Supplementary Information

Ab initio molecular dynamics study of thermal decomposition of 3,6-di(azido)-1,2,4,5-tetrazine

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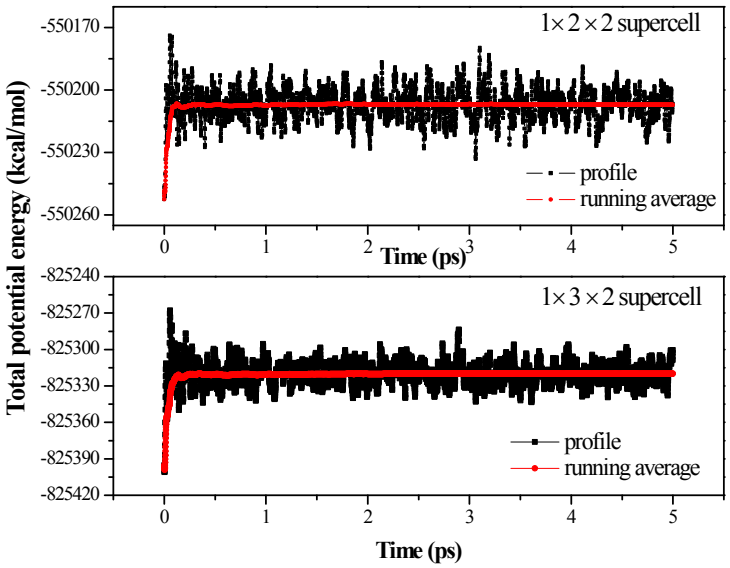

Fig. S1 Time dependences of total potential energy in the 5 ps of equilibration at 300 K.

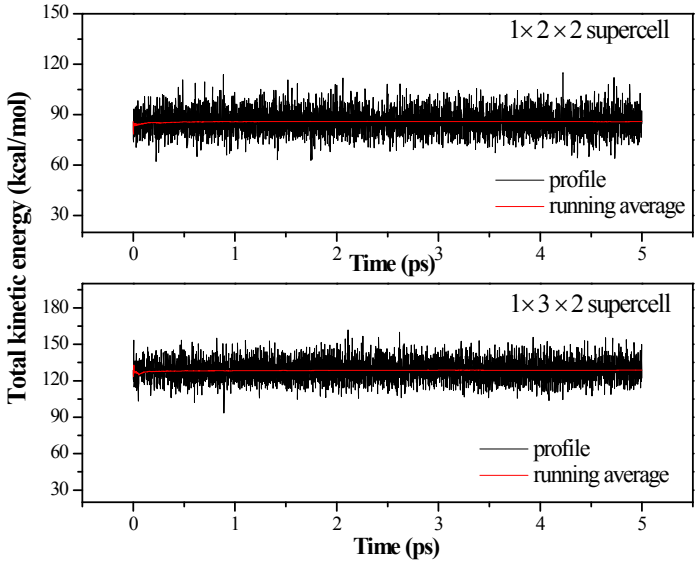

Fig. S2 Time dependences of total kinetic energy in the 5 ps of equilibration at 300 K.

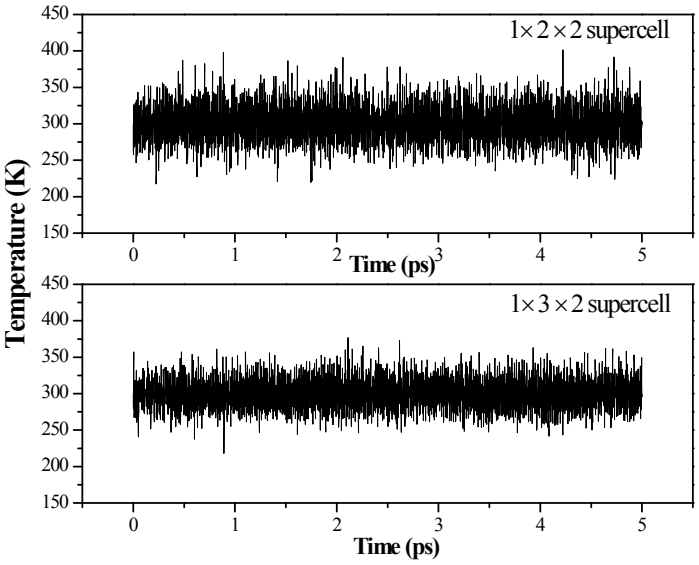

Fig. S3 Time dependences of temperature in the 5 ps of equilibration at 300 K.

