Predicting impact sensitivities for an extended set of energetic materials via the vibrational up-pumping model: molecular-based structure-property relationships identified

Jack M. Hemingway,[1] Heather M. Quayle,[1] Cian Byrne,[1] Colin R. Pulham[1], Subrata Mondal,[2] Adam A. L. Michalchuk,[3,*] and Carole A. Morrison[1,*]

[1]EaStCHEM School of Chemistry and Centre for Science at Extreme Conditions, The University of Edinburgh, King's Buildings, David Brewster Road, Edinburgh EH9 3FJ, U.K.

[2]Federal institute for Materials Research and Testing (BAM), Richard-Wilstaetter-Str 11, Berlin, Germany, 12489

[3]School of Chemistry, University of Birmingham, Edgebaston, Birmingham, B15 2TT, U.K.

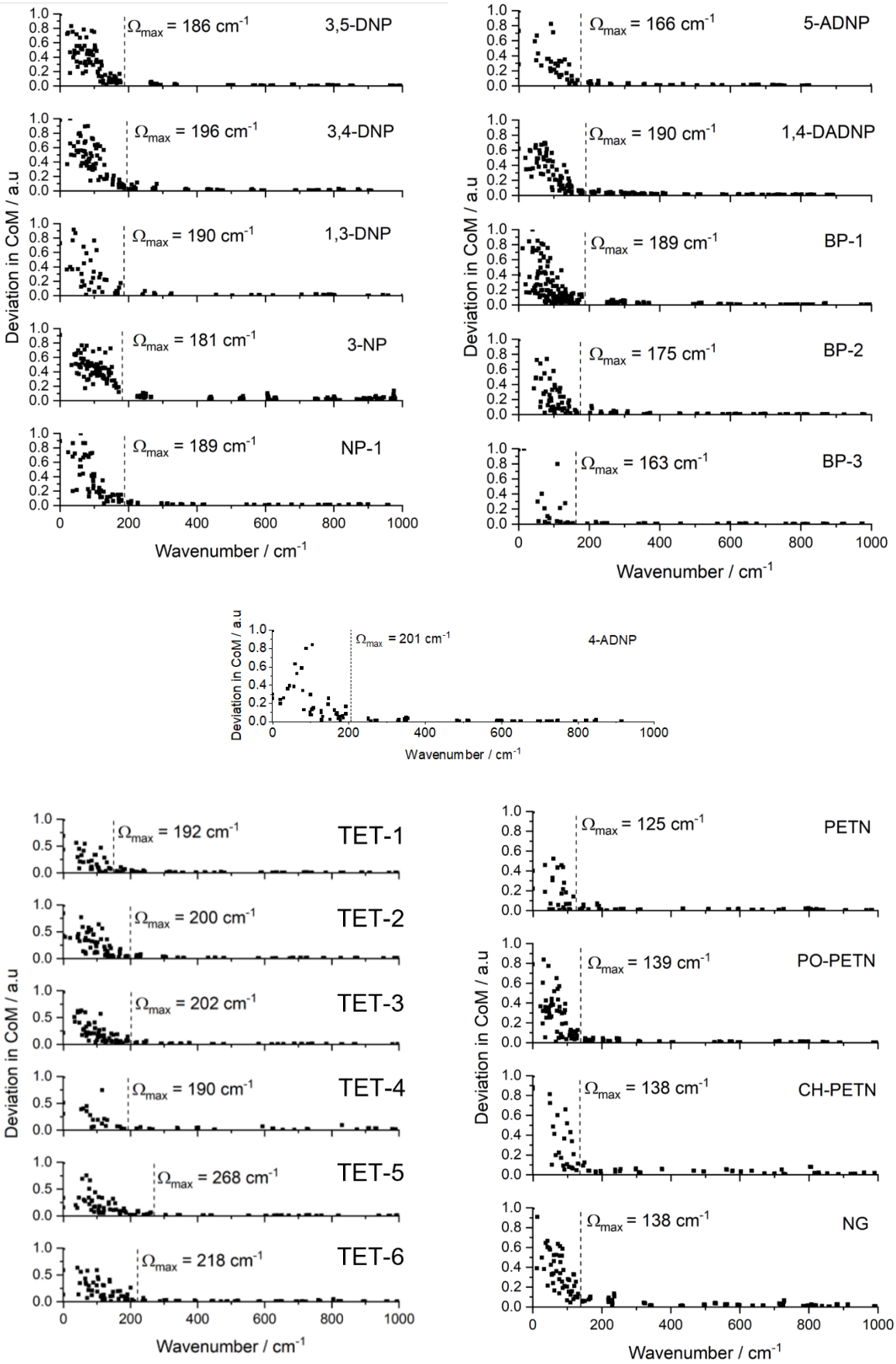
Supplementary material

S1: Crystal structure geometry optimisation data

Table S1: Experimental and calculated unit cell parameters as well as the change in volume for each of the EMs considered in this work. Compounds not listed here that are cited in the main text have been reported previously (ref 28 in main text).

EM	**CCSD code**	a [Å]	b [Å]	c [Å]	α [°]	β [°]	γ [°]	V [Å^3]	Change [%]
3,5-DNP$_{(exp)}$	YIFCAU01	10.6055(3)	10.3711(3)	10.4933(3)	90	90	90	1154.17	-
3,5-DNP$_{(calc)}$		11.0185	10.5158	10.3589	90	90	90	1200.27	+ 3.99
3,4-DNP$_{(exp)}$	UXUKUV	9.7013(13)	12.0797(10)	9.7587(7)	90	93.962(11)	90	1140.88	-
3,4-DNP$_{(calc)}$		9.9718	12.1604	9.8915	90	94.033	90	1196.47	+ 4.87
1,3-DNP$_{(exp)}$	GIMNAU	5.7084(6)	9.2664(8)	11.3570(11)	90	103.315(10)	90	584.59	-
1,3-DNP$_{(calc)}$		5.7283	9.7425	11.2305	90	103.958	90	608.25	+ 4.05
3-NP$_{(exp)}$	RIKNOO	10.1823(12)	12.5014(20)	13.1190(17)	100.26(1)	104.41(1)	111.32(1)	1438.42	-
3-NP$_{(calc)}$		10.3277	12.4509	13.0450	100.75	105.80	112.37	1411.65	- 1.86
NP-1$_{(exp)}$	FIYWAO	10.542(2)	8.4713(17)	10.792(2)	90	106.73(3)	90	922.98	-
NP-1$_{(calc)}$		10.893	8.5626	10.908	90	106.56	90	975.20	+ 5.66
5-ADNP$_{(exp)}$	KAHHUY	7.2132(3)	12.4258(5)	7.1598(3)	90	106.814(2)	90	614.30	-
5-ADNP$_{(calc)}$		7.2002	12.5048	7.1888	90	106.668	90	620.06	+ 0.94
4-ADNP$_{(exp)}$	UFUXOI	4.7257(5)	4.7312(6)	27.063(4)	90	90	90	605.08	-
4-ADNP$_{(calc)}$		4.7957	4.8692	26.836	90	90	90	626.65	+3.56
1,4-DADNP$_{(exp)}$	WETGIN	6.4359(4)	12.7184(7)	15.8769(10)	90	90	90	1299.59	-
1,4-DADNP$_{(calc)}$		6.5686	12.8473	15.9878	90	90	90	1349.18	+ 3.82
BP-1$_{(exp)}$	PITGEH	16.4281(13)	16.4281(13)	8.3705(6)	90	90	90	2259.05	-
BP-1$_{(calc)}$		16.9600	16.9600	8.2518	90	90	90	2373.56	+ 5.07
BP-2$_{(exp)}$	PITGAD	8.6064(8)	11.9636(9)	10.1200(9)	90	114.148(10)	90	950.81	-
BP-2$_{(calc)}$		8.6531	12.1639	10.2112	90	114.127	90	980.89	+ 3.16
BP-3$_{(exp)}$	PITFOQ	15.9744(9)	6.5428(8)	8.9414(8)	90	118.739(10)	90	819.42	-
BP-3$_{(calc)}$		16.1239	6.4231	9.1674	90	118.474	90	834.58	+ 1.85
TET-1$_{(exp)}$	LUVPOI	9.175(1)	6.177(1)	11.171(2)	90	90.382(11)	90	633.09	-
TET-1$_{(calc)}$		9.203	6.175	11.393	90	89.171	90	647.36	+ 2.25
TET-2$_{(exp)}$	LUVNIA	11.1953(6)	9.3248(4)	9.9411(4)	90	111.217(5)	90	967.45	-
TET-2$_{(calc)}$		11.3801	9.4650	10.1046	90	111.130	90	1015.22	+ 4.82
TET-3$_{(exp)}$	LUVPAU	9.2526(5)	11.3617(6)	9.5915(6)	90	106.156(6)	90	968.49	-
TET-3$_{(calc)}$		9.4647	11.1173	9.5742	90	106.391	90	966.47	+ 0.21
TET-4$_{(exp)}$	LUVPIC	6.0193(3)	6.4786(3)	8.4598(4)	90	98.952(5)	90	325.89	-
TET-4$_{(calc)}$		6.0122	6.4823	8.5290	90	98.510	90	328.74	+ 0.87
TET-5$_{(exp)}$	LUVPEY	5.8461(3)	18.4860(7)	8.0667(4)	90	110.769(5)	90	815.13	-
TET-5$_{(calc)}$		5.9000	18.4565	7.8972	90	111.564	90	799.82	- 1.88
TET-6$_{(exp)}$	LUVNAS	8.6244(4)	6.8715(4)	12.0481(6)	90	98.263(4)	90	706.59	-
TET-6$_{(calc)}$		8.6817	6.7677	11.9150	90	98.861	90	691.71	- 2.11
m-TNT$_{(exp)}$	ZZZMUC08	14.9113(1)	6.0340(1)	20.8815(3)	90	110.365(1)	90	1761.37	-
m-TNT$_{(calc)}$		15.070	6.028	20.994	90	110.816	90	1782.64	+ 1.21
TNT-1$_{(exp)}$	YAHJOH01	7.7097(4)	8.2267(6)	8.6514(7)	87.143(3)	64.730(3)	66.439(3)	449.988	-
TNT-1$_{(calc)}$		7.787	8.254	8.699	84.565	64.259	63.822	448.678	-0.29
TNT-2$_{(exp)}$	YAHJIB	8.327	8.327	8.753	115.19	115.19	69.98	487.267	-
TNT-2$_{(calc)}$		8.296	8.306	8.619	117.056	115.018	70.258	471.397	-3.26
PCA$_{(exp)}$	PICRAC12	9.1849(9)	16.8333(19)	9.8061(9)	90	90	90	1696.28	-
PCA$_{(calc)}$		9.3502	18.5549	9.8891	90	90	90	1715.67	+1.14
PETN$_{(exp)}$	PERYTN11	9.3027(3)	9.3027(3)	6.6403(2)	90	90	90	574.653	-
PETN$_{(calc)}$		9.4311	9.4311	6.6968	90	90	90	595.659	+ 3.66
PO-PETN$_{(exp)}$	FICQIU	12.370(3)	8.1257(14)	9.9430(18)	90	97.638(6)	90	990.552	-
PO-PETN$_{(calc)}$		13.133	8.4900	10.1960	90	96.911	90	1128.54	+ 13.93
CH-PETN$_{(exp)}$	FICQOA	7.6451(14)	7.8238(17)	8.9723(15)	100.557(19)	96.753(19)	114.760(14)	467.594	-
CH-PETN$_{(calc)}$		7.7751	7.9840	9.0813	100.416	96.775	115.074	490.074	+ 4.81
NG$_{(exp)}$	CORYIR	8.900(2)	13.608(3)	6.762(2)	90	90	90	818.954	-

