Electronic supplementary information

Ring opening vs direct bond scission of the chain in polymeric triazoles under the influence of an external force[†]

Hans S. Smalø, [a] **and Einar Uggerud**[*a]

1 Theory

The most important parameter in controlling reaction rate is the critical energy $E^{\ddagger}$ which is defined as

$$E^{\ddagger} = E^{TS} - E^{IS} \tag{1}$$

where E^{TS} is the energy of the transition state and E^{IS} is the energy of the initial state. Within the Born Oppenheimer approximation, the energy is viewed as a function of the coordinates of the different nuclei that constitute the molecule, $E(X_i)$. If an external force F is applied to the molecule, a force-modified potential energy may be written as [1]

$$E^{F} = E(X_i) - lF \tag{2}$$

where l is the length of the molecule in the direction of the force, which can be applied both for the initial and transition state.

Further, in an external force both the initial structure, given by X_i^{IS} and the transition state geometry, given by X_i^{TS} is modified, such that

$$X_i^{TS} \rightarrow X_i^{TS} + \Delta_i^{TS} \tag{3}$$
$$X_i^{IS} \rightarrow X_i^{IS} + \Delta_i^{IS} \tag{4}$$

where the displacements Δ_i^{TS} and Δ_i^{IS} represent how the force modifies the geometry of the transition and initial state, respectively. Then the force modified critical energy $E^{\ddagger}$ can be written as

$$\begin{aligned} E^{\ddagger} &= E^{F}(X_i^{TS} + \Delta_i^{TS}) - E^{F}(X_i^{IS} + \Delta_i^{IS}) \\ &= E(X_i^{TS} + \Delta_I^{TS}) - E(X_i^{IS} + \Delta_i^{IS}) - (l^{TS} - l^{IS})F \end{aligned} \tag{5}$$

where l^{TS} and l^{IS} are the distances between the two nuclei to which the force is directed, for the transition state and the equilibrium geometry, respectively. Since the geometry of both the transition state and the initial state is dependent on the applied force, so is l^{TS} and l^{IS}.

By stretching a molecule by its ends with an increasingly strong force, it will reach a point where the weakest bond will break spontaneously. The corresponding force is denoted the critical force F^{crit} and the geometry is denoted the bond-breaking point. By stretching the molecule further, the force required to obtain equilibrium decreases, such that

$$\frac{\partial F}{\partial l} < 0 \tag{6}$$

Thus, beyond the critical point, this may be viewed as a transition state for a given external force F.

2   Computational details and results

Quantum chemical calculations were done using the program system GAUSSIAN 09. Complete optimisation of the molecular geometries was done using the hybrid density functional scheme B3LYP with the 6-31++G(d,p) basis set, B3LYP/6-31++G(d,p). All stationary points were subject to complete geometry optimisation, including a check for the correct number of negative Hessian eigenvalues and imaginary vibrational frequencies. Transition state geometries were carefully checked to ensure they connect the actual minimum energy structures. IRC calculations were performed for the TSes assuring that extrapolation in the forward and the backward directions, respectively, leads to geometries that upon minimization give the indicated minima. In addition, the vibrational motion of the reaction coordinate at the TS was checked for consistency. To obtain more accurate estimates for the energies, G4 theory calculations were done. G4 is a composite technique, which involves geometry optimisations and frequency calculations at rather moderate levels of theory, but with a scheme for extrapolating the energy to essentially include both the qualities of a large atomic basis set and dynamic electron correlation to the CCSD(T) level. G4 employs B3LYP /6-31G(2df,p) for geometry optimisation and frequency calculations.

Table S1 Energetics of the ring opening reaction, Scheme (1) with $R_1 =R_2 =CH_3$, in kJ/mol.

