Comparison of the predictive performance of the Bell-Evans, Taylorexpansion and statistical-mechanics models of mechanochemistry

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Supplemental Information

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General.

All calculations were performed with the Gaussian09.B01¹ software package on trestles.sdsc.edu HPC resource supported by the NSF as part of the XSEDE computational network. Compounds 7-10 are chiral and computations were performed on a single enantiomer (SS for **7-9**, *RSRSRSRS,RSRSRSRSR, RSRSSRS, RSRSRSR, RSSRSRS, RSSRSRSR, RSSRSRS, RSSRS, RSSRSSRS, RSSRSSRS, RSSRSRS, RSSRSSRS, RSSRSRS, RSSRSRS, RSSRSRS, RSSRS, RSSRSRS, RSSRS, RSS*

points; to ensure reliable compliances, very tight convergence criteria and ultrafine integration grids used in all optimizations and analytical frequency calculations. Thermodynamic corrections to electronic energies of individual conformers were calculated statistical-mechanically in the harmonic oscillator/rigid rotor/ideal gas approximations, as $3RT + ZPE + U_{vib} - TS$, where ZPE is the zero-point energy, $U_{\rm vib}$ is the vibrational component of the internal energy and S is total entropy. Vibrational frequencies below 50 cm⁻¹ replaced with 50 cm⁻¹ as previously recommended,² to the artifactually large contribution of such lowfrequency modes to vibrational entropy. The use of this formalism for constrained molecules in this study is justified because the molecule plus its infinitelycompliant constraint is a stationary point and an infinitely compliant potential does not perturb the vibrational frequencies of the coupled molecule.³ The energies of ensembles were calculated as G_{min} –



 $RT\ln \sum g_i e^{-\Delta G_i \beta}$, where G_{\min} is the free energy of the conformational minimum, ΔG_i is the excess free energy of conformer *i* relative to this minimum, g_i is its degeneracy and β is inverse thermal energy. The energy barriers separating individual strain-free conformers were <5 kcal/mol (vs. >30 kcal/mol for ΔG_0^{\dagger}), justifying the use of Boltzmann statistics in calculating properties of ground and transition states and energies of activation. Ensemble averaging was done as $\langle \alpha \rangle = \frac{\sum \alpha_i g_i e^{-G_i \beta}}{\sum g_i e^{-G_i \beta}}$, where α is the quantity of interest (e.g., terminal C...C distances, *q*; or

compliance, λ) and the remaining terms are defined above.

Molecular compliances were calculated as $BH^{1}B^{T}$, where H is the Cartesian Hessians (obtained from frequency calculations on converged geometries), B is a truncated Wilson matrix (typically having only one row for the terminal C⁻⁻C distance); ⁻¹ signifies inversion by the "back-slash" numerical algorithm of Matlab.

Conformational ensembles.

With the exception of ester bonds ((O=)C-O), all rotable bonds in **7-10** can exist in one of the three stable configurations, \pm gauche and anti. The ester bond exists in the endo- or exo configuration, the latter being 5 – 20 kcal/mol higher in energy than the former and hence can be neglected. Consequently, the ester bond is considered to be fixed in the endo configuration. Because of the C₂ symmetry of **1** and **2**, most conformers of **7-10** correspond to two distinct combinations of torsions (i.e., such geometries are doubly degenerate), which reduces the total number of structurally distinct conformers from 3^N-N (where N is the number of rotable bonds) to ~3^N/2+N. The strong coupling between the adjacent torsions closest to the cyclobutene or cyclopropane core eliminates certain torsional combinations (e.g., because they place non-bonded atoms closer than their van der Waals distances).

We used a custom Matlab script to generate all possible conformers of **7-10** by changing the torsions of fully-optimized all-anti conformers of **7-10**. These sets of conformers were analyzed for the presence of short nonbonded contacts. Eliminating such conformers left ~3400, 11811, 11083, ~2420 conformers of **7-10**, respectively. All candidate conformers of **7** and **10** were optimized at the BLYP/6-311+G* level with autofitting. The number of candidate conformers of **8-9** was too large for complete optimization (Table S1): only conformers with up to 5 gauche torsions were optimized at the BLYP/6-311+G* level. Based on our previous demonstration⁴ of good correlation between relative energies of reactant or transition state conformers at the BLYP and B3LYP levels of the DFT, we only reoptimized at the B3LYP level a subset of BLYP-optimized conformers which are likely to account for >85% in aggregate for the corresponding state at any force. For **7** (reactant) B3LYP reoptimization was performed on a subset of conformers comprising the 100 lowest-energy and 50 longest BLYP geometries (only 11 longest BLYP geometries were not among 100 lowest-energy conformers; by longest we mean a geometry with the longest terminal strain-free C...C distance). For **7** (transition state) 100 lowest-energy and 300 longest conformers, with certain conformers satisfying both requirements. Only B3LYP-reoptimized conformers were scanned and have compliances calculated.