S2: Centre of Mass Eigenvector Analysis



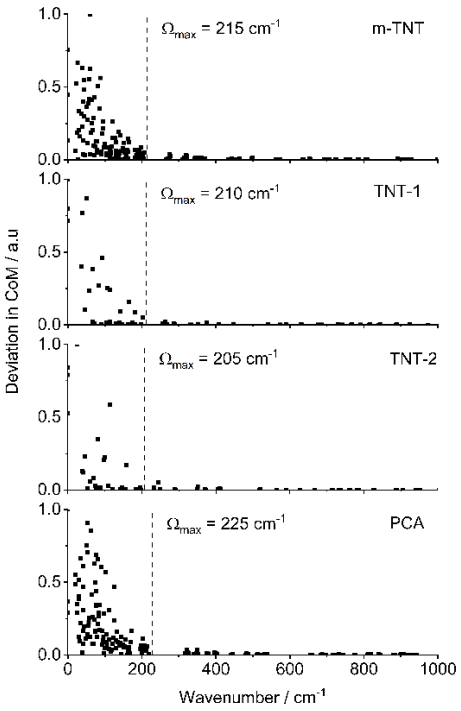
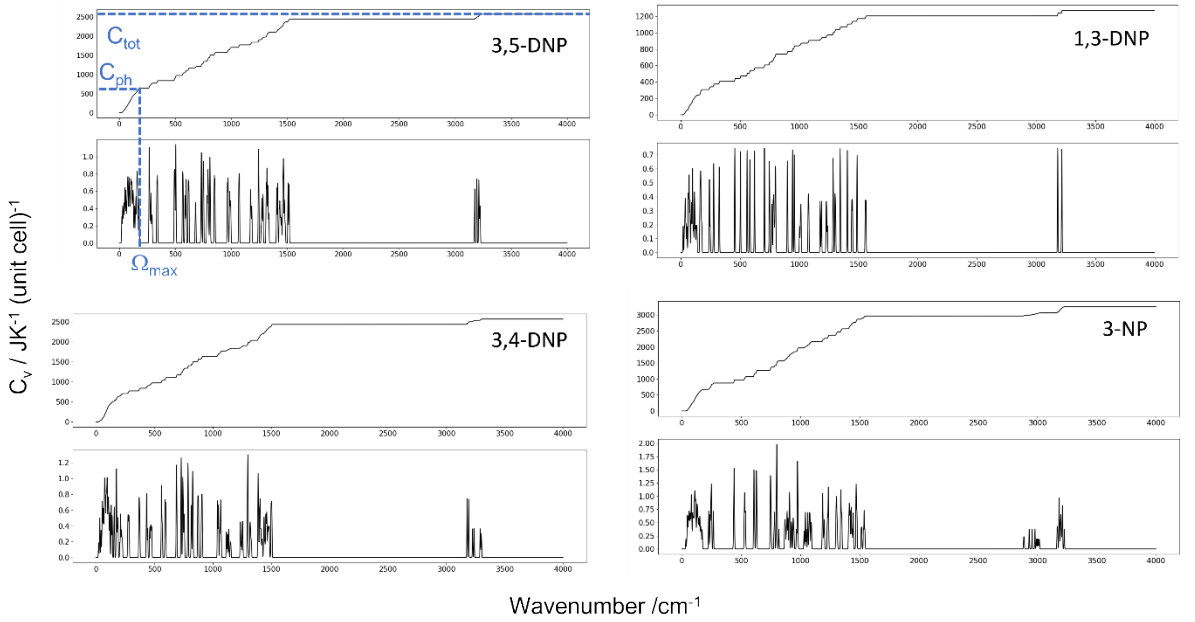
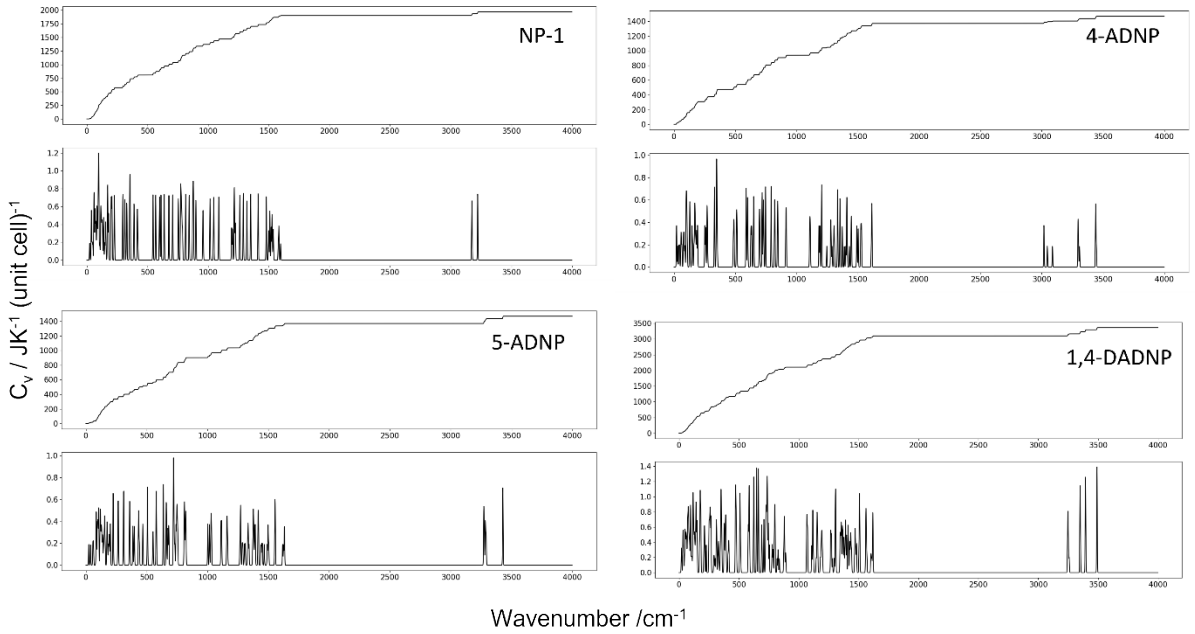
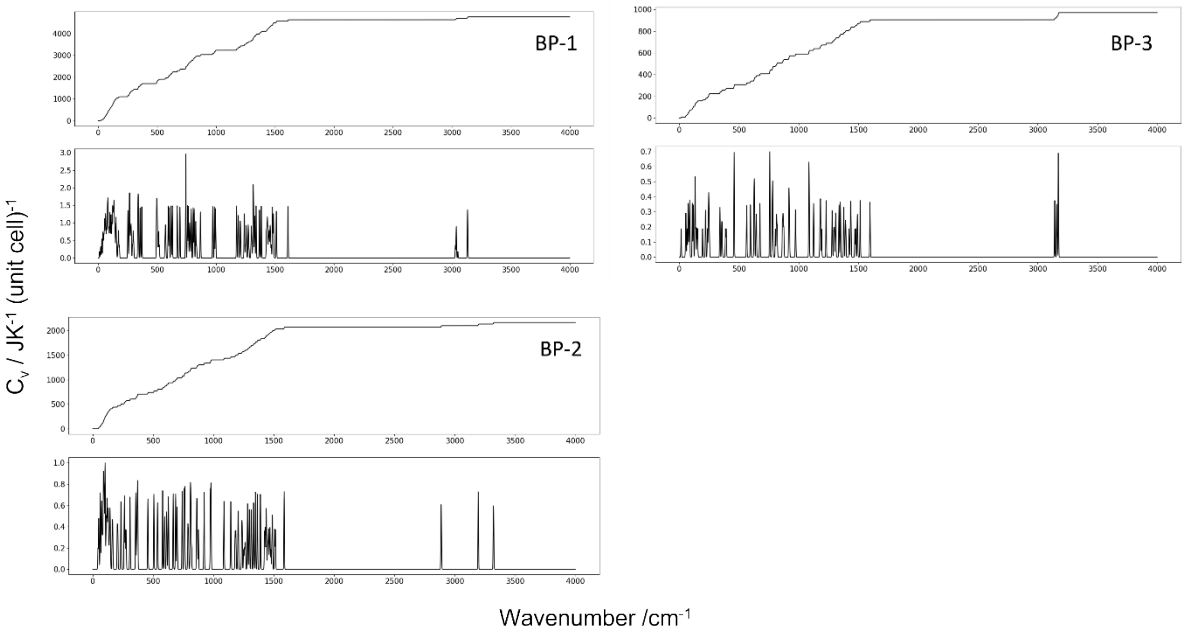


