Supporting Information available for

How stable can the pentanitrogen cation be in kinetics?

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Table S1 The imaginary frequency M_{freq} in (cm^{-1}) and the decomposition barrier $\triangle E^b$ in (kcal/mol) of **TS01/01** (at B3LYP level) and **TS01/02**(at MP2 level) , including zero-point energy corrections (ZPVE) were calculated at different calculation levels. a is from the *Ref.* 1.

	TS01/01		**TS01/02**	
	M_{freq}	$\triangle E^b$	M_{freq}	$\triangle E^b$
B3LYP/6-31G(d)	**-204.69**(-204)[a]	**40.73**(40.87)[a]	**--**	**--**
MP2/6-31G(d)	--	--	**-400.11**	**51.76**(51.86)[a]
MP2/6-311+G(d)	--	--	**-400.55**(-400)[a]	**52.08**(52.10)[a]
CCSD(T)/6-31G(d)//MP2/6-311+G(d)	--	--	**--**	**40.36**(40.39)[a]

Table S2 Relative energies (kcal/mo1) of **01**, **TS01/P1**, **T01/01**, **TS'01/01**, **T01/02**, **TS01/P2** and the corresponding decomposition products **P1 02** and **P2**.

	01	**TS01/P1**	**TS01/01**	**TS'01/01**	**TS01/02**	**TS01/P2**	**P1**	**02**	**P2**
B3LYP/6-31G(d)	0.00	20.51	39.10	42.09	41.40	94.04	15.50	41.52	32.01
MP2/6-311+G(d)	0.00	44.63	*NA*	49.83	51.27	*NA*	35.50	42.57	24.75
MP2/cc-pVTZ	0.00	48.05	*NA*	54.76	51.88	*NA*	41.86	42.96	30.07
CBS-QB3	0.00	22.01	40.77	36.96	40.37	94.94	10.18	38.85	27.65
CCSD/cc-pVTZ	0.00	21.33	36.11	33.65	41.53	*NA*	8.02	39.81	20.64
CCSD(T)_CBS1// CCSD/cc-pVTZ	0.00	24.63	39.27	38.34	41.11	*NA*	15.18	39.04	24.67
CCSD(T)_CBS2// CCSD/cc-pVTZ	0.00	24.42	38.97	38.13	41.32	*NA*	14.45	39.02	23.75
UCCSD(T)// aug-cc-pV5Z	0.00	25.22	--	--	--	--	16.85	--	--

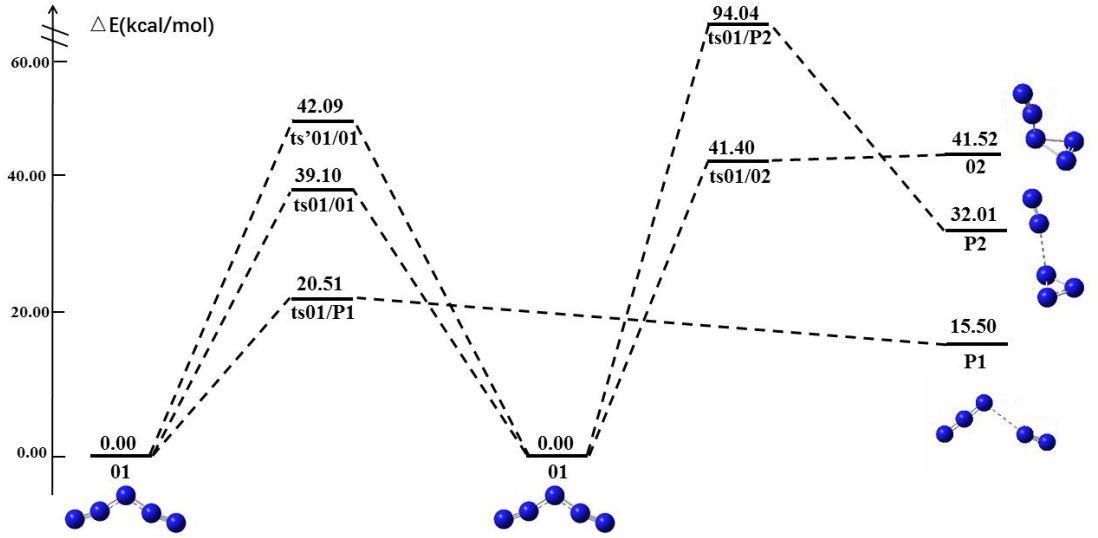


Fig. S1 The potential energy surface of V-shaped isomer N_5^+(**01**) at the B3LYP/6-31G(d) level.

