Electronic Supplementary Material (ESI) for ChemComm.

Quantum Tunneling Instability of the Mythical Hexazine and Pentazine

Supporting Information

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Theoretical method

Table S1. $N_6(D_2)$ to 3 N_2 decomposition energies in kJ mol^{-1} (not including ZPE) with selected methods

Optimization method	$DE^{‡}$
HCTH/Def2-TZVP	5.0
TPSSH/Def2-TZVP	0.8
MN15/Def2-TZVP	8.6
PBE0/Def2-TZVP	4.8
M062X/Def2-TZVP	0.1
CCSD/cc-PVTZ	Unstable
DLPNO-CCSD(T)/cc-PVTZ	Unstable

Table S2. Static correlation diagnostic

	T1		%TAE(T)	
	React.	TS	React.	TS
Hexazine	0.0260	0.0246	9.5	9.3
Pentazine	0.0144	0.0218	5.2	5.8

Table S3. Semiclassical (CVT) and tunneling included (CVT+SCT) decomposition rate constants in s^{-1}.

Hexazine (N_6)

T(K)	CVT	CVT+SCT
4	3.55E-47	3.58E+10
6	7.24E-28	3.58E+10
8	3.56E-18	3.58E+10
10	2.45E-12	3.58E+10
20	1.48E+00	3.59E+10
30	1.50E+04	3.70E+10
40	1.65E+06	3.99E+10
50	2.91E+07	4.50E+10
75	1.50E+09	6.86E+10
77.36	1.92E+09	7.18E+10
100	1.16E+10	1.12E+11
125	4.16E+10	1.78E+11
150	9.98E+10	2.70E+11
175	1.90E+11	3.87E+11
194.7	2.83E+11	4.91E+11
200	3.11E+11	5.23E+11
225	4.61E+11	6.87E+11
250	6.36E+11	8.67E+11
273.15	8.17E+11	1.05E+12
275	8.32E+11	1.06E+12
298.15	1.03E+12	1.25E+12
300	1.05E+12	1.26E+12
325	1.27E+12	1.47E+12
350	1.51E+12	1.69E+12
373.15	1.74E+12	1.88E+12
375	1.75E+12	1.90E+12
400	2.00E+12	2.11E+12

Hexazine ($^{15}N_6$)

T(K)	CVT	CVT+SCT
4	2.17E+10	2.54E+10
6	2.17E+10	2.54E+10
8	2.17E+10	2.54E+10
10	2.17E+10	2.54E+10
20	2.18E+10	2.55E+10
30	2.26E+10	2.64E+10
40	2.48E+10	2.88E+10
50	2.85E+10	3.29E+10
75	4.65E+10	5.20E+10
77.36	4.90E+10	5.46E+10
100	8.05E+10	8.73E+10
125	1.35E+11	1.43E+11
150	2.12E+11	2.25E+11
175	3.12E+11	3.36E+11
194.7	4.07E+11	4.41E+11
200	4.35E+11	4.71E+11
225	5.77E+11	6.26E+11
250	7.37E+11	7.97E+11
273.15	8.97E+11	9.68E+11
275	9.10E+11	9.82E+11
298.15	1.08E+12	1.16E+12
300	1.09E+12	1.18E+12
325	1.29E+12	1.38E+12
350	1.48E+12	1.58E+12
373.15	1.67E+12	1.78E+12
375	1.69E+12	1.79E+12
400	1.89E+12	2.00E+12

Pentazine (N_5CH)

T(K)	CVT	CVT+SCT
4	3.42E-253	3.91E+04
5	2.10E-200	3.91E+04
6	3.38E-165	3.91E+04
8	3.66E-121	3.91E+04
10	1.01E-94	3.91E+04
20	9.97E-42	3.91E+04
30	5.48E-24	3.92E+04
40	4.43E-15	3.96E+04
50	1.03E-09	4.10E+04
75	1.67E-02	5.33E+04
77.36	4.62E-02	5.55E+04
100	7.40E+01	1.01E+05
125	1.21E+04	3.72E+05
150	3.79E+05	2.45E+06
175	4.57E+06	1.53E+07
194.7	2.12E+07	5.27E+07
200	3.04E+07	7.15E+07
225	1.36E+08	2.57E+08
250	4.56E+08	7.50E+08
273.15	1.17E+09	1.74E+09
275	1.25E+09	1.85E+09
298.15	2.76E+09	3.81E+09
300	2.92E+09	4.02E+09
325	6.06E+09	7.84E+09
350	1.14E+10	1.41E+10
373.15	1.91E+10	2.27E+10
375	1.98E+10	2.35E+10
400	3.24E+10	3.71E+10

Pentazine ($^{15}N_5CH$)

T(K)	CVT	CVT+SCT
4	1.84E-257	1.39E+04
5	8.07E-204	1.39E+04
6	4.82E-168	1.39E+04
8	2.69E-123	1.39E+04
10	1.99E-96	1.39E+04
20	1.40E-42	1.39E+04
30	1.48E-24	1.39E+04
40	1.66E-15	1.41E+04
50	4.70E-10	1.47E+04
75	9.89E-03	1.97E+04
77.36	2.78E-02	2.07E+04
100	5.01E+01	4.13E+04
125	8.88E+03	1.99E+05
150	2.93E+05	1.59E+06
175	3.68E+06	1.10E+07
194.7	1.74E+07	4.03E+07
200	2.52E+07	5.52E+07
225	1.15E+08	2.07E+08
250	3.93E+08	6.22E+08
273.15	1.02E+09	1.47E+09
275	1.09E+09	1.57E+09
298.15	2.44E+09	3.28E+09
300	2.59E+09	3.47E+09
325	5.42E+09	6.86E+09
350	1.03E+10	1.24E+10
373.15	1.73E+10	2.03E+10
375	1.80E+10	2.10E+10
400	2.96E+10	3.34E+10

Pentazine (N_5CD)

T(K)	CVT	CVT+SCT
4	1.62E-255	3.02E+04
5	2.90E-202	3.02E+04
6	9.51E-167	3.02E+04
8	2.51E-122	3.02E+04
10	1.19E-95	3.02E+04
20	3.41E-42	3.02E+04
30	2.67E-24	3.03E+04
40	2.58E-15	3.07E+04
50	6.70E-10	3.20E+04
75	1.25E-02	4.25E+04
77.36	3.48E-02	4.44E+04
100	5.94E+01	8.26E+04
125	1.02E+04	3.17E+05
150	3.26E+05	2.12E+06
175	4.02E+06	1.34E+07
194.7	1.89E+07	4.70E+07
200	2.72E+07	6.38E+07
225	1.23E+08	2.33E+08
250	4.17E+08	6.85E+08
273.15	1.08E+09	1.60E+09
275	1.15E+09	1.71E+09
298.15	2.56E+09	3.53E+09
300	2.72E+09	3.73E+09
325	5.66E+09	7.32E+09
350	1.07E+10	1.32E+10
373.15	1.80E+10	2.14E+10
375	1.87E+10	2.21E+10
400	3.07E+10	3.51E+10

