃	112.14	107.78	109.76	118.48
–C=N–CH ₃	119.31	117.22	117.10	124.97
–N=N–CH ₃	110.79	111.74	107.94	117.66
–CH ₂ –CH ₂ –CH ₃	112.66	112.88	113.17	124.67
–CO–O–CH ₃	108.43	114.10	109.08	124.09

Table S11: Initial ($F = 0$) and final (0.01 nN before bond rupture) values of the bond angles β_1 and β_2 in *gem*-dichlorocyclopropane.

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