	$E^{\ddagger}$	ΔE_{rxn}
B3LYP (electronic only)	356	264
G4 (electronic only)	382	246
G4 Energy (0K)	355	268
G4 Energy (T=298K)	337	272
G4 Free Energy (T=298K)	354	220

Table S2 Dependence of the critical energy (Scheme 1) on alkyl substitution and medium, in kJ/mol

Method and molecule	$E^{\ddagger}$
B3LYP ($R_1 =R_2 =CH_3$)	356
B3LYP ($R_1 =R_2 =C_2H_5$)	358
PCM B3LYP(($R_1 =R_2 =CH_3$)	372

Table S3 The lowest frequencies (in cm^{-1}) for the transition state of the ring opening (Scheme 1).

Nr	TS for Scheme 1 with $R_1=R_2=CH_3$	TS for Scheme 1 with $R_1=R_2=C_2H_5$
1	439.3i	439.0i
2	59.9	36.9
3	110.2	65.5

References

[1] J. Ribas-Arino, M. Shiga and D. Marx, *Angew. Chem. Int. Ed.*, 2009, **48**, 4190–4193.

Table S4 Cartesian coordinates (Å) of the reactant of Scheme 1, with $R_1=R_2=CH_3$

C	−3.197429	−0.129521	−4.634145
H	−4.231498	−0.423416	−4.702940
C	−2.370582	0.121168	−3.560795
C	−2.756255	−0.043081	−7.135217
H	−1.860086	0.201754	−7.702079
H	−3.068616	−1.062452	−7.370323
H	−3.554402	0.654418	−7.396789
C	−2.649312	0.064834	−2.094236
H	−3.684269	−0.224647	−1.902352
H	−1.993964	−0.658325	−1.601857
H	−2.473090	1.037593	−1.627814
N	−1.173941	0.432358	−5.355020
N	−1.143699	0.460984	−4.053648
N	−2.417719	0.074414	−5.727189

Table S5 Cartesian coordinates (Å) of the reactant of Scheme 1, with $R_1=R_2=C_2H_5$

C	−3.222017	−0.019749	−4.582575
H	−4.282130	−0.210585	−4.597815
C	−2.327441	0.178372	−3.552748
C	−2.883232	−0.077345	−7.108269
H	−2.150467	0.473249	−7.698930
H	−3.853307	0.408905	−7.236392
C	−2.538266	0.171229	−2.069815
H	−3.610712	0.233201	−1.861028
H	−2.083203	1.073976	−1.650445
N	−1.192285	0.337120	−5.407089
N	−1.098892	0.392175	−4.108807
N	−2.479521	0.090516	−5.714558
C	−2.939335	−1.543170	−7.537458
H	−3.222639	−1.610240	−8.591091
H	−1.963659	−2.016693	−7.412020
H	−3.673180	−2.102284	−6.951983
C	−1.940939	−1.066247	−1.380123
H	−2.090313	−1.016595	−0.298004
H	−2.408576	−1.984542	−1.746218
H	−0.868557	−1.133781	−1.575043

3

Table S6 Cartesian coordinates (Å) of the transition state for Scheme 1, with $R_1=R_2=CH_3$

C	0.419016	−0.315275	0.159301
H	0.334190	−0.529767	1.198014
C	0.901052	−0.106825	−0.956243
C	−2.869390	0.095439	0.638159
H	−3.802001	−0.370214	0.306159
H	−2.668798	−0.239602	1.655914
H	−2.987279	1.184226	0.641034
C	1.943134	0.089450	−1.974981
H	2.939852	0.010987	−1.533313
H	1.852349	−0.655780	−2.768723
H	1.843189	1.071975	−2.442297
N	−1.673189	−0.015361	−1.387568
N	−0.846670	0.121331	−2.200150
N	−1.736836	−0.340564	−0.174330

Table S7 Cartesian coordinates (Å) of the transition state for Scheme 1, with $R_1=R_2=C_2H_5$

C	0.442545	−0.347362	0.089278
H	0.399499	−0.626138	1.114307
C	0.868701	−0.082684	−1.038542
C	−2.857973	0.178328	0.728111
H	−3.805111	−0.133618	0.275743
H	−2.875474	1.271174	0.821695
C	1.890142	0.112353	−2.087996
H	2.861761	0.259405	−1.604514
H	1.663661	1.028639	−2.640325
N	−1.704996	0.149761	−1.331687
N	−0.894909	0.293836	−2.162295
N	−1.746015	−0.240859	−0.138537
C	1.971497	−1.068132	−3.069572
H	2.744287	−0.88074	−3.81972
H	2.219176	−1.994733	−2.54631
H	1.01882	−1.209239	−3.583022
C	−2.699289	−0.468163	2.098878
H	−3.538609	−0.190212	2.740511
H	−2.675312	−1.557093	2.01535