Pentazine ($N_5{}^{13}CH$)

T(K)	CVT	CVT+SCT
4	9.03E-254	3.44E+04
5	7.24E-201	3.44E+04
6	1.39E-165	3.44E+04
8	1.88E-121	3.44E+04
10	5.95E-95	3.44E+04
20	7.63E-42	3.44E+04
30	4.58E-24	3.44E+04
40	3.87E-15	3.48E+04
50	9.27E-10	3.61E+04
75	1.55E-02	4.72E+04
77.36	4.31E-02	4.92E+04
100	7.01E+01	9.08E+04
125	1.16E+04	3.54E+05
150	3.65E+05	2.32E+06
175	4.44E+06	1.46E+07
194.7	2.06E+07	5.09E+07
200	2.96E+07	6.91E+07
225	1.32E+08	2.50E+08
250	4.47E+08	7.32E+08
273.15	1.14E+09	1.70E+09
275	1.23E+09	1.81E+09
298.15	2.71E+09	3.73E+09
300	2.88E+09	3.94E+09
325	5.97E+09	7.70E+09
350	1.12E+10	1.38E+10
373.15	1.88E+10	2.23E+10
375	1.96E+10	2.32E+10
400	3.20E+10	3.66E+10

Pentazine ($^{15}N_5{}^{12}CD$)

T(K)	CVT	CVT+SCT
4	2.30E-260	9.52E+03
5	3.84E-206	9.52E+03
6	5.59E-170	9.52E+03
8	9.48E-125	9.52E+03
10	1.37E-97	9.52E+03
20	3.66E-43	9.52E+03
30	6.04E-25	9.55E+03
40	8.47E-16	9.71E+03
50	2.75E-10	1.02E+04
75	6.90E-03	1.41E+04
77.36	1.96E-02	1.48E+04
100	3.81E+01	3.07E+04
125	7.13E+03	1.48E+05
150	2.44E+05	1.31E+06
175	3.14E+06	9.36E+06
194.7	1.51E+07	3.47E+07
200	2.19E+07	4.78E+07
225	1.02E+08	1.82E+08
250	3.53E+08	5.55E+08
273.15	9.23E+08	1.33E+09
275	9.91E+08	1.42E+09
298.15	2.23E+09	2.99E+09
300	2.37E+09	3.16E+09
325	5.00E+09	6.30E+09
350	9.54E+09	1.15E+10
373.15	1.62E+10	1.88E+10
375	1.68E+10	1.95E+10
400	2.77E+10	3.12E+10

$N(Me)_2$-Pentazine

T(K)	CVT	CVT+SCT
4		
5		
6		
8	1.08E-265	1.36E-06
10	2.31E-210	1.37E-06
20	1.15E-99	1.46E-06
30	9.08E-63	1.56E-06
40	2.51E-44	1.69E-06
50	2.89E-33	1.88E-06
75	1.66E-18	3.00E-06
77.36	1.32E-17	3.19E-06
100	4.20E-11	7.75E-06
125	1.22E-06	1.06E-04
150	1.21E-03	1.15E-02
175	1.72E-01	7.45E-01
194.7	3.58E+00	1.09E+01
200	7.33E+00	2.08E+01
225	1.39E+02	3.04E+02
250	1.48E+03	2.74E+03
273.15	9.19E+03	1.51E+04
275	1.05E+04	1.71E+04
298.15	4.85E+04	7.22E+04
300	5.42E+04	8.03E+04
325	2.20E+05	3.03E+05
350	7.36E+05	9.57E+05
373.15	1.96E+06	2.44E+06
375	2.11E+06	2.62E+06
400	5.34E+06	6.36E+06

NH_2-Pentazine

T(K)	CVT	CVT+SCT
4		
5		
6	4.38E-285	2.06E-02
8	4.42E-211	2.06E-02
10	1.18E-166	2.06E-02
20	1.06E-77	2.07E-02
30	5.61E-48	2.13E-02
40	4.38E-33	2.29E-02
50	3.92E-24	2.58E-02
75	3.72E-12	4.31E-02
77.36	2.01E-11	4.61E-02
100	3.98E-06	1.14E-01
125	1.76E-02	9.91E-01
150	5.01E+00	3.60E+01
175	2.95E+02	1.02E+03
194.7	3.58E+03	9.13E+03
200	6.46E+03	1.55E+04
225	7.31E+04	1.41E+05
250	5.19E+05	8.61E+05
273.15	2.35E+06	3.53E+06
275	2.62E+06	3.92E+06
298.15	9.33E+06	1.29E+07
300	1.02E+07	1.41E+07
325	3.28E+07	4.25E+07
350	8.96E+07	1.10E+08
373.15	2.03E+08	2.40E+08
375	2.15E+08	2.54E+08
400	4.66E+08	5.32E+08

OH-Pentazine

T(K)	CVT	CVT+SCT
4		
5		
6	2.23E-289	1.50E-02
8	2.67E-214	1.50E-02
10	3.13E-169	1.50E-02
20	5.48E-79	1.50E-02
30	7.85E-49	1.53E-02
40	1.02E-33	1.61E-02
50	1.24E-24	1.77E-02
75	1.79E-12	2.81E-02
77.36	9.91E-12	2.99E-02
100	2.36E-06	7.20E-02
125	1.18E-02	6.66E-01
150	3.61E+00	2.56E+01
175	2.24E+02	7.68E+02
194.7	2.80E+03	7.12E+03
200	5.10E+03	1.22E+04
225	5.94E+04	1.14E+05
250	4.32E+05	7.19E+05
273.15	1.99E+06	3.01E+06
275	2.23E+06	3.34E+06
298.15	8.04E+06	1.12E+07
300	8.84E+06	1.23E+07
325	2.87E+07	3.76E+07
350	7.93E+07	9.91E+07
373.15	1.81E+08	2.18E+08
375	1.93E+08	2.32E+08
400	4.22E+08	4.90E+08

OMe-Pentazine

T(K)	CVT	CVT+SCT
4		
5	5.47E-290	8.40E-01
6	7.46E-240	8.40E-01
8	3.69E-177	8.40E-01
10	1.60E-139	8.40E-01
20	3.88E-64	8.44E-01
30	6.14E-39	8.76E-01
40	2.63E-26	9.57E-01
50	1.04E-18	1.10E+00
75	1.56E-08	1.98E+00
77.36	6.53E-08	2.14E+00
100	2.09E-03	6.54E+00
125	2.65E+00	9.53E+01
150	3.26E+02	2.50E+03
175	1.05E+04	4.08E+04
194.7	8.86E+04	2.51E+05
200	1.47E+05	3.90E+05
225	1.17E+06	2.45E+06
250	6.24E+06	1.12E+07
273.15	2.27E+07	3.66E+07
275	2.50E+07	3.99E+07
298.15	7.42E+07	1.10E+08
300	8.04E+07	1.18E+08
325	2.18E+08	3.00E+08
350	5.18E+08	6.77E+08
373.15	1.05E+09	1.32E+09
375	1.10E+09	1.38E+09
400	2.15E+09	2.60E+09