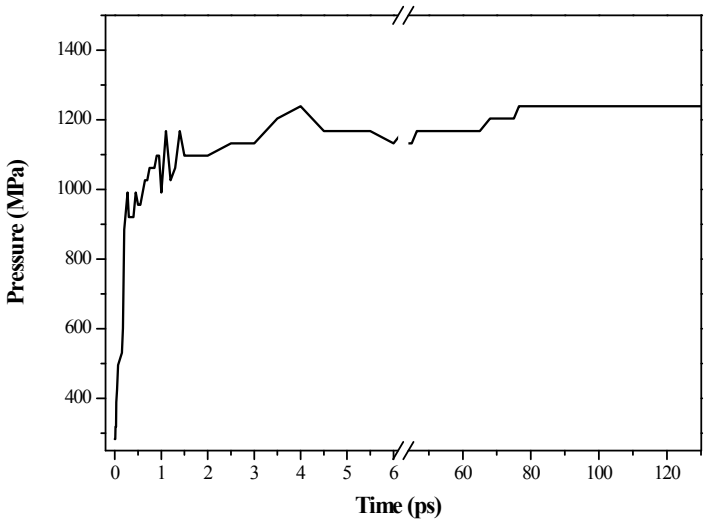

Fig. S4 Rough estimating of change trend of pressure as a function of time in the system of 1 × 2 × 2 supercell.

Table S1 The calculated Mulliken bond orders and bond dissociation energies (BDE) of unimolecular DiAT at 300 K.

Bonds	Mulliken	BDE ($kJ \cdot mol^{-1}$)
N1-N2	1.300	743.9
N2-N3	0.810	728.9
N3-C4	0.790	370.6
C4-N5	0.880	258.4
N5-N6	0.870	332.6

Table S2 The observed times of the three initiation reactions from the simulations by using a time step of 0.1 fs.

Initiation reactions	Observed times	
	1 × 2 × 2 supercell	1 × 3 × 2 supercell
N-N_2 cleavage	16	9
Ring opening	6	2
Isomerization	2	1

Table S3. A comparison of the numbers of released nitrogen gas in 0.5 and 1.0 ps for systems of 1 × 2 × 2 supercell and 1 × 3 × 2 supercell by using a time step of 0.1 and 1.0 fs.

Systems	Numbers of released nitrogen gas	
	0.5 ps	1.0 ps
1 × 2 × 2 supercell (1.0 fs) [a]	22	26
1 × 2 × 2 supercell (0.1 fs) [a]	21	25
1 × 3 × 2 supercell (1.0 fs)	26	32
1 × 3 × 2 supercell (0.1 fs)	24	31

[a] The values are the averaged results of the three independent simulations.

Table S4. The global endothermic reactions rate constant (τ_{endo}) and the time when the maximum in total energy is obtained (t_{max}) for systems of 1 × 2 × 2 supercell and 1 × 3 × 2 supercell by using a time step of 1.0 fs and 0.1 fs.

Systems	t_{max} (ps)	τ_{endo} (ps)
1 × 2 × 2 supercell (1.0 fs) [a]	0.20	0.1
1 × 2 × 2 supercell (0.1 fs) [a]	0.15	0.08
1 × 3 × 2 supercell (1.0 fs)	0.27	0.14
1 × 3 × 2 supercell (0.1 fs)	0.25	0.12

[a] The values are the averaged results of the three independent simulations.