		# rotable bonds	Total number of conformers	Re-optimize at B3LYP/6- level of DFT	ed conform. -311+G(d) -	# of conform. respo 85% of the ensemb force at BLYP/6-311	onsible for le at any L+G* level
				Reactant Transition I		Reactant	Transition state
7		8	3281 ^(a)	111 ^(b)	176 ^(b)	65	99
8		10	11811 ^(c)	278 ^(d)	267 ^(d)	254	249
9		10	11083 ^(c)	597 ^(b)	594 ^(b)	175	140
	Br Br	9	2292 ^(a)	505	420 ^(e)	79	114
	RSRSRSRS,RSRSRSSR,						

Table S1. Statistics on the optimized conformational ensembles.

	# rotable bonds	Total number of conformers	Re-optimize at B3LYP/6- level of DFT	ed conform. -311+G(d) -	# of conform. responsible for 85% of the ensemble at any force at BLYP/6-311+G* level				
RSRSSRRS, RSSRRSSR,									
RSSRSRRS, RSRSSRSR									
enantiomers									

(a) all conformers optimized at the BLYP/6-311+G* level; (b) all conformers with 1 or 0 gauche torsions in the side chains; (c) all conformers with up to 5 gauche torsions were optimized at the BLYP/6-311+G* level; (d) all conformers with 0 or 1 gauche torsions in the side chains + all conformers with both OCCO torsions and both H_3 COCC torsions in gauche configuration; (e) only one of the two central cyclopropane moieties undergoes the isomerization; all other moieties are intact in the transition state.

The statistical mechanics model and the determination of vanishing forces.

Consider a macromolecule constrained by a harmonic potential with equilibrium distance q_c and compliance λ_c acting between a pair of atoms with an equilibrium uncoupled separation of q° . In the harmonic limit, the potential energy of coupled conformer *i*, $U_i(q_c, \lambda_c)$ is given by eq. S1, where λ_i° is the harmonic stretching compliance of the constrained molecular degree of freedom and U_i° is the potential energy of uncoupled conformer *i* relative to that of the uncoupled constraining potential.

$$U_i(q_c, \lambda_c) = U_i^o + \frac{(q_i^o - q_c)^2}{2(\lambda_i^o + \lambda_c)} \qquad eq.S1$$

Conformer *i* will not exist in the coupled system if another conformer *j* exist for which:

$$\begin{pmatrix} \boldsymbol{Q}_{i}^{o} - \boldsymbol{Q}_{j}^{o} - (q_{i}^{o} - q_{c}) \frac{\boldsymbol{H}_{i}^{-1}(:,1)}{\lambda_{c} + \lambda_{i}^{o}} + (q_{j}^{o} - q_{c}) \frac{\boldsymbol{H}_{j}^{-1}(:,1)}{\lambda_{c} + \lambda_{j}^{o}} \end{pmatrix}^{T} \boldsymbol{H}_{j}^{c} \begin{pmatrix} \boldsymbol{Q}_{i}^{o} - \boldsymbol{Q}_{j}^{o} - (q_{i}^{o} - q_{c}) \frac{\boldsymbol{H}_{i}^{-1}(:,1)}{\lambda_{c} + \lambda_{i}^{o}} \\ + (q_{j}^{o} - q_{c}) \frac{\boldsymbol{H}_{j}^{-1}(:,1)}{\lambda_{c} + \lambda_{j}^{o}} \end{pmatrix} + U_{j}^{o} + \frac{1}{2} \frac{(q_{j}^{o} - q_{c})^{2}}{\lambda_{c} + \lambda_{j}^{o}} \leq U_{i}^{o} + \frac{1}{2} \frac{(q_{i}^{o} - q_{c})^{2}}{\lambda_{c} + \lambda_{i}^{o}} \quad eq.S2$$