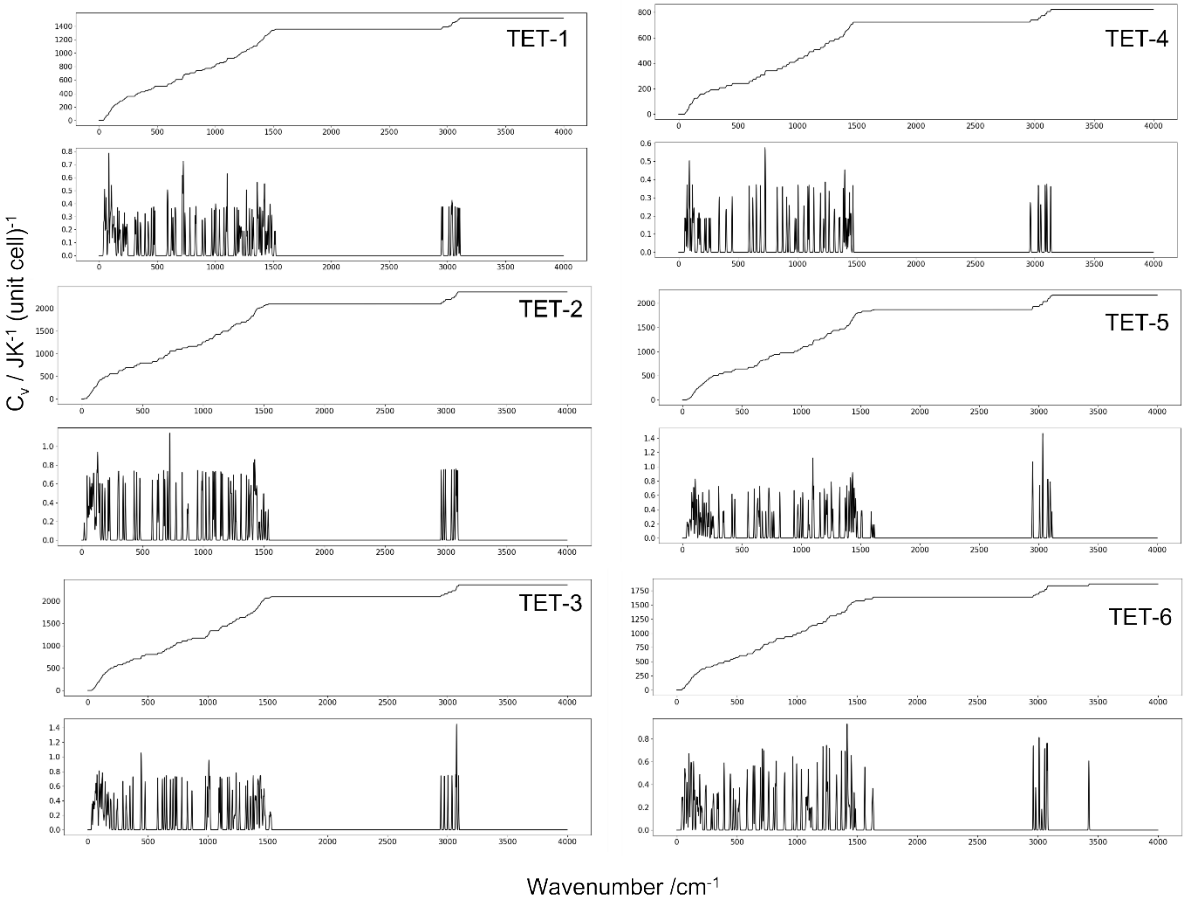
Figure S1: Centre of mass (CoM) deviation and Ω_{max} derivation for the pyrazoles, tetrazoles and nitrate esters studied in this work. Compounds not listed here that are cited in the main text have been reported in previous papers. [ref 22 and 28 in the main text]

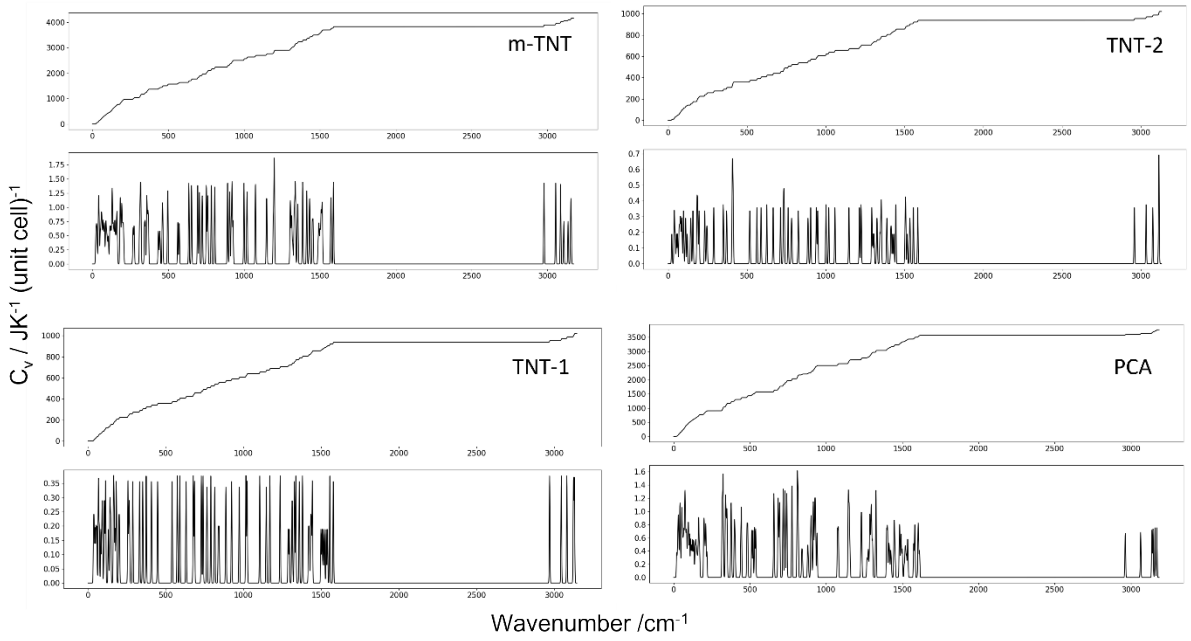
S3: Energetic Material Heat Capacity Calculations