Table S8 Cartesian coordinates (Å) of product 1 of Scheme 1, with $R_1=R_2=CH_3$

C	−1.547572	0.282099	0.000022
H	−1.560023	0.915837	−0.892721
H	−2.436286	−0.344579	−0.000485
H	−1.560582	0.915202	0.893224
N	0.717707	−0.096323	−0.000564
N	1.792002	0.271487	0.000303
N	−0.389377	−0.629315	0.000239

4

Table S9 Cartesian coordinates (Å) of product 2 of Scheme 1, with $R_1=R_2=CH_3$

C	0.548578	−0.336326	0.227541
H	−0.01974	−0.506771	1.108738
C	1.191603	−0.143372	−0.769848
C	1.971248	0.090729	−1.978148
H	3.043012	0.056323	−1.764289
H	1.754081	−0.666775	−2.736179
H	1.743999	1.070956	−2.406057

Table S10 Cartesian coordinates (Å) of product 1 of Scheme 1, with $R_1=R_2=C_2H_5$

N	−1.665937	0.135199	−5.195755
N	−0.678766	0.04044	−4.64156
N	−2.788614	0.286137	−5.671307
C	−2.930659	0.001012	−7.12083
H	−2.182173	0.571234	−7.683493
H	−3.911903	0.394102	−7.384897
C	−2.840743	−1.487345	−7.4499
H	−2.999772	−1.642846	−8.520686
H	−1.858426	−1.894236	−7.194871
H	−3.599523	−2.051462	−6.903298

Table S11 Cartesian coordinates (Å) of product 2 of Scheme 1, with $R_1=R_2=C_2H_5$

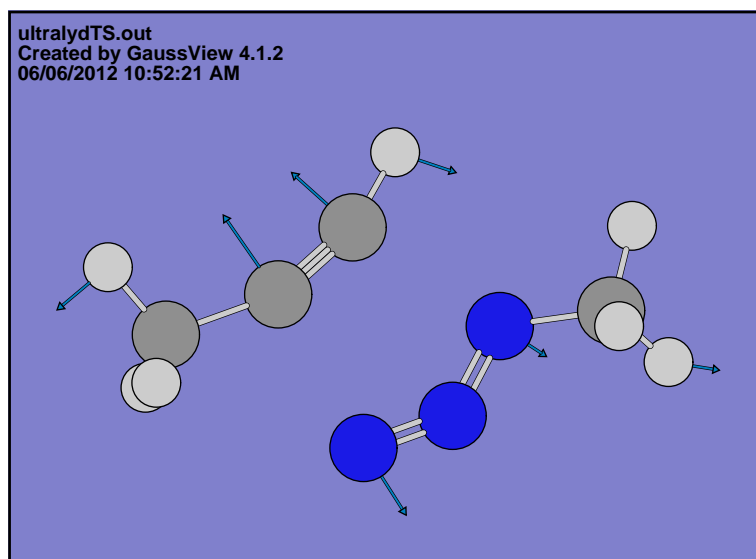|			
C	−3.35237	−0.041654	−4.462956
H	−3.624916	−0.124135	−5.486382
C	−3.050513	0.051209	−3.30222
C	−2.670244	0.160776	−1.896154
H	−3.573268	0.315439	−1.295101
H	−2.058478	1.060272	−1.765436
C	−1.904476	−1.068757	−1.375335
H	−1.644638	−0.934307	−0.322341
H	−2.51067	−1.972442	−1.467352
H	−0.982581	−1.221122	−1.940535