where \mathbf{Q}_{l}° is a 3N-6 column vector of non-redundant internal coordinates of uncoupled N-atomic conformer *I*, such that $q_{l}^{\circ} \equiv \mathbf{Q}_{l}^{\circ}(1)$; \mathbf{H}_{l} is the Hessian of uncoupled conformer *I* in coordinates \mathbf{Q}_{l} , i.e., $\mathbf{H}_{l}(n,m) = \partial^{2}U_{l}/\partial \mathbf{Q}_{l}^{\circ}(n)\partial \mathbf{Q}_{l}^{\circ}(m)$; \mathbf{H}_{l}^{-1} is its inverse such that $\mathbf{H}_{l}^{-1}(1,1) \equiv \lambda_{l}^{\circ}$; $\mathbf{H}_{l}^{-1}(:,1)$ is a 3N-6 column vector containing the compliance of the constrained degree of freedom and coupling constants of the constrained degree of freedom to the other 3N-7 coordinates of conformer *I*; and \mathbf{H}_{l}° is the Hessian of the coupled system, $\mathbf{H}_{l}^{\circ}(n,m) = \mathbf{H}_{l}(n,m) + \delta_{n,m}\lambda_{c}$ (δ is Kronicker's delta).

If the constraining potential is soft compared to the constrained degree of freedom for all conformers (i.e., $\forall i \lambda_c >> \lambda_i^\circ$),³ eq. S2 can be written in free energies G_i and G_j and constraining force $-f = q_c/\lambda_c$:

$$\left(\boldsymbol{Q}_{i}^{o} - \boldsymbol{Q}_{j}^{o} - f_{v} \left(\boldsymbol{H}_{i}^{-1}(:,1) - \boldsymbol{H}_{j}^{-1}(:,1) \right) \right)^{T} \boldsymbol{H}_{j} \left(\boldsymbol{Q}_{i}^{o} - \boldsymbol{Q}_{j}^{o} - f_{v} \left(\boldsymbol{H}_{i}^{-1}(:,1) - \boldsymbol{H}_{j}^{-1}(:,1) \right) \right)$$

$$= \frac{G_{i}^{o} - G_{j}^{o}}{N_{A}} + f_{v} \left(q_{j}^{o} - q_{i}^{o} \right) + \frac{f_{v}^{2} \left(\lambda_{j}^{o} - \lambda_{i}^{o} \right)}{2} \quad eq.S3$$

where f_v is the lowest force at which conformer *i* vanishes and N_A is the Avogadro number. The left-hand-side of eq. S3 is the difference of molecular strain energies of conformers *i* and *j* coupled to force f_v , and the last two terms in the right-hand-side is the difference of the strain energies of the constraining potential coupled to conformers *i* and *j* and exerting force f_v .

The free energy of a chemical reaction of a coupled system is now:

$$\Delta G^{\ddagger}(f) = -RT ln \left[\sum_{i(f_{v} > f)} e^{-\frac{\left(G_{i}^{o} - N_{A}f\left[q_{i}^{o} + \frac{f\lambda_{i}^{o}}{2}\right]\right)_{ts}}{RT}} - \sum_{j(f_{v} > f)} e^{-\frac{\left(G_{j}^{o} - N_{A}f\left[q_{j}^{o} + \frac{f\lambda_{j}^{o}}{2}\right]\right)_{gs}}{RT}} \right] eq. 2$$

where $i(f_v > f)$ indicates summation over only conformational minima whose vanishing force exceeds constraining force f and ()_{ts} and ()_{gs} signify transition-state and ground-state conformational ensembles.

Eq. 2, which is copied from the main text, is exact within the harmonic oscillator approximation. It can be used only if vanishing forces are known for the conformers comprising the two kinetically significant states. Brute-force solution of eq. S3 to obtain vanishing forces is impractical because of the size of **Q** and **H** and the number of coupled equations. However, since only a small fraction of the 3N-6 molecular degrees of freedom that define the strain-free geometry deform at forces of interest in this work, both matrices can be reduced considerably by eliminating coordinates that define the positions of H atoms, the C-C distances and the dimensions of the reactive site which are distorted only negligibly at forces below 1.5 nN. This procedure allowed us to reduce **Q** to vector of size 28 (**7**), 32 (**8**), 40 (**9**) and 33 (**10**) and **H** to a symmetrical square matrix of the same number of columns and rows.

We then calculated for a set of forces [10, 50:50:1500] pN (see below) $X^2/2-X$ (where X is the number of conformers comprising the state) pairwise differences of the molecular strain energies (lhs of eq. S3) and the same number of the rhs values. Pairwise combinations of conformers for which the two corresponding parameters were within 10% of each other were assumed to satisfy eq. S3. The positive sum of the lhs and rhs of eq. S3 for such a pair of conformers means that conformer *i* (as defined in eq. S3) is unstable above force f_v ; otherwise, conformer *j* is unstable. When eq. S3 for a single conformer could be satisfied for different values of f_v (because the conformer is unstable with respect to rearranging to multiple conformers), the smallest f_v was used as the vanishing force for such conformer. Depending on the compound, no solutions for eq. S3 could be found for between 1 and 17 conformers up to $f_v = 1.5$ nN. Because of increasingly important anharmonicity of the constrained distances, forces above 1.5 nN were not used. There's a reasonably good agreement between f_v found from eq. S3 and those obtained from relaxed potential energy scans as described previously (Fig. S1).