OEt-Pentazine

T(K)	CVT	CVT+SCT
4		
5	3.68E-236	2.14E+02
6	5.36E-195	2.14E+02
8	1.61E-143	2.14E+02
10	1.31E-112	2.14E+02
20	1.10E-50	2.19E+02
30	5.62E-30	2.38E+02
40	1.37E-19	2.74E+02
50	2.46E-13	3.28E+02
75	6.02E-05	6.03E+02
77.36	1.96E-04	6.47E+02
100	1.04E+00	1.59E+03
125	3.88E+02	1.00E+04
150	2.11E+04	1.20E+05
175	3.82E+05	1.17E+06
194.7	2.26E+06	5.29E+06
200	3.44E+06	7.62E+06
225	1.95E+07	3.53E+07
250	7.98E+07	1.26E+08
273.15	2.37E+08	3.40E+08
275	2.57E+08	3.66E+08
298.15	6.42E+08	8.53E+08
300	6.87E+08	9.08E+08
325	1.60E+09	1.99E+09
350	3.32E+09	3.94E+09
373.15	6.01E+09	6.88E+09
375	6.29E+09	7.18E+09
400	1.11E+10	1.22E+10

Me-Pentazine

T(K)	CVT	CVT+SCT
4	5.52E-236	6.51E+03
5	1.22E-186	6.51E+03
6	9.89E-154	6.51E+03
8	1.43E-112	6.53E+03
10	7.43E-88	6.56E+03
20	2.29E-38	6.99E+03
30	7.55E-22	7.69E+03
40	1.39E-13	8.66E+03
50	1.27E-08	1.00E+04
75	5.42E-02	1.70E+04
77.36	1.38E-01	1.81E+04
100	1.18E+02	4.29E+04
125	1.25E+04	2.16E+05
150	2.89E+05	1.48E+06
175	2.81E+06	8.28E+06
194.7	1.14E+07	2.61E+07
200	1.59E+07	3.45E+07
225	6.22E+07	1.12E+08
250	1.89E+08	2.97E+08
273.15	4.44E+08	6.41E+08
275	4.73E+08	6.78E+08
298.15	9.76E+08	1.31E+09
300	1.03E+09	1.36E+09
325	2.00E+09	2.50E+09
350	3.57E+09	4.26E+09
373.15	5.72E+09	6.58E+09
375	5.93E+09	6.80E+09
400	9.27E+09	1.03E+10

F-Pentazine

T(K)	CVT	CVT+SCT
4		
5		
6	5.51E-263	1.78E-01
8	1.66E-194	1.78E-01
10	2.13E-153	1.78E-01
20	4.51E-71	1.78E-01
30	1.49E-43	1.81E-01
40	9.31E-30	1.89E-01
50	1.86E-21	2.09E-01
75	2.45E-10	3.37E-01
77.36	1.18E-09	3.60E-01
100	9.84E-05	9.32E-01
125	2.42E-01	9.80E+00
150	4.61E+01	3.07E+02
175	2.04E+03	6.85E+03
194.7	2.07E+04	5.20E+04
200	3.59E+04	8.47E+04
225	3.42E+05	6.51E+05
250	2.11E+06	3.48E+06
273.15	8.58E+06	1.29E+07
275	9.51E+06	1.42E+07
298.15	3.09E+07	4.29E+07
300	3.37E+07	4.65E+07
325	9.94E+07	1.29E+08
350	2.53E+08	3.13E+08
373.15	5.40E+08	6.45E+08
375	5.71E+08	6.81E+08
400	1.17E+09	1.35E+09

Cl-Pentazine

T(K)	CVT	CVT+SCT
4	6.32E-278	1.09E+03
5	3.40E-220	1.09E+03
6	1.08E-181	1.09E+03
8	1.54E-133	1.09E+03
10	1.26E-104	1.09E+03
20	1.08E-46	1.09E+03
30	2.60E-27	1.13E+03
40	1.37E-17	1.23E+03
50	9.71E-12	1.40E+03
75	6.75E-04	2.33E+03
77.36	2.04E-03	2.49E+03
100	6.13E+00	5.90E+03
125	1.54E+03	3.49E+04
150	6.43E+04	3.54E+05
175	9.55E+05	2.87E+06
194.7	5.01E+06	1.15E+07
200	7.42E+06	1.62E+07
225	3.74E+07	6.67E+07
250	1.39E+08	2.16E+08
273.15	3.82E+08	5.44E+08
275	4.11E+08	5.82E+08
298.15	9.65E+08	1.28E+09
300	1.03E+09	1.36E+09
325	2.25E+09	2.81E+09
350	4.45E+09	5.30E+09
373.15	7.75E+09	8.91E+09
375	8.08E+09	9.27E+09
400	1.37E+10	1.52E+10

Br-Pentazine

T(K)	CVT	CVT+SCT
4	2.26E-257	4.57E+03
5	9.41E-204	4.57E+03
6	5.42E-168	4.57E+03
8	2.89E-123	4.57E+03
10	2.08E-96	4.57E+03
20	1.38E-42	4.62E+03
30	1.40E-24	4.83E+03
40	1.50E-15	5.30E+03
50	4.07E-10	6.07E+03
75	7.82E-03	1.02E+04
77.36	2.18E-02	1.09E+04
100	3.72E+01	2.54E+04
125	6.34E+03	1.32E+05
150	2.03E+05	1.10E+06
175	2.49E+06	7.54E+06
194.7	1.17E+07	2.71E+07
200	1.68E+07	3.70E+07
225	7.56E+07	1.37E+08
250	2.56E+08	4.05E+08
273.15	6.58E+08	9.52E+08
275	7.05E+08	1.01E+09
298.15	1.56E+09	2.10E+09
300	1.66E+09	2.22E+09
325	3.45E+09	4.36E+09
350	6.50E+09	7.86E+09
373.15	1.09E+10	1.27E+10
375	1.13E+10	1.32E+10
400	1.85E+10	2.09E+10