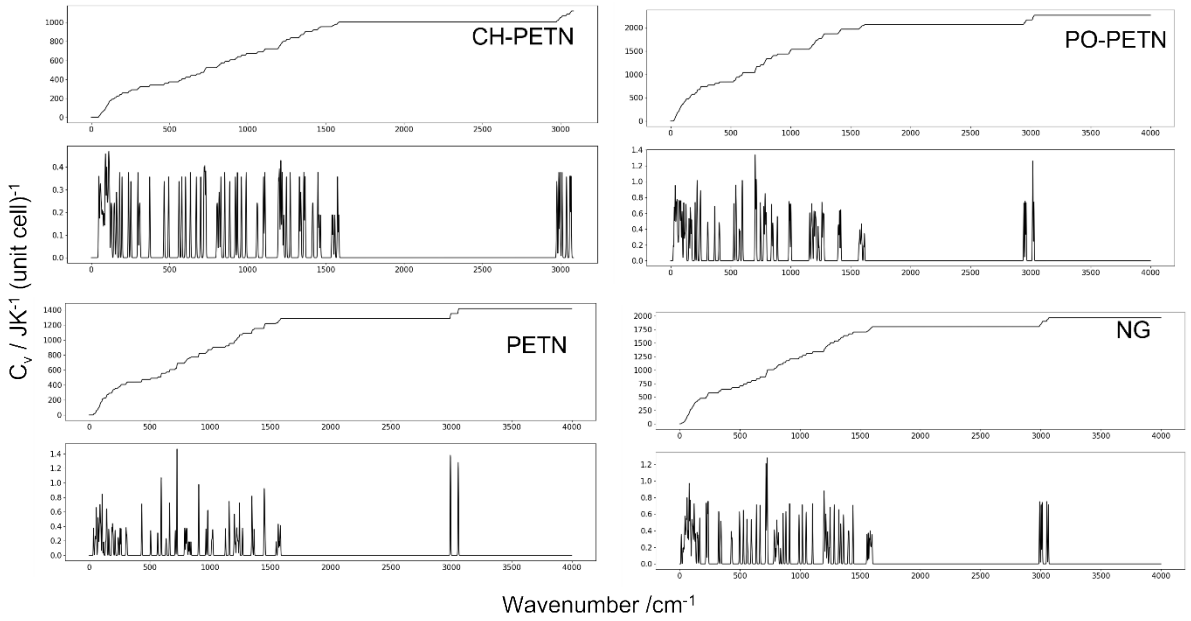





BP-1
BP-3
BP-2
C_v / JK^{-1} (unit cell)$^{-1}$
Wavenumber /cm^{-1}


TET-1
TET-4
TET-2
TET-5
TET-3
TET-6
C_v / JK^{-1} (unit cell)$^{-1}$
Wavenumber /cm^{-1}


m-TNT
TNT-2
TNT-1
PCA
C_v / JK^{-1} (unit cell)$^{-1}$
Wavenumber /cm^{-1}


CH-PETN
PO-PETN
PETN
NG
C_v / JK^{-1} (unit cell)$^{-1}$
Wavenumber /cm^{-1}

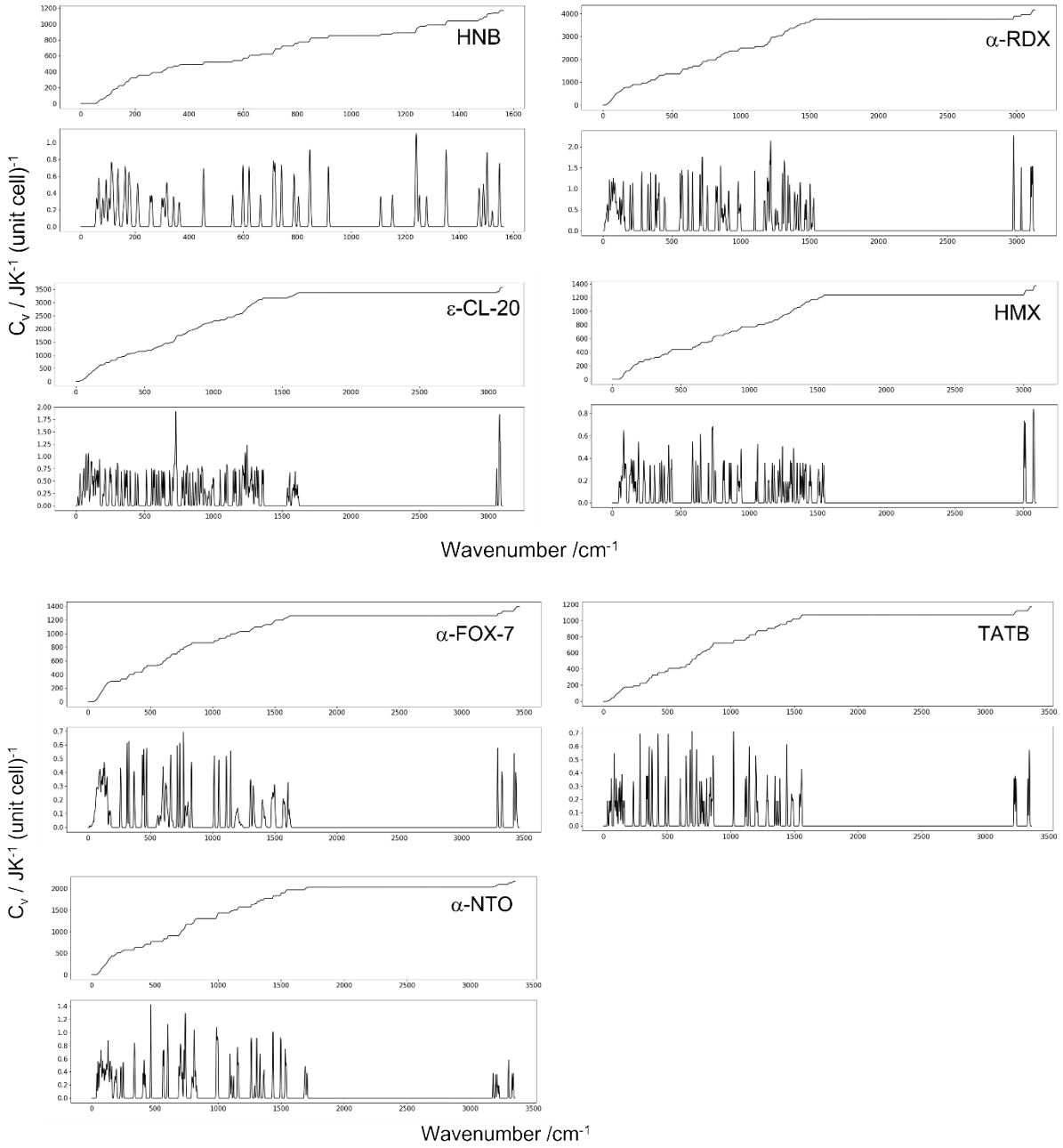


Figure S2: Cumulative contributions to the vibrational heat capacity by wavenumber for the pyrazoles, tetrazoles and nitrate esters studied in this work. Determination of C_{total}/C_{phonon} ratio is denoted on the 3,5-DNP plot.

S4: Parameters used in vibrational up-pumping model

Table S2: Vibrational frequencies denoting the top of the phonon bath (Ω_{max}), Phonon mode shock temperatures (T_{shock}), number of phonon modes residing in the phonon baths (#q), and number of molecules in the unit cell (Z).

EM	W_{max}[a] / cm^{-1}	C_{phon}/C_{tot}[b]	T_{shock}[c]	#q[d]	Z[d]
HNB	155	5.22	3423	30	2
e-Cl20	222	5.00	3278	88	4
b-HMX	200	5.32	3488	34	2
a-RDX	164	4.98	3265	96	8
a-FOX-7	180	5.00	3278	36	4
a-NTO	200	4.03	2642	64	8
TATB	151	6.71	4399	24	2
TNP	214	3.49	2288	156	12
3,5-DNP	186	4.01	2630	80	8
3,4-DNP	196	3.64	2387	80	8
1,3-DNP	190	4.13	2708	40	4
3-NP	181	4.85	3180	84	12
NP-1	189	4.16	2728	60	4
5-ADNP	166	6.29	4124	36	4
4-ADNP	201	4.78	3134	40	4
1,4-DADNP	190	5.26	3449	80	8
BP-1	189	4.31	2826	136	8
BP-2	175	4.92	3226	56	4
BP-3	163	6.16	4039	22	2
TET-1	192	5.23	3430	38	2
TET-2	200	4.80	3062	64	4
TET-3	202	4.67	3416	64	4
TET-4	190	5.21	2807	22	2
TET-5	268	4.28	2807	60	4
TET-6	218	5.00	3279	48	4
m-TNT	215	4.26	2793	120	8
TNT-1	210	5.55	3639	30	2
TNT-2	205	4.71	3088	30	2
PCA	225	4.18	2741	112	8
PETN	125	6.33	4147	30	2
PO-PETN	139	4.51	2963	60	4
CH-PETN	138	4.51	2956	26	2
NG	138	4.84	3168	52	4

[a]Determined from eigenvector centre of mass displacements, shown in Figure S1

[b]Determined from cumulative contributions to the vibrational heat capacity, shown in Figure S2.

[c] Temperature used to scale the occupancies of the phonon bath modes (ie. adsorption of impact energy), determined relative to C_{phon}/C_{tot} = 5.0 equates to 3279 K, based on previous work (ref 22 in main text).

[d]Vibrational up pumping intensity is scaled on a per phonon bath mode, per molecule basis (where Z denotes the number of molecules contained in the crystallographic unit cell).