A simpler way of estimating f_v is to use what appears to be a general relationship between f_v and the strain-free terminal C...C distance, q° : $f_v \sim 500/(q^\circ_{max}-q^\circ)$, where f_v is in pN and q° is in Å (Fig. S2). We do not know the significance of the numerator nor how general this fit is.

The force-energy correlations shown in Figure 1 (main text), blue line, were obtained using f_v values from direct quantum-chemical computations of the conformational ensembles coupled to stretching force, to be consistent with the reference data (black line). Using f_v values derived from the approximation solution of eq. S3 approximately triples the error at 1 nN but has only negligible effects at forces above ~1.2 nN, where only very few (1 – 10) conformers comprise the ensembles; f_v values from the empirical f_v vs. q_o correlations (Fig. S2) approximately doubles the errors further. Yet, even with these increased errors, the statistical-mechanical model (eq. 2) remains by far the most accurate of all considered by us.

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Figure S1. Comparison of the vanishing forces obtained from quantum-chemical calculations of conformational ensembles coupled to the stretching force (x axis) and those obtained from solution of eq. S3. Solid lines are linear least-squares fits with the equation and the residuals shown. Results are at the B3LYP/6311+G* level of DFT in the gas phase.

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Figure S2. Correlation between the vanishing force of a conformer and its strain-free terminal C...C separation, q° obtained from quantumchemical calculations of the conformational ensembles coupled to a stretching force (blue points) and the equation $f_v = 500/(q^{\circ}_{max} - q^{\circ})$ (red line). The values of q°_{max} are listed in Table 1 (main text). The data are at the B3LYP/6311+G* level of DFT in the gas phase.