CF_3-Pentazine

T(K)	CVT	CVT+SCT
4	1.45E-184	5.68E+05
5	1.64E-145	5.69E+05
6	1.82E-119	5.70E+05
8	6.91E-87	5.73E+05
10	2.51E-67	5.79E+05
20	3.62E-28	6.28E+05
30	4.32E-15	7.10E+05
40	1.54E-08	8.27E+05
50	1.35E-04	9.86E+05
75	2.65E+01	1.71E+06
77.36	5.60E+01	1.82E+06
100	1.26E+04	3.76E+06
125	5.38E+05	1.16E+07
150	6.81E+06	4.28E+07
175	4.30E+07	1.46E+08
194.7	1.34E+08	3.41E+08
200	1.75E+08	4.21E+08
225	5.31E+08	1.03E+09
250	1.31E+09	2.19E+09
273.15	2.64E+09	3.98E+09
275	2.78E+09	4.17E+09
298.15	5.02E+09	6.98E+09
300	5.25E+09	7.25E+09
325	9.06E+09	1.16E+10
350	1.45E+10	1.77E+10
373.15	2.14E+10	2.50E+10
375	2.20E+10	2.57E+10
400	3.18E+10	3.58E+10

CN-Pentazine

T(K)	CVT	CVT+SCT
4	3.13E-227	1.09E+05
5	1.22E-179	1.09E+05
6	6.70E-148	1.09E+05
8	3.38E-108	1.09E+05
10	2.35E-84	1.09E+05
20	1.46E-36	1.09E+05
30	1.46E-20	1.13E+05
40	1.57E-12	1.21E+05
50	1.07E-07	1.35E+05
75	3.21E-01	2.11E+05
77.36	7.99E-01	2.22E+05
100	5.93E+02	4.47E+05
125	5.65E+04	1.59E+06
150	1.22E+06	8.18E+06
175	1.12E+07	3.89E+07
194.7	4.40E+07	1.14E+08
200	6.08E+07	1.48E+08
225	2.30E+08	4.50E+08
250	6.79E+08	1.15E+09
273.15	1.57E+09	2.40E+09
275	1.67E+09	2.53E+09
298.15	3.38E+09	4.77E+09
300	3.56E+09	5.00E+09
325	6.82E+09	9.01E+09
350	1.20E+10	1.51E+10
373.15	1.90E+10	2.30E+10
375	1.96E+10	2.38E+10
400	3.04E+10	3.56E+10

NO_2-Pentazine

T(K)	CVT	CVT+SCT
4	1.05E-212	6.33E+04
5	5.09E-168	6.33E+04
6	3.24E-138	6.33E+04
8	6.20E-101	6.33E+04
10	1.52E-78	6.34E+04
20	1.13E-33	6.60E+04
30	1.15E-18	7.30E+04
40	3.88E-11	8.46E+04
50	1.32E-06	1.02E+05
75	1.61E+00	1.87E+05
77.36	3.79E+00	2.01E+05
100	1.93E+03	4.87E+05
125	1.44E+05	2.25E+06
150	2.67E+06	1.32E+07
175	2.22E+07	6.39E+07
194.7	8.18E+07	1.84E+08
200	1.11E+08	2.38E+08
225	4.00E+08	7.06E+08
250	1.13E+09	1.75E+09
273.15	2.52E+09	3.58E+09
275	2.68E+09	3.77E+09
298.15	5.28E+09	6.95E+09
300	5.55E+09	7.28E+09
325	1.04E+10	1.27E+10
350	1.79E+10	2.08E+10
373.15	2.78E+10	3.12E+10
375	2.88E+10	3.22E+10
400	4.38E+10	4.75E+10

LCT (Large Curvature Tunneling) test for hexazine and pentazine decomposition.

To examine the impact of LCT on the decomposition rate, we tested its performance using the MN15 functional, but with a smaller basis set and larger steps (sstep=0.005). The results showed that for both pentazine and hexazine, SCT is the preferred path for QTI.

Pentazine (MN15/6-31G)

T(K)	CVT	CVT+SCT	CVT+LCG4
4	6.06E-103	2.20E+08	1.46E+08
5	3.28E-80	2.20E+08	1.46E+08
6	4.86E-65	2.20E+08	1.46E+08
8	4.73E-46	2.20E+08	1.46E+08
10	1.23E-34	2.20E+08	1.46E+08
20	1.07E-11	2.20E+08	1.46E+08
30	5.63E-04	2.20E+08	1.47E+08
40	4.47E+00	2.24E+08	1.49E+08
50	1.04E+03	2.37E+08	1.59E+08
75	1.69E+06	3.73E+08	2.65E+08
77.36	2.68E+06	4.01E+08	2.88E+08
100	7.67E+07	1.01E+09	8.16E+08
125	8.07E+08	3.39E+09	2.99E+09
150	4.05E+09	1.00E+10	9.23E+09
175	1.32E+10	2.44E+10	2.31E+10
194.7	2.74E+10	4.39E+10	4.20E+10
200	3.26E+10	5.06E+10	4.86E+10
225	6.70E+10	9.25E+10	8.96E+10
250	1.21E+11	1.53E+11	1.49E+11
273.15	1.90E+11	2.28E+11	2.23E+11
275	1.97E+11	2.35E+11	2.30E+11
298.15	2.89E+11	3.31E+11	3.25E+11
300	2.98E+11	3.39E+11	3.33E+11
325	4.25E+11	4.66E+11	4.59E+11
350	5.78E+11	6.14E+11	6.06E+11
373.15	7.43E+11	7.70E+11	7.61E+11
375	7.57E+11	7.83E+11	7.74E+11
400	9.60E+11	9.70E+11	9.61E+11

Hexazine (MN15/Def2-SVP)

T(K)	CVT	CVT+SCT	CVT+LCG4
4	7.01E-119	3.24E+08	2.66E+08
5	5.35E-93	2.96E+08	2.43E+08
6	9.80E-76	2.73E+08	2.25E+08
8	3.85E-54	2.41E+08	1.98E+08
10	3.59E-41	2.20E+08	1.81E+08
20	3.80E-15	1.83E+08	1.51E+08
30	8.41E-06	6.76E+08	5.57E+08
40	2.15E-01	7.41E+08	6.13E+08
50	9.96E+01	8.36E+08	6.95E+08
75	3.99E+05	1.29E+09	1.10E+09
77.36	6.65E+05	1.36E+09	1.17E+09
100	2.74E+07	2.42E+09	2.16E+09
125	2.17E+08	3.16E+09	2.93E+09
150	1.26E+09	7.03E+09	6.72E+09
175	4.50E+09	1.47E+10	1.42E+10
194.7	9.88E+09	2.45E+10	2.40E+10
200	1.19E+10	2.79E+10	2.73E+10
225	2.57E+10	4.84E+10	4.77E+10
250	4.80E+10	7.76E+10	7.69E+10
273.15	7.79E+10	1.14E+11	1.13E+11
275	8.07E+10	1.17E+11	1.16E+11
298.15	1.22E+11	1.62E+11	1.61E+11
300	1.25E+11	1.66E+11	1.65E+11
325	1.82E+11	2.27E+11	2.25E+11
350	2.52E+11	2.97E+11	2.96E+11
373.15	3.29E+11	3.72E+11	3.70E+11
375	3.36E+11	3.78E+11	3.77E+11
400	4.32E+11	4.69E+11	4.68E+11