S5: Vibrational up-pumping output data

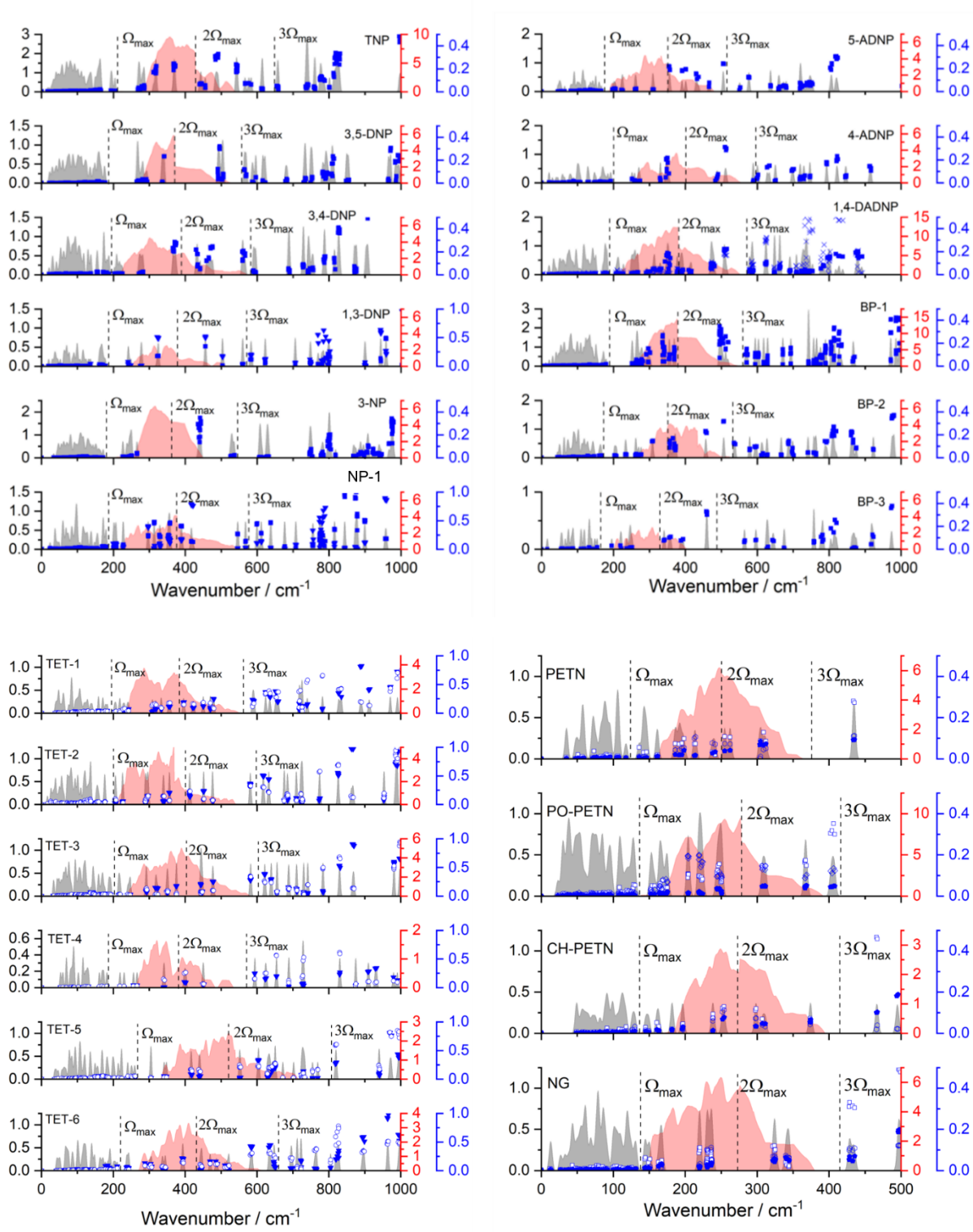


Figure S3: g(w) (grey) , $\Omega^{(2)}$ (red), along with eigenvector displacement contributions from the weakest bonds (blue) for each EM. Colour scheme: C-NO2 (filled squares), C-N ring or side chain bonds (open circles), N-NO2 (solid triangles), N-NH2 bonds (crosses), O-N (open squares), C-O (solid pentagons) and C-P (open diamonds).

Table S3: Experimental and predicted impact sensitivities (projected onto all vibrational modes in the up-pumping window, alongside the number of trigger bonds (TBs), number of doorway modes (Q_d) per molecule and Kier Molecular Flexibility (KMF) parameters

EM	Exp IS / J	Ref	Total relative up-pumped density / 10^3 a.u	Relative up-pumped density (Q_T modes only)/ $\times 10^3$ a.u	Total # TBs	# Q_d per Z	KMF
HNB	2.75	1	107.3	65.5	6	12	4.26
e-Cl20	3.75	2	182.2	181.9	18	12	3.33
b-HMX	8	2	63.5	47.6	12	7	4.18
a-RDX	13	3	48.1	21.6	9	6	2.68
a-FOX-7	31.5	4	14.7	4.7	2	3	2.13
a-NTO	73	5	12.4	8.2	1	3	1.03
TATB	120*	5	17.1	5.4	3	3	2.87
TNP	17	6	31.9	21.5	3	4	2.06
3,5-DNP	25	7	14.7	10.8	2	3	1.51
3,4-DNP	40	7	22.9	13.2	2	3	1.51
1,3-DNP	25	7	13.1	7.4	2	3	0.96
3-NP	> 100	8	2.5	1.0	1	2	2.86
NP-1	2.5	9	54.9	54.9	4	8	2.86
5-ADNP	23	10	51.6	18.7	2	4	1.62
4-ADNP	41	11	27.5	20.0	2	5	1.62
1,4-DADNP	> 40	12	164.7	31.3	3	5	1.73
BP-1	4.5	13	105.2	78.7	4	9	3.18
BP-2	20	13	51.6	37.3	3	5	2.63
BP-3	30	13	41.8	20.7	2	4	2.08
TET-1	2	14	103.5	98.0	9	8	4.65
TET-2	5	14	49.3	42.3	5	6	3.12
TET-3	8	14	67.3	51.9	5	6	3.12
TET-4	15	14	19.7	16.3	4	3	1.95
TET-5	40	14	24.3	20.1	4	4	2.57
TET-6	> 100	14	47.7	25.4	4	4	2.03
m-TNT	24.5	15	77.8	57.1	3	6	2.79
TNT-1	14	15	56.8	54.0	3	7	2.79
TNT-2	26.8	15	40.4	37.4	3	7	2.79
PCA	16	15	91.8	43.2	3	7	2.66
PETN	3	16	176.8	104.7	8	9	6.84
PO-PETN	2	16	104.9	100.8	9	8	5.60
CH-PETN	6	16	66.4	32.4	6	6	5.92
NG	14	17	64.3	43.4	6	10	5.14

*Experimental IS quoted for TATB in ref 5 is an estimated value.

S6: Local mode analysis

Table S4: Calculated mass-independent local force constants (in mDynÅ^{-1}), derived by LModeA-nano based on Cartesian force constants calculated at the B3LYP/6-31G* level using Gaussian16.