Force	Quantu	ım-chen	nical solu	ution	$\Delta G^{*}(f) = \Delta$	$\Delta G^{*\circ} - f \Delta q^{\circ}_{ }$	minimal n	nodel)	$\Delta G^{\dagger}(f) =$	$= \Delta G^{*0} - f\Delta$	Δq°_{max}		$\Delta G^{*}(f) =$	$\Delta G^{i0} - f\langle$	$\Delta q^{\circ} \rangle$		Eq. 1 (T	aylor-exp	ansion)		Eq. 2 (statistical me		al mecha	anics)
рN	7	8	9	10	7	8	9	10	7	8	9	10	7	8	9	10	7	8	9	10	7	8	9	10
0	29.3	29.8	30.3	32.2	29.3	29.8	30.3	32.2	29.3	29.8	30.3	32.2	29.3	29.8	30.3	32.2	29.3	29.8	30.3	32.2	29.3	29.8	30.3	32.2
10	29.2	29.8	30.2	32.4	29.2	29.7	30.2	32.0	29.3	29.9	30.4	32.0	29.3	29.9	30.3	32.3	29.3	29.9	30.4	32.0	29.2	30.2	30.8	32.0
25	29.2	29.7	30.1	32.5	29.0	29.5	30.0	31.7	29.2	30.0	30.5	31.7	29.3	30.0	30.4	32.5	29.2	30.0	30.5	31.7	29.1	30.5	30.6	31.7
50	29.1	29.7	30.0	32.3	28.7	29.2	29.7	31.2	29.1	30.2	30.7	31.3	29.3	30.3	30.5	32.7	29.1	30.2	30.7	31.3	29.0	30.4	30.2	31.3
75	29.0	29.8	29.7	31.9	28.5	29.0	29.5	30.7	29.0	30.4	30.9	30.8	29.2	30.5	30.6	33.0	28.9	30.3	30.8	30.9	28.9	30.3	29.9	30.9
100	28.9	29.9	29.6	31.6	28.2	28.7	29.2	30.2	28.9	30.5	31.1	30.4	29.2	30.7	30.6	33.2	28.8	30.4	30.9	30.4	28.8	30.1	29.7	30.4
125	28.7	30.0	29.5	31.3	27.9	28.4	28.9	29.7	28.8	30.7	31.3	29.9	29.2	31.0	30.7	33.5	28.7	30.6	31.1	30.0	28.6	29.8	29.5	30.0
150	28.5	30.0	29.3	30.9	27.6	28.1	28.6	29.2	28.7	30.9	31.5	29.4	29.2	31.2	30.8	33.8	28.5	30.7	31.1	29.6	28.3	29.7	29.2	29.6
200	28.0	30.1	29.0	30.2	27.0	27.5	28.0	28.2	28.4	31.3	31.9	28.5	29.1	31.7	31.0	34.3	28.2	30.9	31.3	28.8	28.0	29.6	28.8	28.9
250	27.6	30.1	28.7	29.5	26.5	27.0	27.5	27.2	28.2	31.7	32.2	27.6	29.1	32.2	31.2	34.8	27.9	31.0	31.4	28.0	27.7	29.4	28.3	28.1
300	27.1	29.9	28.2	28.6	25.9	26.4	26.9	26.2	28.0	32.0	32.6	26.7	29.0	32.6	31.3	35.3	27.6	31.1	31.4	27.2	27.1	29.2	27.9	27.5
350	26.6	29.6	27.8	27.7	25.4	25.9	26.4	25.2	27.8	32.4	33.0	25.8	29.0	33.1	31.5	35.9	27.2	31.1	31.3	26.5	26.7	29.0	27.4	26.9
400	26.1	29.3	27.3	26.8	24.8	25.3	25.8	24.1	27.6	32.8	33.4	24.8	28.9	33.6	31.7	36.4	26.8	31.1	31.1	25.8	26.2	28.7	27.0	26.0
450	25.6	28.9	26.8	25.8	24.2	24.7	25.2	23.1	27.4	33.1	33.8	23.9	28.9	34.0	31.8	36.9	26.4	31.0	30.9	25.1	25.5	28.3	26.5	25.3
500	25.1	28.4	26.4	24.8	23.7	24.2	24.7	22.1	27.2	33.5	34.2	23.0	28.8	34.5	32.0	37.4	26.0	30.9	30.6	24.5	25.0	28.0	26.0	24.7
550	24.6	28.0	26.0	23.9	23.1	23.6	24.1	21.1	26.9	33.9	34.6	22.1	28.8	35.0	32.2	37.9	25.6	30.7	30.3	23.8	24.3	27.6	25.6	24.0