Kinetic Isotope Effect from CVT+SCT rate constants

Table S4. Hexazine KIE

T(K)	$^{14}N_6/^{15}N_6$
4	1.41
6	1.41
8	1.41
10	1.41
20	1.41
30	1.40
40	1.39
50	1.37
75	1.32
77.36	1.32
100	1.28
125	1.24
150	1.20
175	1.15
194.7	1.11
200	1.11
225	1.10
250	1.09
273.15	1.08
275	1.08
298.15	1.08
300	1.07
325	1.07
350	1.07
373.15	1.06
375	1.06
400	1.06

Table S5. Pentazine- KIE

T(K)	N_5CH/N_5CD	$N_5{}^{12}CH/N_5{}^{13}CH$	$^{14}N_5CH/^{15}N_5CH$	$^{14}N_5{}^{12}CH/^{15}N_5{}^{13}CD$
4	1.29	1.14	2.81	4.11
5	1.29	1.14	2.81	4.11
6	1.29	1.14	2.81	4.11
8	1.29	1.14	2.81	4.11
10	1.29	1.14	2.81	4.11
20	1.29	1.14	2.81	4.11
30	1.29	1.14	2.82	4.10
40	1.29	1.14	2.81	4.08
50	1.28	1.14	2.79	4.02
75	1.25	1.13	2.71	3.78
77.36	1.25	1.13	2.68	3.75
100	1.22	1.11	2.45	3.29
125	1.17	1.05	1.87	2.51
150	1.16	1.06	1.54	1.87
175	1.14	1.05	1.39	1.63
194.7	1.12	1.04	1.31	1.52
200	1.12	1.03	1.30	1.50
225	1.10	1.03	1.24	1.41
250	1.09	1.02	1.21	1.35
273.15	1.09	1.02	1.18	1.31
275	1.08	1.02	1.18	1.30
298.15	1.08	1.02	1.16	1.27
300	1.08	1.02	1.16	1.27
325	1.07	1.02	1.14	1.24
350	1.07	1.02	1.14	1.23
373.15	1.06	1.02	1.12	1.21
375	1.06	1.01	1.12	1.21
400	1.06	1.01	1.11	1.19

Correlation between $\Delta E^{\ddagger}$+ZPE and the Swain-Lupton resonance parameter (R) / Hammet sigma-para

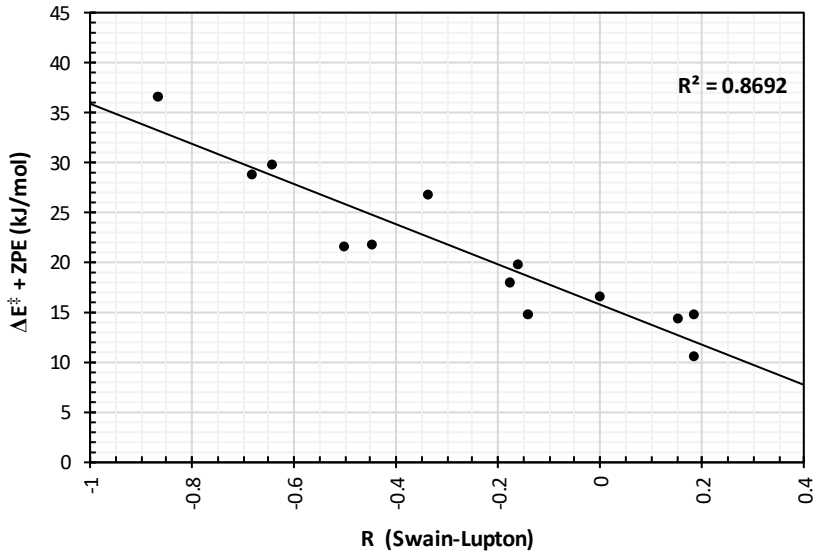

Figure S1. $\Delta E^{\ddagger}$+ZPE vs. Swain-Lupton R parameter, using the Hammet equation substituents for replacing the pentazine hydrogen (see table 2 in the main text).

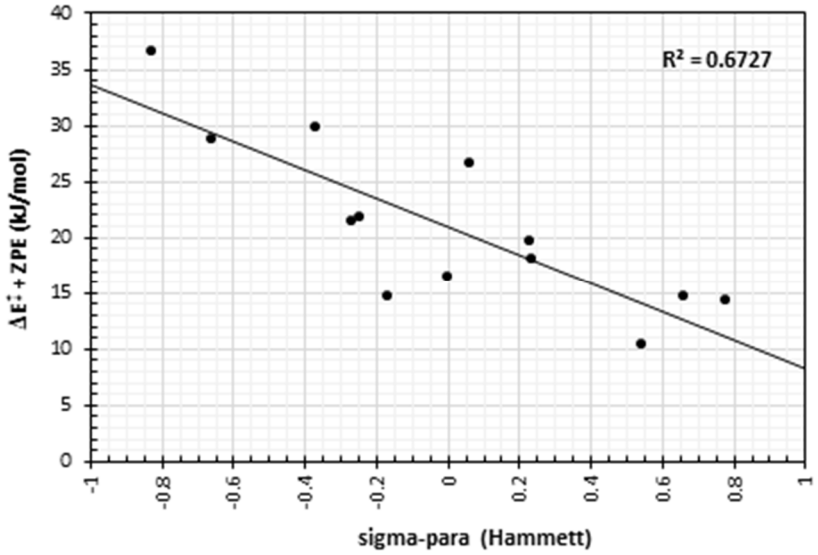

Figure S2. $\Delta E^{\ddagger}$+ZPE vs. Hammett sigma-para parameter.