HNB			CL-20			HMX			RDX			FOX-7		
Ntrig	6		Ntrig	19		Ntrig	12		Ntrig	9		Ntrig	2	
Θ	0.30		Θ	0.30		Θ	0.26		Θ	0.28		Θ	0.25	
Bonds	K^{loc}	$(K^{loc})^{-1}$	Bonds	K^{loc}	$(K^{loc})^{-1}$	Bonds	K^{loc}	$(K^{loc})^{-1}$	Bonds	K^{loc}	$(K^{loc})^{-1}$	Bonds	K^{loc}	$(K^{loc})^{-1}$
CC	6.6394	0.15061602	N-N	2.585	0.386847	N-N	3.814	0.262192	N-N	2.774	0.36049	C-N	4.051	0.246853
CC	6.6394	0.15061602	N-N	3.151	0.31736	N-N	3.324	0.300842	N-N	2.776	0.360231	C-N	4.05	0.246914
CC	6.6394	0.15061602	N-N	2.548	0.392465	N-N	3.807	0.262674	N-N	3.536	0.282805	C-N	6.688	0.149522
CC	6.6394	0.15061602	N-N	2.51	0.398406	N-N	3.314	0.30175	C-N	3.896	0.256674	C-N	6.684	0.149611
CC	6.6394	0.15061602	C-N	3.722	0.268673	C-N	4.018	0.24888	C-N	3.897	0.256608	C-C	5.1	0.196078
CC	6.6394	0.15061602	C-N	3.453	0.289603	C-N	3.808	0.262605	C-N	4.343	0.230256	N-O	8.087	0.123655
CN	3.292	0.30376671	C-N	3.479	0.287439	C-N	3.903	0.256213	C-N	3.723	0.268601	N-O	10.128	0.098736
CN	3.292	0.30376671	C-N	3.774	0.264971	C-N	4.715	0.212089	C-N	3.721	0.268745	N-O	10.128	0.098736
CN	3.292	0.30376671	C-N	4.486	0.222916	C-N	4.019	0.248818	C-N	4.344	0.230203	N-O	8.104	0.123396
CN	3.292	0.30376671	C-N	4.232	0.236295	C-N	3.809	0.262536	N-O	10.038	0.099621	N-H	6.482	0.154273
CN	3.292	0.30376671	C-N	4.088	0.244618	C-N	3.9	0.25641	N-O	10.1	0.09901	N-H	7.281	0.137344
CN	3.292	0.30376671	C-N	4.021	0.248694	C-N	4.715	0.212089	N-O	10.098	0.09903	N-H	7.279	0.137382
NO	10.341	0.09670245	C-N	3.98	0.251256	N-O	9.765	0.102407	N-O	10.036	0.099641	N-H	6.473	0.154488
NO	10.341	0.09670245	C-N	3.475	0.28777	N-O	9.715	0.102934	N-O	9.806	0.101978	TATB		
NO	10.341	0.09670245	C-N	3.337	0.29967	N-O	9.769	0.102365	N-O	9.08	0.110132	Ntrig	3	
NO	10.341	0.09670245	C-N	4.111	0.24325	N-O	9.364	0.106792	C-H	5.292	0.188964	Θ	0.23	
NO	10.341	0.09670245	C-C	3.089	0.323729	N-O	9.716	0.102923	C-H	5.706	0.175254	Bonds	K^{loc}	$(K^{loc})^{-1}$
NO	10.341	0.09670245	C-C	3.003	0.333	N-O	9.762	0.102438	C-H	5.056	0.197785	C-C	5.223	0.191461
NO	10.341	0.09670245	C-C	3.218	0.310752	N-O	9.371	0.106712	C-H	5.717	0.174917	C-C	5.223	0.191461
NO	10.341	0.09670245	N-O	10.196	0.098078	N-O	9.772	0.102333	C-H	5.056	0.197785	C-C	5.223	0.191461
NO	10.341	0.09670245	N-O	10.125	0.098765	C-H	5.481	0.182448	C-H	5.717	0.174917	C-C	5.028	0.198886
NO	10.341	0.09670245	N-O	9.851	0.101513	C-H	5.328	0.187688				C-C	5.028	0.198886
NTO			N-O	10.047	0.099532	C-H	5.248	0.190549				C-C	5.028	0.198886
Ntrig	1		N-O	10.012	0.09988	C-H	5.472	0.182749				C-N	4.091	0.244439
Θ	0.23		N-O	10.063	0.099374	C-H	5.328	0.187688				C-N	4.091	0.244439
Bonds	K^{loc}	$(K^{loc})^{-1}$	N-O	10.179	0.098241	C-H	5.481	0.182448				C-N	4.091	0.244439
N-N	5.524	0.181028	N-O	10.152	0.098503	C-H	5.473	0.182715				C-N	8.028	0.124564
C-N	8.955	0.111669	N-O	10.191	0.098126	C-H	5.249	0.190512				C-N	8.028	0.124564
C-N	6.646	0.150466	N-O	10.131	0.098707							C-N	8.028	0.124564
C-N	5.023	0.199084	N-O	10.096	0.099049							N-O	8.366	0.119531
C-N	5.059	0.197668	N-O	10.056	0.099443							N-O	8.371	0.11946
C-N	4.247	0.23546	C-H	5.583	0.179115							N-O	8.366	0.119531
N-O	10.4	0.096154	C-H	5.606	0.17838							N-O	8.365	0.119546
N-O	9.599	0.104178	C-H	5.631	0.177588							N-O	8.373	0.119432
C-O	12.869	0.077706	C-H	5.666	0.176491							N-O	8.37	0.119474
N-H	7.416	0.134844	C-H	5.661	0.176647							NH1	6.545	0.152788
N-H	7.444	0.134336	C-H	5.614	0.178126							NH1	6.548	0.152718
N-N	5.524	0.181028										NH1	6.549	0.152695
TNP			3,5-DNP			3,4-DNP			3-NP			NP1		
Ntrig	3		Ntrig	2		Ntrig	2		Ntrig	1		Ntrig	5	
Θ	0.24		Θ	0.23		Θ	0.24		Θ	0.23		Θ	0.40	
Bonds	K^{loc}	$(K^{loc})^{-1}$	Bonds	K^{loc}	$(K^{loc})^{-1}$	Bonds	K^{loc}	$(K^{loc})^{-1}$	Bonds	K^{loc}	$(K^{loc})^{-1}$	Bonds	K^{loc}	$(K^{loc})^{-1}$
N-N	6.672	0.14988	N-N	6.594	0.151653	N-N	5.835	0.17138	N-N	6.351	0.157456	N-N	5.889	0.169808
C-N	7.111	0.140627	C-N	6.757	0.147995	C-N	7.629	0.131079	C-N	7.36	0.13587	N-N	2.766	0.361533
C-N	4.143	0.241371	C-N	7.015	0.142552	C-N	7.136	0.140135	C-N	6.596	0.151607	C-N	6.063	0.164935
C-N	6.873	0.145497	C-N	4.493	0.222568	C-N	3.99	0.250627	C-N	4.305	0.232288	C-N	7.337	0.136295
C-N	4.394	0.227583	C-N	4.214	0.237304	C-N	4.333	0.230787	C-C	7.352	0.136017	C-N	1.862	0.537057
C-N	3.962	0.252398	N-O	9.645	0.103681	N-O	10.332	0.096787	C-C	6.177	0.161891	C-N	2.233	0.447828
C-C	6.132	0.163079	N-O	10.223	0.097819	N-O	10.246	0.097599	N-O	9.832	0.101709	C-N	2.218	0.450857
C-C	7.194	0.139005	N-O	9.942	0.100583	N-O	10.102	0.09899	N-O	10.3	0.097087	N-O	10.315	0.096946
N-O	10.505	0.095193	N-O	10.42	0.095969	N-O	9.744	0.102627	C-H	5.892	0.169722	N-O	11.095	0.090131
N-O	9.969	0.100311	C-C	7.218	0.138543	C-C	5.905	0.169348	C-H	6.007	0.166472	N-O	10.651	0.093888
N-O	10.45	0.095694	C-C	6.243	0.160179	C-C	7.155	0.139762	N-H	7.361	0.135851	N-O	10.543	0.09485
N-O	10.23	0.097752	C-H	6.052	0.165235	C-H	5.973	0.16742	BP-1			N-O	10.704	0.093423
N-O	9.72	0.102881	N-H	7.253	0.137874	N-H	7.344	0.136166	Ntrig	4		N-O	10.217	0.097876
N-O	10.451	0.095685	4-ADNP			1,4-DADNP			Θ	0.23		N-O	10.492	0.095311
N-H	7.202	0.13885	Ntrig	1		Ntrig	2		Bonds	K^{loc}	$(K^{loc})^{-1}$	N-O	10.694	0.09351
5-ADNP			Θ	0.22		Θ	0.21		N-N	6.718	0.148854	C-C	7.506	0.133227
Ntrig	1		Bonds	K^{loc}	$(K^{loc})^{-1}$	Bonds	K^{loc}	$(K^{loc})^{-1}$	N-N	6.719	0.148832	C-C	5.656	0.176803
Θ	0.21		N-N	7.189	0.139101	N-N	7.375	0.135593	C-N	6.988	0.143102	C-C	4.501	0.222173
Bonds	K^{loc}	$(K^{loc})^{-1}$	C-N	6.84	0.146199	N-N	4.747	0.210659	C-N	7.142	0.140017	C-H	6.029	0.165865
N-N	5.232	0.191131	C-N	6.502	0.153799	C-N	6.419	0.155788	C-N	7.141	0.140036	C-H	6.01	0.166389
C-N	6.866	0.145645	C-N	4.574	0.218627	C-N	5.868	0.170416	C-N	6.987	0.143123	BP-2		
C-N	8.181	0.122234	C-N	5.232	0.191131	C-N	4.796	0.208507	C-N	4.417	0.226398	Ntrig	0	
C-N	4.767	0.209776	C-N	8.07	0.123916	C-N	8.063	0.124023	C-N	4.125	0.242424	Θ	0	
C-N	6.13	0.163132	C-C	6.679	0.149723	C-N	5.202	0.192234	C-N	4.125	0.242424	Bonds	K^{loc}	$(K^{loc})^{-1}$
C-N	6.866	0.145645	C-C	5.751	0.173883	C-C	6.104	0.163827	C-N	4.418	0.226347	N-N	8.142	0.12282
C-C	6.437	0.155352	N-O	9.001	0.111099	C-C	6.338	0.157778	N-O	10.488	0.095347	N-N	7.614	0.131337
C-C	5.836	0.17135	N-O	9.403	0.106349	N-O	10.158	0.098445	N-O	9.87	0.101317	C-N	8.086	0.123671
N-O	8.64	0.115741	N-O	9.063	0.110339	N-O	8.793	0.113727	N-O	9.671	0.103402	C-N	8.993	0.111198
N-O	10.054	0.099463	N-O	10.383	0.096311	N-O	9.043	0.110583	N-O	10.129	0.098726	C-N	9.685	0.103252
N-O	10.261	0.097456	N-H	7.323	0.136556	N-O	8.874	0.112689	N-O	9.87	0.101317	C-N	7.977	0.12536