600	24.1	27.5	25.6	23.0	22.5	23.0	23.5	20.1	26.7	34.3	35.0	21.1	28.7	35.5	32.4	38.5	25.1	30.4	29.8	23.3	23.7	27.2	25.1	23.3
650	23.6	27.0	25.2	22.0	22.0	22.5	23.0	19.1	26.5	34.6	35.4	20.2	28.7	35.9	32.5	39.0	24.7	30.1	29.3	22.7	23.2	26.8	24.6	22.5
700	23.1	26.5	24.8	21.1	21.4	21.9	22.4	18.1	26.3	35.0	35.7	19.3	28.6	36.4	32.7	39.5	24.2	29.8	28.7	22.2	22.6	26.4	24.2	21.8
750	22.6	26.0	24.3	20.3	20.8	21.3	21.8	17.1	26.1	35.4	36.1	18.4	28.6	36.9	32.9	40.0	23.7	29.4	28.1	21.7	22.1	26.0	23.7	21.0
800	22.1	25.5	23.9	19.5	20.3	20.8	21.3	16.1	25.9	35.7	36.5	17.5	28.5	37.3	33.0	40.5	23.1	28.9	27.4	21.2	21.5	25.6	23.3	20.3
850	21.6	25.0	23.4	18.8	19.7	20.2	20.7	15.1	25.7	36.1	36.9	16.5	28.5	37.8	33.2	41.1	22.6	28.4	26.6	20.8	21.0	25.2	22.8	19.7
900	21.1	24.5	23.0	18.2	19.1	19.6	20.1	14.1	25.4	36.5	37.3	15.6	28.4	38.3	33.4	41.6	22.0	27.8	25.7	20.4	20.5	24.8	22.3	19.2
950	20.6	24.0	22.5	17.6	18.6	19.1	19.6	13.1	25.2	36.9	37.7	14.7	28.4	38.8	33.6	42.1	21.4	27.2	24.8	20.0	19.9	24.5	21.9	18.6
1000	20.2	23.5	22.0	17.0	18.0	18.5	19.0	12.1	25.0	37.2	38.1	13.8	28.3	39.2	33.7	42.6	20.8	26.6	23.8	19.6	19.4	24.1	21.4	18.1
1050	19.7	22.9	21.5	16.5	17.5	18.0	18.5	11.1	24.8	37.6	38.5	12.9	28.3	39.7	33.9	43.2	20.2	25.8	22.7	19.3	19.0	23.8	21.0	17.7
1100	19.2	22.4	21.0	16.0	16.9	17.4	17.9	10.0	24.6	38.0	38.9	11.9	28.2	40.2	34.1	43.7	19.5	25.1	21.6	19.0	18.5	23.5	20.3	17.2
1150	18.8	21.9	20.5	15.5	16.3	16.8	17.3	9.0	24.4	38.3	39.2	11.0	28.2	40.6	34.2	44.2	18.9	24.2	20.3	18.8	18.0	23.0	19.7	16.8
1200	18.3	21.4	19.9	15.0	15.8	16.3	16.8	8.0	24.2	38.7	39.6	10.1	28.2	41.1	34.4	44.7	18.2	23.3	19.1	18.5	17.5	22.5	19.0	16.4
1250	17.8	20.9	19.4	14.5	15.2	15.7	16.2	7.0	23.9	39.1	40.0	9.2	28.1	41.6	34.6	45.2	17.5	22.4	17.7	18.3	17.0	21.9	18.3	16.0
1300	17.4	20.4	18.9	14.0	14.6	15.1	15.6	6.0	23.7	39.5	40.4	8.2	28.1	42.1	34.8	45.8	16.7	21.4	16.3	18.1	16.5	21.4	17.6	15.6
1350	16.9	19.9	18.3	13.6	14.1	14.6	15.1	5.0	23.5	39.8	40.8	7.3	28.0	42.5	34.9	46.3	16.0	20.4	14.8	18.0	15.9	20.6	16.8	15.0
1400	16.4	19.4	17.8	13.1	13.5	14.0	14.5	4.0	23.3	40.2	41.2	6.4	28.0	43.0	35.1	46.8	15.2	19.3	13.2	17.9	15.3	19.5	16.0	14.5
1450	15.9	18.9	17.3	12.6	12.9	13.4	13.9	3.0	23.1	40.6	41.6	5.5	27.9	43.5	35.3	47.3	14.5	18.1	11.5	17.8	14.5	18.4	15.2	14.0
1500	15.4	18.4	16.7	12.1	12.4	12.9	13.4	2.0	22.9	40.9	42.0	4.6	27.9	43.9	35.4	47.8	13.7	16.9	9.8	17.7	13.8	17.1	14.0	13.4