Free energy along the reaction path coordinates

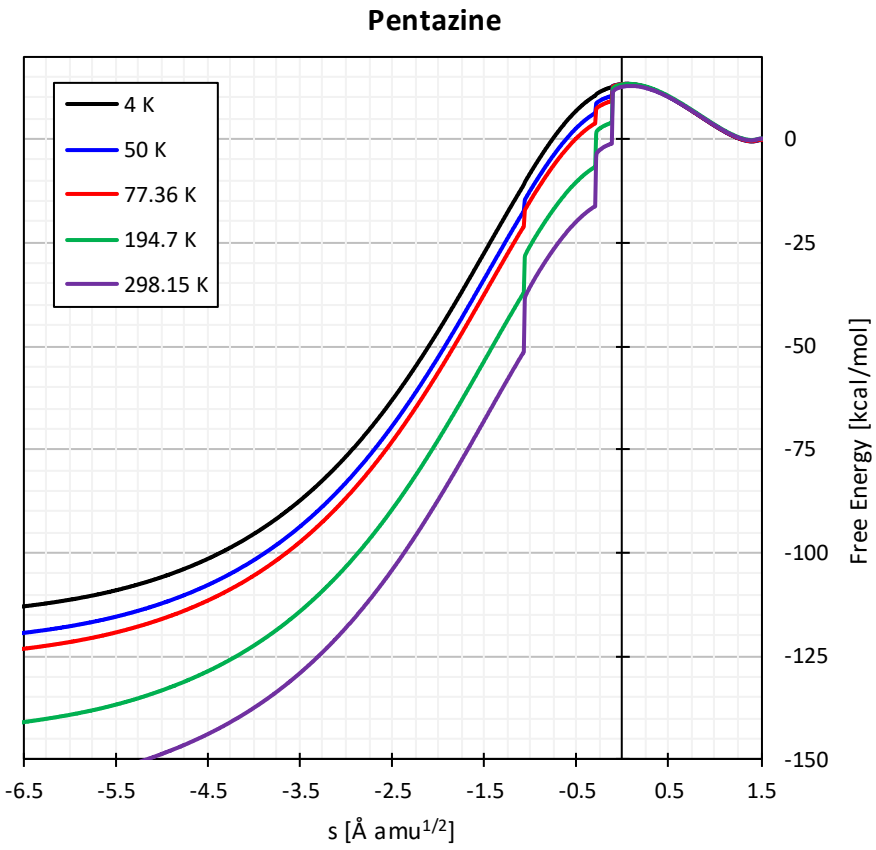

Figure S3. Free energy vs. reaction path coordinate of pentazine, in various temperatures.

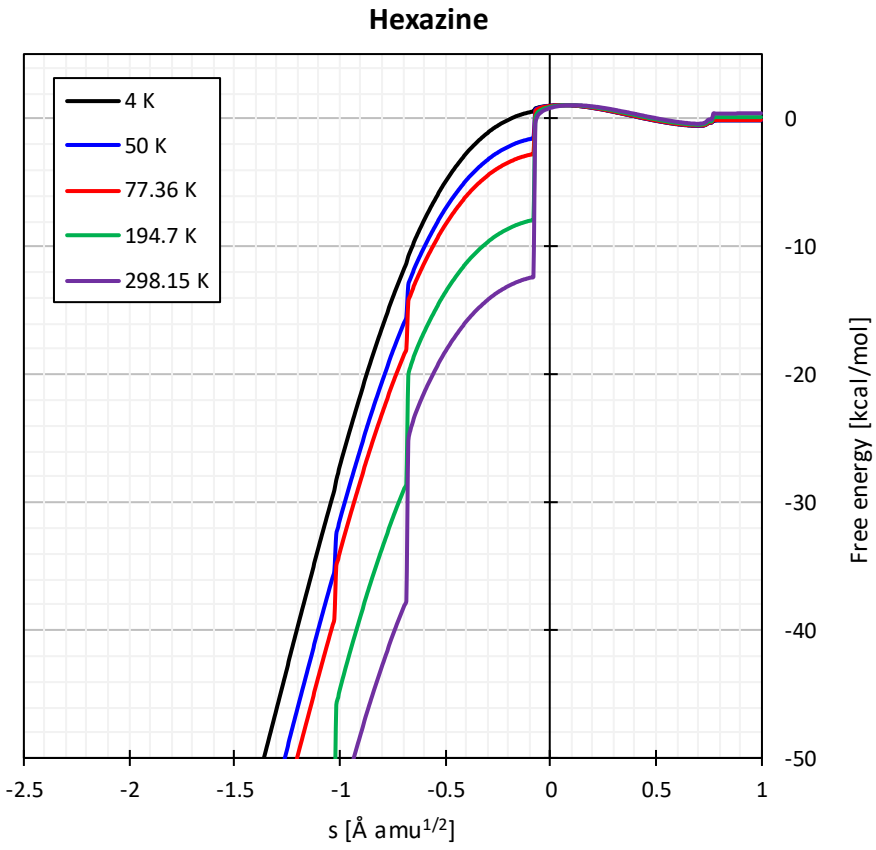

Figure S4. Free energy vs. reaction path coordinate of hexazine, in various temperatures.

XYZ optimized geometries at the MN15/Def2-TZVP level.

Hexazine (N_6)

Reactant

N	1.127765	0.640791	0.133137
N	1.127757	-0.640801	-0.133149
N	0.000006	1.287474	0.000126
N	-0.000006	-1.287474	-0.000125
N	-1.127759	0.640827	-0.133012
N	-1.127763	-0.640817	0.133025

Transition state

N	-1.192705	-0.589226	0.164252
N	-1.192745	0.589170	-0.164158
N	0.073493	-1.320175	0.005447
N	0.073426	1.320176	-0.005438
N	1.119276	-0.713914	-0.145550
N	1.119254	0.713968	0.145447

Pentazine (N_5CH)

Reactant

C	0.000000	0.000000	-1.250593
N	0.000000	1.171841	-0.631606
N	-0.000000	-1.171841	-0.631606
N	0.000000	1.145996	0.675704
N	-0.000000	-1.145996	0.675704
N	0.000000	-0.000000	1.317064
H	0.000000	0.000000	-2.333265

Transition state

C	-1.145320	-0.640051	0.090252
N	-0.193972	-1.407692	-0.103049
N	-1.077228	0.849699	-0.024552
N	1.260437	-0.682346	-0.015609
N	-0.056156	1.444900	-0.068409
N	1.357572	0.482693	0.098958
H	-2.162653	-0.970476	0.247118

<u>Pentazine substituents</u>

$N(Me)_2$-Pentazine

Reactant

C	-0.013729	0.092859	0.000000
N	-0.057114	-0.561699	1.178834
N	-0.057114	-0.561699	-1.178834
N	-0.057114	-1.854546	1.140179
N	-0.057114	-1.854546	-1.140179
N	-0.028246	-2.512819	0.000000
N	0.057039	1.429121	0.000000
C	0.080145	2.201455	-1.227375
H	0.972078	2.831375	-1.244286
H	0.086580	1.540220	-2.086884
H	-0.799525	2.847759	-1.274037
C	0.080145	2.201455	1.227375
H	-0.799525	2.847759	1.274037
H	0.086580	1.540220	2.086884
H	0.972078	2.831375	1.244286

Transition state

C	0.134274	-0.148810	-0.035269
N	-0.478272	-1.234270	0.048883
N	-0.524679	1.219742	-0.118434
N	-2.121710	-1.116323	0.081928
N	-1.679997	1.407952	-0.083332
N	-2.679624	-0.094233	0.062280
N	1.477574	-0.013751	-0.127316
C	2.201734	1.208466	0.170860
H	3.028266	1.310376	-0.533188
H	1.557198	2.075408	0.075524
H	2.611988	1.179828	1.185340
C	2.248512	-1.240511	-0.069333
H	2.318589	-1.622802	0.953917
H	1.772203	-2.002292	-0.683333
H	3.251595	-1.039203	-0.443872