N-O	10.293	0.097153	N-H	7.321	0.136593	N-H	7.258	0.137779	N-O	10.488	0.095347	C-N	5.449	0.18352
N-H	6.825	0.14652	N-H	7.28	0.137363	N-H	7.338	0.136277	N-O	10.128	0.098736	C-N	5.646	0.177117
N-H	7.125	0.140351				N-H	6.823	0.146563	N-O	9.672	0.103391	C-N	5.456	0.183284
N-H	7.376	0.135575				N-H	6.637	0.15067	C-C	5.759	0.173641	N-O	12.627	0.079195
BP-3									C-C	6.845	0.146092	N-O	13.409	0.074577
Ntrig	2								C-C	6.845	0.146092	N-O	13.77	0.072622
Θ	0.24								C-C	5.76	0.173611	N-O	12.743	0.078474
Bonds	K^{loc}	$(K^{loc})^{-1}$							C-C	5.44	0.183824	N-O	12.572	0.079542
N-N	6.401	0.156226							N-H	7.228	0.138351	N-O	13.849	0.072207
N-N	6.401	0.156226							N-H	7.228	0.138351	C-C	8.105	0.123381
C-N	6.787	0.147341										C-C	6.249	0.160026
C-N	7.433	0.134535										C-C	6.402	0.156201
C-N	6.787	0.147341										C-C	8.155	0.122624
C-N	7.433	0.134535										C-C	5.977	0.167308
C-N	4.218	0.237079										N-H	8.302	0.120453
C-N	4.218	0.237079										N-H	8.433	0.118582
C-C	7.052	0.141804										C-H	6.633	0.150761
C-C	5.764	0.173491												
C-C	7.051	0.141824												
C-C	5.764	0.173491												
C-C	5.414	0.184706												
N-O	10.294	0.097144												
N-O	9.844	0.101585												
N-O	9.844	0.101585												
N-O	10.295	0.097135												
C-H	5.885	0.169924												
C-H	5.885	0.169924												
N-H	7.364	0.135796												
TET-1			TET-2			TET-3			TET-4			TET-5		
Ntrig	9		Ntrig	8		Ntrig	7		Ntrig	5		Ntrig	7	
Θ	0.25		Θ	0.25		Θ	0.28		Θ	0.25		Θ	0.23	
Bonds	K^{loc}	$(K^{loc})^{-1}$	Bonds	K^{loc}	$(K^{loc})^{-1}$	Bonds	K^{loc}	$(K^{loc})^{-1}$	Bonds	K^{loc}	$(K^{loc})^{-1}$	Bonds	K^{loc}	$(K^{loc})^{-1}$
N-N	5.651	0.17696	N-N	4.73	0.211416	N-N	5.457	0.183251	N-N	6.579	0.151999	N-N	4.476	0.223414
N-N	4.557	0.219443	N-N	5.335	0.187441	N-N	4.957	0.201735	N-N	4.248	0.235405	N-N	6.051	0.165262
N-N	5.328	0.187688	N-N	4.301	0.232504	N-N	5.354	0.186776	N-N	6.441	0.155255	N-N	4.801	0.20829
N-N	3.998	0.250125	N-N	2.793	0.358038	N-N	2.292	0.4363	N-N	3.922	0.254972	N-N	4.4	0.227273
N-N	3.198	0.312695	N-N	4.211	0.237473	N-N	3.895	0.256739	C-N	6.131	0.163106	C-N	4.342	0.230309
C-N	4.988	0.200481	C-N	4.274	0.233973	C-N	6.217	0.160849	C-N	6.579	0.151999	C-N	6.777	0.147558
C-N	4.051	0.246853	C-N	5.632	0.177557	C-N	5.544	0.180375	C-N	3.81	0.262467	C-N	4.279	0.233699
C-N	4.143	0.241371	C-N	3.55	0.28169	C-N	5.334	0.187477	C-N	4.12	0.242718	C-N	3.368	0.296912
C-N	5.603	0.178476	C-N	3.876	0.257998	C-N	3.329	0.300391	C-N	4.058	0.246427	C-N	4.671	0.214087
C-N	3.457	0.289268	C-N	4.582	0.218245	C-N	3.901	0.256345	N-O	9.949	0.100513	N-O	9.75	0.102564
C-N	4.061	0.246245	N-O	9.822	0.101812	C-N	4.245	0.235571	N-O	9.32	0.107296	N-O	8.802	0.113611
C-N	4.673	0.213995	N-O	9.133	0.109493	C-N	4.16	0.240385	C-H	5.411	0.184809	C-H	5.449	0.18352
C-N	5.188	0.192753	N-O	9.816	0.101874	N-O	10.202	0.09802	C-H	5.445	0.183655	C-H	5.12	0.195313
N-O	9.906	0.100949	N-O	9.92	0.100806	N-O	9.608	0.10408	C-H	5.234	0.191058	C-H	5.288	0.189107
N-O	9.73	0.102775	C-H	5.342	0.187196	N-O	9.407	0.106304	C-H	5.478	0.182548	C-H	5.502	0.181752
N-O	10.072	0.099285	C-H	5.285	0.189215	N-O	9.761	0.102449	C-H	5.572	0.179469	C-H	5.288	0.189107
N-O	9.752	0.102543	C-H	5.496	0.181951	C-H	5.37	0.18622	C-H	5.986	0.167056	C-H	5.239	0.190876
N-O	9.353	0.106918	C-H	5.38	0.185874	C-H	5.534	0.180701				C-H	5.504	0.181686
N-O	9.923	0.100776	C-H	5.382	0.185805	C-H	5.374	0.186081				C-H	5.386	0.185667
C-H	5.43	0.184162	C-H	5.529	0.180865	C-H	5.495	0.181984				N-H	6.91	0.144718
C-H	5.247	0.190585	C-H	5.479	0.182515	C-H	5.222	0.191498						
C-H	5.441	0.18379	C-H	5.498	0.181884	C-H	5.383	0.18577						
C-H	5.245	0.190658				C-H	5.512	0.181422						
C-H	5.541	0.180473				C-H	5.556	0.179986						
C-H	5.581	0.179179												
C-H	5.621	0.177904												
C-H	5.437	0.183925												
C-H	5.421	0.184468												
C-H	5.411	0.184809												
TET-6														
Ntrig	4													
Θ	0.24													
Bonds	K^{loc}	$(K^{loc})^{-1}$												
N-N	4.223	0.236798												
N-N	6.259	0.15977												
N-N	4.25	0.235294												
N-N	3.809	0.262536												
C-N	6.418	0.155812												
C-N	5.939	0.168379												
C-N	6.375	0.156863												
C-N	4.058	0.246427												
N-O	9.94	0.100604												
N-O	8.841	0.113109												
C-H	5.344	0.187126												
C-H	5.477	0.182582												
C-H	5.255	0.190295												
C-H	5.533	0.180734												
C-H	5.449	0.18352												
N-H	6.896	0.145012												
N-H	7.133	0.140193												
TNT			TNT-1			TNT-2			PCA					
Ntrig	4		Ntrig	4		Ntrig	8		Ntrig	3				
Θ	0.27		Θ	0.27		Θ	0.24		Θ	0.27				
Bonds	K^{loc}	$(K^{loc})^{-1}$	Bonds	K^{loc}	$(K^{loc})^{-1}$	Bonds	K^{loc}	$(K^{loc})^{-1}$	Bonds	K^{loc}	$(K^{loc})^{-1}$			