Table S2. Free energies of activation of isomerization (in kcal/mol at 298 K) of molecules **7-10** in stretched polymers from full quantum-chemical calculations of constrained conformational ensembles (from refs. ⁴ and ⁵, both at the B3LYP/6-311+G* level of DFT) and chemomechanical models.

Table S3 Contributions of the strain energy of the constraining potential and the molecular segment to the force-induced changes in the activation free energy of compounds **7-10** coupled to a stretching force from complete quantum-chemical calculations of constrained ensembles up to 1.5 nN. All values are in kcal/mol at 298 K. The data are at the B3LYP/6311+G* level of DFT in the gas phase.

$\Delta G^{\dagger 0}$	$-\Delta G^{\dagger}(f)$			strain en	ergy of co	nstraining	molecular strain energy					
7	8	9	10	7	8	9	10	7	8	9	10	
0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.02	-0.01	0.03	0.00	
0.1	0.0	0.1	-0.2	0.1	0.0	0.0	-0.1	-0.01	0.00	0.16	-0.16	
0.1	0.1	0.2	-0.3	0.3	0.1	0.1	0.0	-0.18	0.01	0.14	-0.22	
0.2	0.1	0.3	-0.1	0.4	-0.1	0.4	0.2	-0.28	0.17	-0.11	-0.28	
0.3	0.0	0.6	0.3	0.6	-0.2	0.6	0.6	-0.32	0.23	0.00	-0.28	
0.4	-0.1	0.7	0.6	0.8	-0.3	0.7	1.0	-0.34	0.20	0.06	-0.43	
0.6	-0.2	0.8	0.9	1.0	-0.3	0.8	1.6	-0.37	0.11	-0.04	-0.71	
0.8	-0.2	1.0	1.3	1.3	-0.2	1.0	2.1	-0.50	-0.03	0.03	-0.73	
1.3	-0.3	1.3	2.0	1.9	0.1	1.5	3.0	-0.64	-0.38	-0.27	-0.96	
1.7	-0.3	1.6	2.7	2.5	0.6	2.0	3.7	-0.80	-0.88	-0.39	-1.03	
2.2	-0.1	2.1	3.6	3.1	1.4	2.5	4.7	-0.91	-1.46	-0.39	-1.06	
2.7	0.2	2.5	4.5	3.7	2.3	2.8	5.6	-0.97	-2.08	-0.28	-1.13	
3.2	0.5	3.0	5.4	4.2	3.1	3.4	6.6	-1.00	-2.63	-0.39	-1.17	
3.7	0.9	3.5	6.4	4.7	4.0	3.9	7.6	-1.02	-3.05	-0.46	-1.18	
4.2	1.4	3.9	7.4	5.2	4.7	4.4	8.5	-1.03	-3.33	-0.53	-1.12	
4.7	1.8	4.3	8.3	5.7	5.4	4.9	9.3	-1.02	-3.52	-0.65	-0.97	
5.2	2.3	4.7	9.2	6.2	6.0	5.4	10.0	-0.96	-3.62	-0.73	-0.72	
5.7	2.8	5.1	10.2	6.7	6.5	5.9	10.6	-0.94	-3.72	-0.79	-0.40	
6.2	3.3	5.5	11.1	7.1	7.1	6.4	11.1	-0.91	-3.83	-0.87	-0.04	
6.7	3.8	6.0	11.9	7.6	7.7	6.9	11.5	-0.88	-3.90	-0.93	0.36	
7.2	4.3	6.4	12.7	8.1	8.2	7.4	12.0	-0.87	-3.96	-0.96	0.70	
7.7	4.8	6.9	13.4	8.5	8.8	7.7	12.4	-0.80	-3.96	-0.82	1.02	
8.2	5.3	7.3	14.0	8.9	9.3	8.4	12.7	-0.74	-3.95	-1.10	1.35	
8.7	5.8	7.8	14.6	9.4	9.8	9.0	13.0	-0.73	-3.98	-1.13	1.65	
9.1	6.3	8.3	15.2	9.8	10.3	9.5	13.2	-0.70	-4.00	-1.17	1.95	
9.6	6.9	8.8	15.7	10.2	10.9	10.0	13.4	-0.62	-4.00	-1.22	2.27	
10.1	7.4	9.3	16.2	10.6	11.3	10.5	13.6	-0.55	-3.97	-1.27	2.57	
10.5	7.9	9.8	16.7	11.1	11.8	11.2	13.8	-0.52	-3.94	-1.34	2.87	
11.0	8.4	10.4	17.2	11.4	12.3	11.6	14.0	-0.38	-3.91	-1.21	3.17	
11.5	8.9	10.9	17.7	11.8	12.7	12.0	14.2	-0.31	-3.87	-1.06	3.47	
11.9	9.4	11.4	18.2	12.2	13.2	12.4	14.4	-0.30	-3.80	-0.95	3.75	
12.4	9.9	12.0	18.6	12.6	13.7	12.8	14.6	-0.19	-3.73	-0.78	4.04	
12.9	10.4	12.5	19.1	12.9	14.1	13.2	14.8	0.00	-3.67	-0.63	4.31	
13.4	10.9	13.0	19.6	13.3	14.5	13.5	15.1	0.10	-3.62	-0.47	4.56	
13.9	11.4	13.6	20.1	13.7	15.0	13.9	15.3	0.18	-3.53	-0.25	4.80	

Table S4. Terminal C...C distances in compounds 7-10 coupled to stretching force. The conformers of 8 and 9 with the longest strain-free terminal C...C distance do not exist above stretching force of 750 and 650 pN, respectively. The data are at the B3LYP/6311+G* level of DFT in the gas phase.