Figure S1 Visualization of the imaginary vibrational mode, TS for Scheme 1 with $R_1=R_2=CH_3$
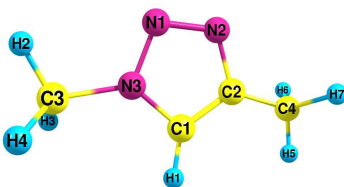

Figure S2 1,4-dimethyl-1,2,3-triazole
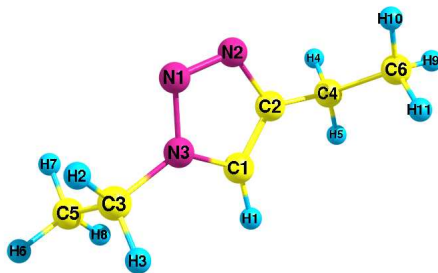

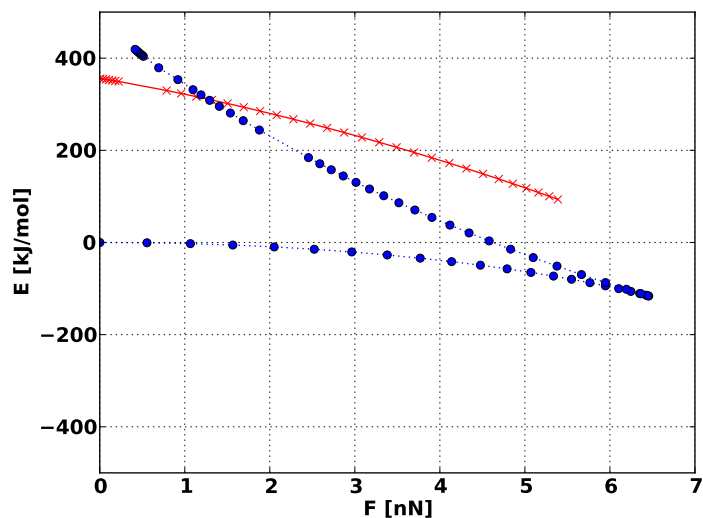**Figure S3** 1,4-diethyl-1,2,3-triazole

Figure S4 Force modified potential energy (Eq 2) for $R_1 = R_2 = CH_3$ with $\times$ being the transition state as a function of applied force and $\circ$ the stretched initial state. When stretching the initial state, a critical point is reached where the *weakest* bond automaticly breaks, and when stretching the initial state further, the force will be reduced. Thus for the initial state there are two sets of data, one before and one after the critical point.
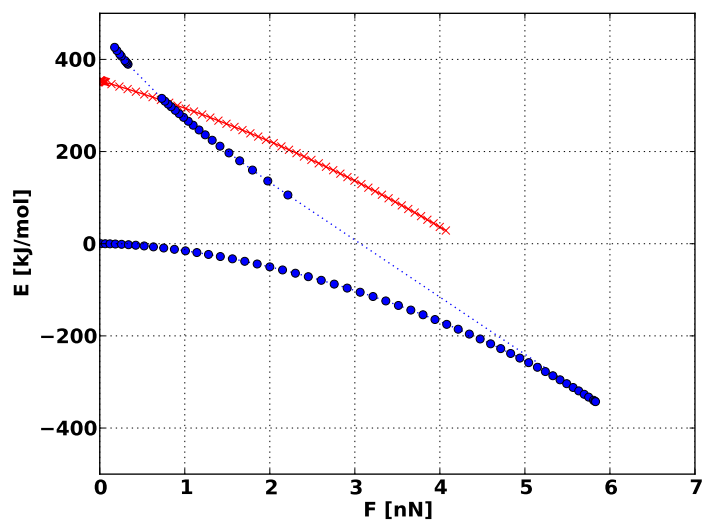

Figure S5 Force modified potential energy (Eq 2) for $(R_1 = R_2 = C_2H_5)$ with $\times$ being the transition state as a function of applied force and $\circ$ the stretched initial state. When stretching the initial state, a critical point is reached where the *weakest* bond automaticly breaks, and when stretching the initial state further, the force will be reduced. Thus for the initial state there are two sets of data, one before and one after the critical point.