C-N	3.535	0.282885	C-N	3.61	0.277008	C-N	3.56	0.280899	C-N	3.528	0.283447			
C-N	3.535	0.282885	C-N	3.446	0.290192	C-N	3.417	0.292654	C-N	3.87	0.258398			
C-N	3.798	0.263296	C-N	3.679	0.271813	C-N	3.567	0.280348	C-N	3.848	0.259875			
C-C	5.837	0.171321	C-C	6	0.166667	C-C	4.846	0.206356	C-C	5.739	0.174246			
C-C	6.582	0.15193	C-C	6.243	0.160179	C-C	5.085	0.196657	C-C	6.81	0.146843			
C-C	6.805	0.146951	C-C	6.426	0.155618	C-C	5.054	0.197863	C-C	6.61	0.151286			
C-C	6.805	0.146951	C-C	6.579	0.151999	C-C	5.174	0.193274	C-C	6.947	0.143947			
C-C	6.581	0.151953	C-C	6.79	0.147275	C-C	5.049	0.198059	C-C	6.65	0.150376			
C-C	5.837	0.171321	C-C	6.356	0.157332	C-C	4.792	0.208681	C-C	5.519	0.181192			
C-C	4.221	0.236911	C-C	4.369	0.228885	C-C	4.462	0.224115	C-O	7.312	0.136761			
N-O	10.074	0.099265	N-O	10.185	0.098184	N-O	10.02	0.0998	N-O	10.315	0.096946			
N-O	10.121	0.098804	N-O	10.221	0.097838	N-O	10.271	0.097362	N-O	9.823	0.101802			
N-O	10.119	0.098824	N-O	10.308	0.097012	N-O	10.387	0.096274	N-O	10.03	0.099701			
N-O	10.075	0.099256	N-O	10.392	0.096228	N-O	10.361	0.096516	N-O	10.061	0.099394			
N-O	10.121	0.098804	N-O	10.214	0.097905	N-O	10.255	0.097513	N-O	10.434	0.095841			
N-O	10.121	0.098804	N-O	10.033	0.099671	N-O	10.045	0.099552	N-O	8.518	0.117398			
C-H	5.385	0.185701	C-H	5.346	0.187056	C-H	4.694	0.213038	C-H	5.844	0.171116			
C-H	5.295	0.188857	C-H	5.266	0.189897	C-H	5.184	0.192901	C-H	5.845	0.171086			
C-H	5.384	0.185736	C-H	5.233	0.191095	C-H	4.714	0.212134	O-H	5.591	0.178859			
C-H	5.847	0.171028	C-H	5.655	0.176835	C-H	5.697	0.175531						
C-H	5.842	0.171174	C-H	5.766	0.17343	C-H	5.689	0.175778						
PETN			PO-PETN			CH-PETN			NG					
Ntrig	12		Ntrig	9		Ntrig	9		Ntrig	8				
Θ	0.34		Θ	0.43		Θ	0.34		Θ	0.36				
Bonds	K^{loc}	$(K^{loc})^{-1}$	Bonds	K^{loc}	$(K^{loc})^{-1}$	Bonds	K^{loc}	$(K^{loc})^{-1}$	Bonds	K^{loc}	$(K^{loc})^{-1}$			
C-C	3.696	0.270563	P-O	6.03	0.165837	C-C	3.952	0.253036	C-O	3.165	0.315956			
C-O	3.35	0.298507	P-C	2.322	0.430663	C-C	3.892	0.256937	C-O	3.413	0.292997			
O-N	2.071	0.482859	P-C	2.356	0.424448	C-C	3.825	0.261438	C-O	3.449	0.289939			
N-O	8.478	0.117952	P-C	2.279	0.438789	C-O	3.218	0.310752	C-C	3.94	0.253807			
N-O	9.243	0.10819	C-O	3.564	0.280584	C-O	3.354	0.298151	C-C	3.988	0.250752			
C-H	5.397	0.185288	C-O	3.597	0.278009	C-O	3.332	0.30012	O-N	1.97	0.507614			
C-H	5.398	0.185254	C-O	3.603	0.277546	O-N	2.181	0.458505	N-O	8.156	0.122609			
C-C	3.696	0.270563	O-N	1.689	0.592066	O-N	2.146	0.465983	N-O	9.408	0.106293			
C-O	3.35	0.298507	O-N	1.796	0.556793	O-N	1.996	0.501002	O-N	2.011	0.497265			
O-N	2.071	0.482859	O-N	1.771	0.564653	N-O	9.152	0.109266	N-O	8.169	0.122414			
N-O	8.478	0.117952	N-O	9.423	0.106123	N-O	8.448	0.118371	N-O	9.449	0.105831			
N-O	9.243	0.10819	N-O	8.73	0.114548	N-O	8.402	0.119019	O-N	2.112	0.473485			
C-H	5.397	0.185288	N-O	9.41	0.10627	N-O	9.22	0.10846	N-O	8.399	0.119062			
C-H	5.398	0.185254	N-O	8.606	0.116198	N-O	8.296	0.12054	N-O	9.293	0.107608			
C-C	3.696	0.270563	N-O	9.465	0.105652	N-O	9.338	0.107089	C-H	5.409	0.184877			
C-O	3.35	0.298507	N-O	8.645	0.115674	C-H	5.382	0.185805	C-H	5.29	0.189036			
O-N	2.071	0.482859	C-H	5.374	0.186081	C-H	5.42	0.184502	C-H	5.374	0.186081			
N-O	8.478	0.117952	C-H	5.453	0.183385	C-H	5.37	0.18622	C-H	5.48	0.182482			
N-O	9.243	0.10819	C-H	5.392	0.18546	C-H	5.298	0.18875	C-H	5.338	0.187336			
C-H	5.397	0.185288	C-H	5.465	0.182983	C-H	5.402	0.185117						
C-H	5.398	0.185254	C-H	5.372	0.18615	C-H	5.364	0.186428						
C-C	3.696	0.270563	C-H	5.413	0.18474	C-H	5.164	0.193648						
C-O	3.35	0.298507												
O-N	2.071	0.482859												
N-O	8.478	0.117952												
N-O	9.243	0.10819												
C-H	5.397	0.185288												
C-H	5.398	0.185254												

Table S5: Local force constants calculated by LMODEA-nano (B3LYP/6-31G*) for the different bond types listed in Table S4.

Bond Type	No. of bonds in sample	Local Force Constant / mDyn/Å			
		Min value	Max value	Mean	Std. Dev.
$C–NO_2$	50	1.862	5.645	3.969	0.755
$N–NO_2$	25	2.51	5.049	3.302	0.571
$O–NO_2$	13	1.689	2.181	1.997	0.146
$N–NH_2$	1	4.747	4.747	4.747	0
$C_{aliphatic}–N_{aromatic/ring}$	6	4.22	4.89	4.582	0.235
$(C–N)_{aliphatic}$	43	3.337	4.715	4.051	0.357
$(C–O)_{aliphatic}$	13	3.165	3.603	3.392	0.128
C–P	3	2.279	2.356	2.319	0.032
$C_{aromatic}–N_{aliphatic}$	3	5.75	5.99	5.85	0.102
$(N–N)_{aromatic}$	33	4.436	8.142	6.101	1.039
$(C\text{-}C)_{aromatic}$	69	4.792	8.155	6.210	0.755
$C_{aromatic}–N_{aromatic/ring}$	43	5.77	9.685	7.047	0.770
N-H	30	6.473	8.433	7.107	0.479
$C–NH_2$	9	6.13	8.07	7.318	0.827
N–O (in NO_2)	175	8.087	13.849	9.873	0.916

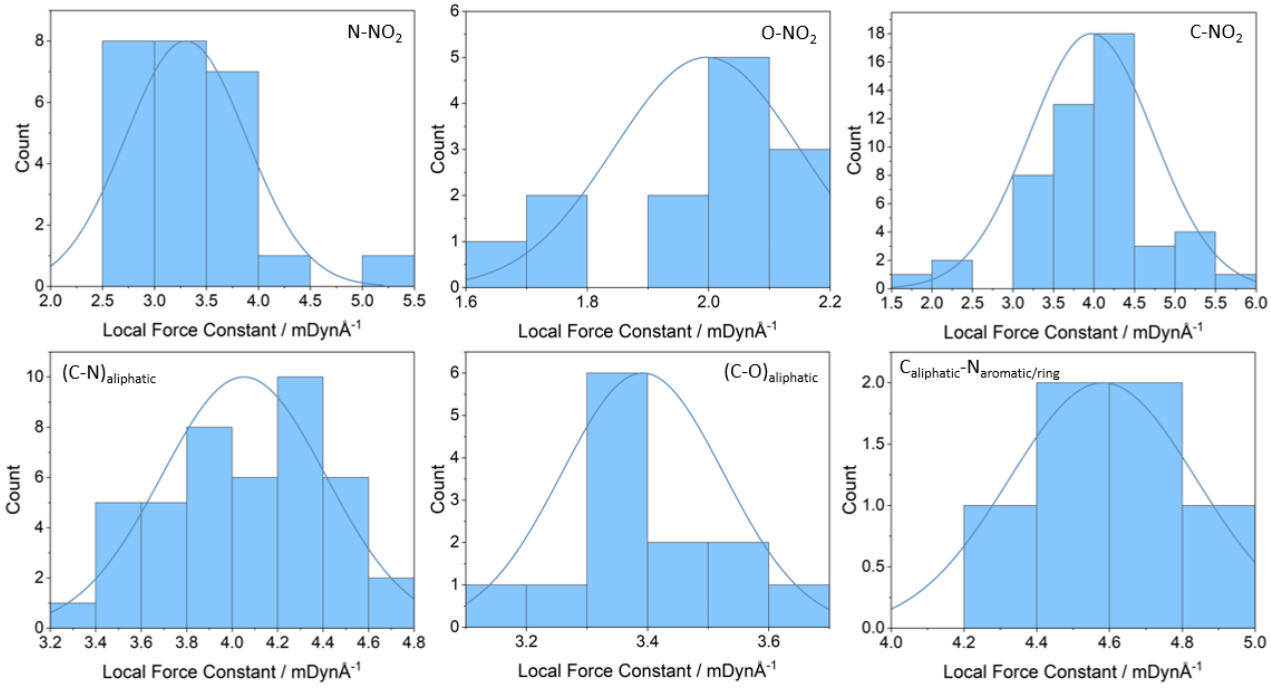


Figure S5: Local force constant analysis for bond types in EM test set (calculated at B3LYP/6-31G*).

S7: Keir Molecular Flexibility calculation

The following python code converts a SMILES string (given in the input file 'listofsmiles_short.txt'), calculates the one-bond ($^{1}\kappa$) and two-bond ($^{2}\kappa$) Kappa shape indices, and normalises their product with respect to the number of heavy atoms present in the string.

```
#!/usr/bin/env python3
# -*- coding: utf-8 -*-
"""
Created on Fri Jan 15 15:58:06 2021

@author: jackhemingway
"""
import rdkit

from rdkit import Chem
from rdkit.Chem import Descriptors
from rdkit.Chem import AllChem
from collections import OrderedDict
import numpy as np
from rdkit.Chem import GraphDescriptors as gdesc


with open('listofsmiles_short.txt') as f:
    lines = f.readlines()

finalvalues = []
for line in lines:

    line=Chem.MolFromSmiles(line)
    K1=gdesc.Kappa1(line)
    K2=gdesc.Kappa2(line)
    heavy_atom_count=Descriptors.HeavyAtomCount(line)
    TOT=(K1*K2)/heavy_atom_count
    print(TOT)
    finalvalues.append(TOT)

with open('outputvalues.txt', 'w') as f:
    for value in finalvalues:
        f.write(str(value) + '\n')

```

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