NH_2-Pentazine

Reactant

C	0.000000	0.000000	0.821049
N	0.000000	1.180658	0.184103
N	0.000000	-1.180658	0.184103
N	0.000000	1.142763	-1.111758
N	0.000000	-1.142763	-1.111758
N	0.000000	0.000000	-1.765214
N	0.000000	0.000000	2.158364
H	0.000000	0.877251	2.654416
H	0.000000	-0.877251	2.654416

Transition state

C	0.000000	0.887982	0.000000
N	1.187803	0.518045	0.000000
N	-1.233758	-0.022165	0.000000
N	1.388290	-1.098804	0.000000
N	-1.173648	-1.193265	0.000000
N	0.498069	-1.852649	0.000000
N	-0.476806	2.144181	0.000000
H	0.148659	2.932561	0.000000
H	-1.478312	2.272147	0.000000

OH-Pentazine

Reactant

C	0.000000	0.828501	0.000000
N	1.190625	0.235701	0.000000
N	-1.159744	0.181358	0.000000
N	1.179739	-1.064711	0.000000
N	-1.105540	-1.120789	0.000000
N	0.048971	-1.740779	0.000000
O	-0.017130	2.143762	0.000000
H	-0.941313	2.443442	0.000000

Transition state

C	0.000000	0.903986	0.000000
N	1.187512	0.561730	0.000000
N	-1.200445	-0.005633	0.000000
N	1.390874	-1.077382	0.000000
N	-1.156337	-1.179714	0.000000
N	0.498700	-1.827757	0.000000
O	-0.452055	2.145392	0.000000
H	-1.425689	2.114239	0.000000

OMe-Pentazine

Reactant

C	0.000000	0.463959	0.000000
N	-1.337324	0.374606	0.000000
N	0.812273	-0.582228	0.000000
N	-1.833709	-0.817478	0.000000
N	0.246114	-1.765723	0.000000
N	-1.048922	-1.888866	0.000000
C	1.910550	1.822829	0.000000
H	2.093276	2.891976	0.000000
H	2.337885	1.358131	0.887072
H	2.337885	1.358131	-0.887072
O	0.487329	1.678606	0.000000

Transition state

C	0.000000	0.451270	0.000000
N	-1.378850	-0.092078	0.000000
N	1.054295	-0.201033	0.000000
N	-1.648726	-1.236463	0.000000
N	0.826352	-1.842118	0.000000
N	-0.242311	-2.312780	0.000000
C	1.098419	2.490017	0.000000
H	0.828187	3.540862	0.000000
H	1.679913	2.239529	0.887011
H	1.679913	2.239529	-0.887011
O	-0.131731	1.765458	0.000000

OEt-Pentazine

Reactant

C	0.000000	0.274766	0.000000
N	0.282364	1.585519	0.000000
N	0.920176	-0.679543	0.000000
N	1.533455	1.905475	0.000000
N	2.172120	-0.288853	0.000000
N	2.480786	0.975228	0.000000
O	-1.271198	-0.032003	0.000000
C	-1.632369	-1.427353	0.000000
H	-1.194957	-1.898619	0.881340
H	-1.194957	-1.898619	-0.881340
C	-3.137261	-1.494391	0.000000
H	-3.544379	-1.006692	0.884852
H	-3.544379	-1.006692	-0.884852
H	-3.456264	-2.536271	0.000000

Transition state

C	0.000000	0.100240	0.000000
N	-0.258342	1.562206	0.000000
N	1.108845	-0.455101	0.000000
N	0.575942	2.390526	0.000000
N	2.386813	0.597690	0.000000
N	2.229779	1.754862	0.000000
O	-1.188057	-0.474233	0.000000
C	-1.172565	-1.911556	0.000000
H	-0.623243	-2.248810	0.881443
H	-0.623243	-2.248810	-0.881443
C	-2.604308	-2.380450	0.000000
H	-3.127520	-2.019737	0.884910
H	-3.127520	-2.019737	-0.884910
H	-2.634037	-3.469739	0.000000

Me-Pentazine

Reactant

C	0.000000	0.797171	0.000000
N	-1.167226	0.147789	0.000000
N	1.170460	0.165433	0.000000
N	-1.134883	-1.152703	0.000000
N	1.150898	-1.142825	0.000000
N	0.015576	-1.793885	0.000000
C	-0.020433	2.282787	0.000000
H	-0.557909	2.641848	0.877868
H	0.994643	2.669889	0.000000
H	-0.557909	2.641848	-0.877868

Transition state

C	0.841673	-0.187553	0.000003
N	0.196555	-1.243687	0.000004
N	0.227002	1.199562	0.000020
N	-1.415512	-1.086518	0.000009
N	-0.938174	1.390904	-0.000003
N	-1.930150	-0.030840	-0.000026
C	2.320279	-0.070737	-0.000005
H	2.631640	0.497469	0.878104
H	2.786977	-1.051166	-0.000022
H	2.631628	0.497493	-0.878103

F-Pentazine

Reactant

C	0.000000	-0.000000	0.822176
N	0.000000	1.173383	0.226398
N	-0.000000	-1.173383	0.226398
N	-0.000000	1.144022	-1.080828
N	-0.000000	-1.144022	-1.080828
N	-0.000000	0.000000	-1.723615
F	0.000000	-0.000000	2.121585

Transition state

C	0.000000	0.887752	0.000000
N	1.177455	0.534124	0.000000
N	-1.188980	0.052816	0.000000
N	1.334595	-1.132395	0.000000
N	-1.190992	-1.127567	0.000000
N	0.397272	-1.829848	0.000000
F	-0.411716	2.132621	0.000000

Cl-Pentazine

Reactant

C	0.000000	0.000000	0.426454
N	0.000000	1.172977	-0.188716
N	-0.000000	-1.172977	-0.188716
N	0.000000	1.143176	-1.494922
N	-0.000000	-1.143176	-1.494922
N	0.000000	-0.000000	-2.139136
Cl	0.000000	0.000000	2.116833

Transition state

C	-0.465554	-0.163737	0.072634
N	0.135347	-1.232814	0.232123
N	0.152226	1.168633	0.133186
N	1.756413	-1.081637	-0.046086
N	1.314683	1.370701	0.057498
N	2.255886	-0.036372	-0.218169
Cl	-2.147562	-0.019833	-0.090921

Br-Pentazine

Reactant

C	-0.000000	-0.000000	-0.149745
N	0.000000	1.172470	-0.765434
N	-0.000000	-1.172470	-0.765434
N	0.000000	1.143293	-2.072558
N	-0.000000	-1.143293	-2.072558
N	-0.000000	-0.000000	-2.716142
Br	0.000000	0.000000	1.704096

Transition state

C	0.119767	-0.156736	0.109280
N	0.719211	-1.226945	0.269366
N	0.746339	1.168703	0.163986
N	2.328994	-1.084724	-0.060684
N	1.909942	1.360311	0.054901
N	2.824648	-0.041489	-0.261623
Br	-1.726358	-0.008302	-0.051923