Force	Ensemble-average terminal CC distances, A								Terminal CC distances in longest strain-free conformers, A							
рN	Reactant Transition state								Reactant Transition state							
	7	8	9	10	7	8	9	10	7	8	9	10	7	8	9	10
0	11.01	11.56	9.91	16.33	11.07	10.90	9.67	15.60	13.82	15.53	20.25	17.35	14.14	15.01	19.71	18.64
10	12.02	12.59	13.74	16.37	12.57	12.84	13.59	16.00	13.85	15.53	20.36	17.36	14.24	15.04	20.08	18.64
25	12.62	13.59	18.05	16.43	13.34	13.76	18.22	16.30	13.89	15.54	20.46	17.39	14.42	15.09	20.16	18.66
50	13.19	14.63	18.96	16.54	13.81	14.47	19.58	16.80	13.92	15.56	20.54	17.42	14.59	15.15	20.26	18.68
75	13.48	15.08	19.56	16.65	14.04	14.85	20.09	17.20	13.96	15.57	20.58	17.46	14.67	15.21	20.32	18.71
100	13.68	15.30	19.96	16.78	14.22	15.09	20.42	17.50	13.99	15.59	20.61	17.50	14.74	15.27	20.37	18.73
125	13.81	15.41	20.21	16.90	14.37	15.26	20.68	17.80	14.03	15.60	20.64	17.53	14.78	15.31	20.41	18.75
150	13.91	15.48	20.38	17.02	14.52	15.39	20.83	17.98	14.06	15.61	20.65	17.57	14.80	15.36	20.45	18.77
200	14.03	15.57	20.50	17.21	14.70	15.61	21.03	18.26	14.10	15.63	20.68	17.64	14.86	15.44	20.52	18.81
250	14.10	15.62	20.58	17.36	14.81	15.80	21.20	18.40	14.14	15.65	20.71	17.71	14.89	15.51	20.60	18.85
300	14.15	15.65	20.73	17.47	14.88	15.97	21.28	18.56	14.17	15.66	20.74	17.79	14.92	15.57	20.67	18.89
350	14.19	15.68	20.76	17.56	14.93	16.13	21.33	18.68	14.20	15.68	20.76	17.86	14.95	15.64	20.75	18.94
400	14.22	15.70	20.79	17.64	14.96	16.25	21.38	18.80	14.22	15.70	20.79	17.94	14.97	15.70	20.82	18.98
450	14.25	15.72	20.81	17.72	14.98	16.33	21.42	18.90	14.25	15.72	20.81	18.01	14.99	15.75	20.89	19.03
500	14.27	15.73	20.83	17.79	15.00	16.39	21.45	18.98	14.27	15.74	20.83	18.09	15.01	15.80	20.96	19.07
550	14.30	15.75	20.85	17.86	15.02	16.43	21.48	19.04	14.30	15.75	20.85	18.16	15.02	15.85	21.03	19.12
600	14.32	15.77	20.88	17.93	15.04	16.47	21.51	19.09	14.32	15.77	20.88	18.24	15.04	15.90	21.11	19.17
650	14.34	15.79	20.90	18.00	15.06	16.49	21.53	19.14	14.34	15.79	20.90	18.32	15.06	15.95	21.22	19.23
700	14.36	15.81	20.92	18.07	15.07	16.52	21.56	19.18	14.36	15.81	20.92	18.39	15.07	16.01		19.29
750	14.38	15.82	20.94	18.14	15.09	16.54	21.59	19.22	14.38	15.82	20.94	18.47	15.09	16.06		19.36
800	14.40	15.84	20.96	18.21	15.11	16.56	21.61	19.26	14.40	15.84	20.96	18.55	15.11			19.43
850	14.42	15.86	20.98	18.28	15.12	16.58	21.62	19.30	14.42	15.86	20.98	18.62	15.12			19.49
900	14.44	15.88	21.01	18.35	15.14	16.60	21.66	19.34	14.44	15.88	21.01	18.70	15.14			19.56
950	14.46	15.89	21.03	18.42	15.15	16.62	21.69	19.38	14.46	15.89	21.03	18.78	15.15			19.62
1000	14.48	15.91	21.05	18.49	15.17	16.63	21.71	19.42	14.48	15.91	21.05	18.85	15.17			19.68
1050	14.50	15.93	21.07	18.56	15.18	16.65	21.74	19.46	14.50	15.93	21.07	18.93	15.18			19.74
1100	14.52	15.94	21.09	18.63	15.20	16.66	21.77	19.50	14.52	15.94	21.09	19.00	15.20			19.81
1150	14.54	15.96	21.12	18.70	15.21	16.68	21.80	19.54	14.54	15.96	21.12	19.08	15.21			19.88
1200	14.56	15.98	21.14	18.77	15.22	16.69	21.81	19.59	14.56	15.98	21.14	19.16	15.22			19.95
1250	14.58	15.99	21.16	18.84	15.24	16.71	21.83	19.64	14.58	15.99	21.16	19.23	15.24			20.02
1300	14.60	16.01	21.18	18.91	15.25	16.72	21.85	19.69	14.60	16.01	21.18	19.31	15.25			20.08
1350	14.61	16.03	21.20	18.98	15.27	16.74	21.87	19.73	14.61	16.03	21.20	19.38	15.27			20.19
1400	14.64	16.05	21.23	19.05	15.28	16.75	21.88	19.79	14.64	16.05	21.23	19.45	15.28			20.31
1450	14.65	16.06	21.25	19.11	15.30	16.77	21.90	19.84	14.65	16.06	21.25	19.53	15.30			20.43
1500	14.67	16.08	21.27	19.18	15.31	16.78	21.92	19.89	14.67	16.08	21.27	19.60	15.31			20.59

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