CF_3-Pentazine

Reactant

C	-0.011062	0.130202	0.000000
N	1.243204	0.557919	0.000000
N	-1.074299	0.906531	0.000000
N	1.418156	1.848599	0.000000
N	-0.848471	2.200376	0.000000
N	0.376574	2.657739	0.000000
C	-0.199848	-1.385642	0.000000
F	0.376574	-1.905437	1.077812
F	-1.479892	-1.707516	0.000000
F	0.376574	-1.905437	-1.077812

Transition state

C	-0.091116	0.169725	-0.067948
N	-0.689782	1.241207	-0.215446
N	-0.703923	-1.175294	-0.109563
N	-2.288767	1.110199	0.032319
N	-1.874803	-1.347257	-0.062230
N	-2.799083	0.061620	0.180286
C	1.418440	0.039959	0.023956
F	1.998328	1.220119	0.120250
F	1.731410	-0.686276	1.095419
F	1.884768	-0.588446	-1.050515

CN-Pentazine

Reactant

C	0.000000	0.494933	0.000000
N	0.000000	-0.122745	1.176228
N	0.000000	-0.122745	-1.176228
N	0.000000	-1.428037	1.146551
N	0.000000	-1.428037	-1.146551
N	-0.000002	-2.069601	0.000000
C	0.000000	1.937083	0.000000
N	0.000003	3.086580	0.000000

Transition state

C	0.536186	-0.147394	0.091776
N	-0.079335	-1.202857	0.362167
N	-0.116844	1.178968	0.159591
N	-1.609057	-1.089196	-0.103395
N	-1.283294	1.347301	0.091535
N	-2.143038	-0.068846	-0.327640
C	1.956157	-0.061188	-0.063260
N	3.095274	0.013416	-0.206700

NO_2-Pentazine

Reactant

C	0.236280	0.182440	0.000000
N	0.261569	-0.415102	1.174220
N	0.261569	-0.415102	-1.174220
N	0.261569	-1.722220	1.146372
N	0.261569	-1.722220	-1.146372
N	0.243605	-2.363003	0.000000
N	0.296560	1.613995	0.000000
O	-0.782672	2.129433	0.716587
O	-0.782672	2.129433	-0.716587

Transition state

C	-0.170392	-0.106032	0.234850
N	0.335818	-1.216012	0.069192
N	0.479093	1.214476	0.171713
N	1.966233	-1.150684	-0.123611
N	1.635930	1.347402	-0.038130
N	2.527457	-0.122524	-0.171571
N	-1.539572	0.126300	0.598450
O	-2.381020	-0.727400	-0.101048
O	-2.220525	0.632835	-0.517879

XYZ optimized geometries of Hexazine using different functionals

Hexazine (D_2)

HCTH/Def2-TZVP

N	1.119333	0.241435	-0.629667
N	1.119333	-0.241435	0.629667
N	0.000000	0.000000	-1.232201
N	0.000000	0.000000	1.232201
N	-1.119333	-0.241435	-0.629667
N	-1.119333	0.241435	0.629667

TPSSH/Def2-TZVP

N	1.127678	0.216207	-0.632138
N	1.127678	-0.216207	0.632138
N	0.000000	0.000000	-1.257501
N	0.000000	0.000000	1.257501
N	-1.127678	-0.216207	-0.632138
N	-1.127678	0.216207	0.632138

PBE0/Def2-TZVP

N	1.121367	0.184213	-0.630708
N	1.121367	-0.184213	0.630708
N	0.000000	0.000000	-1.264029
N	0.000000	0.000000	1.264029
N	-1.121367	-0.184213	-0.630708
N	-1.121367	0.184213	0.630708

M062X/Def2-TZVP

N	1.125744	0.118898	-0.641703
N	1.125744	-0.118898	0.641703
N	0.000000	0.000000	-1.289770
N	0.000000	0.000000	1.289770
N	-1.125744	-0.118898	-0.641703
N	-1.125744	0.118898	0.641703

Orca Input files

Pentazine

```
%pal nprocs 16 end
%maxcore 7000
! ccsd(t)  extrapolate(3/4,cc) TightSCF
*xyz 0 1
C     0.000000    0.000000   -1.250593
N     0.000000    1.171841   -0.631606
N    -0.000000   -1.171841   -0.631606
N     0.000000    1.145996    0.675704
N    -0.000000   -1.145996    0.675704
N     0.000000   -0.000000    1.317064
H     0.000000    0.000000   -2.333265
*
```

Hexazine

```
%pal nprocs 16 end
%maxcore 7000
! dlpno-ccsd(t) cc-pVTZ cc-pVTZ/C TIGHTSCF opt freq
*xyz 0 1
  N   1.140867      0.144241     -0.646921
  N   1.140867     -0.144241      0.646921
  N   -0.000000      0.000000     -1.301970
  N   0.000000      0.000000      1.301970
  N   -1.140867     -0.144241     -0.646921
  N   -1.140867      0.144241      0.646921
*
```

Example of Polyrate input file (.dat file):

```
*GENERAL

TITLE
 QMT_computation
END

#DL ISPE

ATOMS
1 N
2 N
3 N
4 N
5 N
6 N
END

NOSUPERMOL

*SECOND

HESSCAL hhook

FPRINT

*OPTIMIZATION

PRINT

OPTMIN ohook
OPTTS ohook

*REACT1
INITGEO hooks
GEOM
1
2
3
4
5
6
END
SPECIES nonlinrp

*PROD1
INITGEO hooks
GEOM
1
2
3
4
5
6
END
SPECIES nonlinrp

*START
INITGEO hooks
GEOM
1
2
3
4
5
6
END
SPECIES nonlints
PROJECT

*PATH
#SYMMETRY
INTMU 3
SSTEP 0.001
RPM pagem
SRANGE
 SLP 20.
 SLM -20.
END
SPECSTOP
 CURVE VMEP
 PERCENTDOWN 99.9
END
PRPATH
 coord 1 2
 xmol
 freq 15
END

*TUNNEL
ZCT
SCT
QRST
 harmonic
 mode 15
 states all
END

*RATE
FORWARDK
SIGMAF 1
TST
CVT
PRDELG
PRPART rtp

TEMP
4
5
6
7
8
9
10
12
14
16
18
20
22
24
26
28
30
40
50
75
77.355
100
125
150
175
194.7
200
225
250
273.15
275
298.15
300
325
350
373.15
375
400
END

ANALYSIS
4
5
6
7
8
9
10
12
14
16
18
20
22
24
26
28
30
40
50
75
77.355
100
125
150
175
194.7
200
225
250
273.15
275
298.15
300
325
350
373.15
375
400
END

EACT
6. 10.
10. 20.
20. 50.
50. 100.
200. 225.
300. 325.
END

GTLOG
```

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