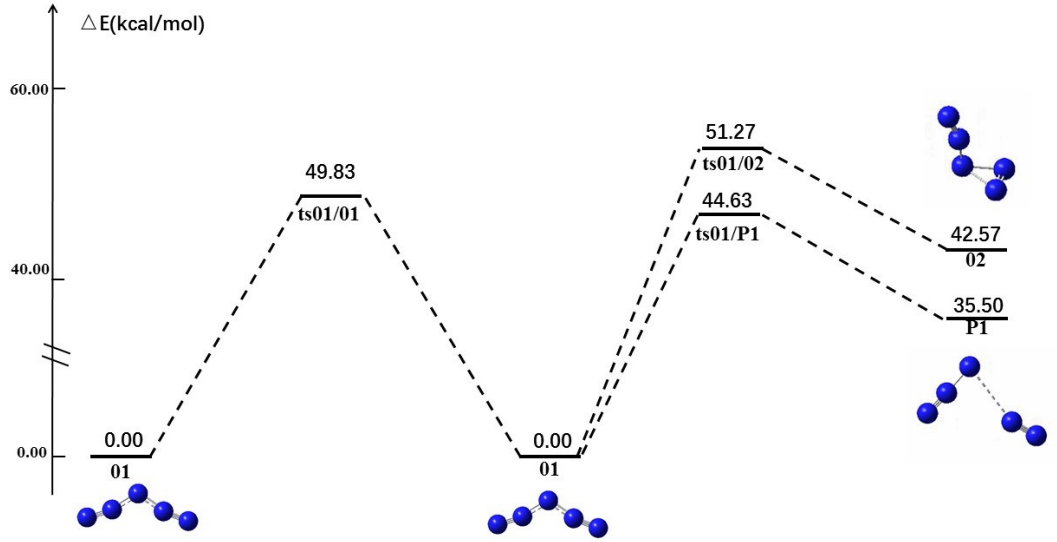


Fig. S2 The potential energy surface of V-shaped isomer N_5^+(**01**) at the MP2/6-311+G(d) level.

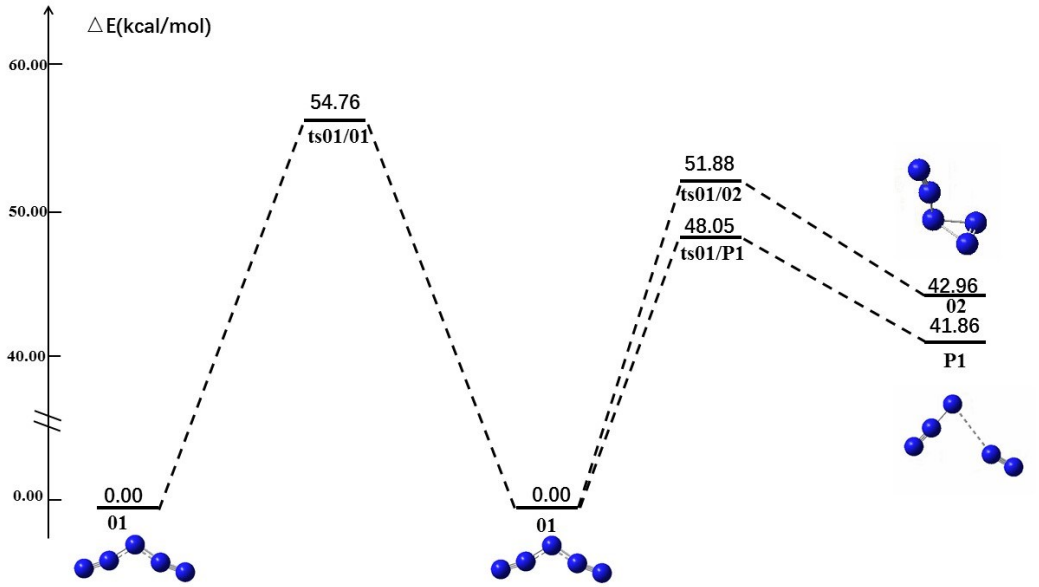


Fig. S3 The potential energy surface of V-shaped isomer N_5^+(**01**) at the MP2/cc-pVTZ level.

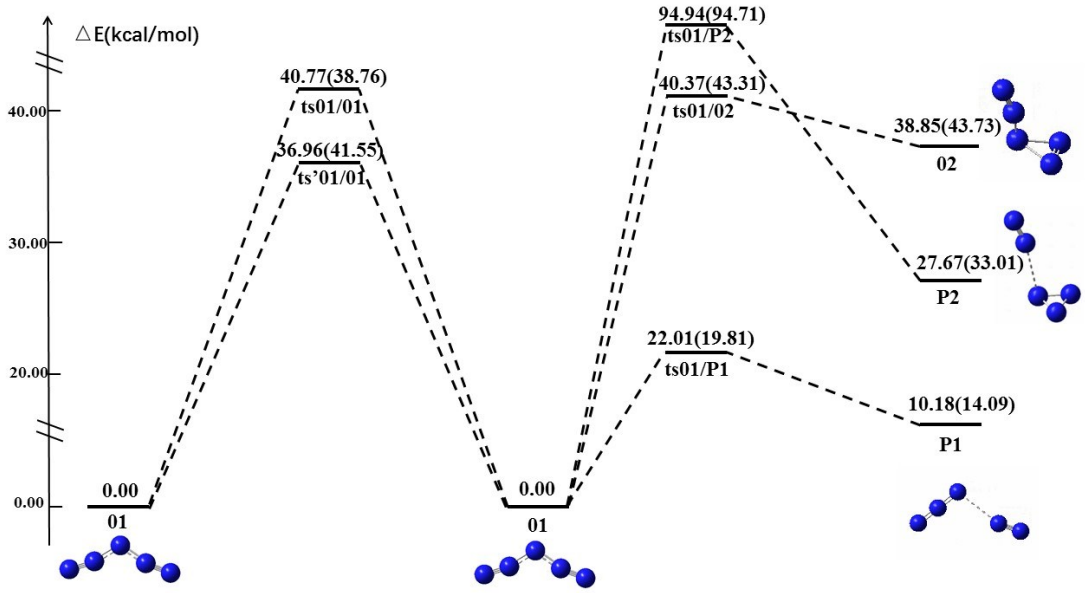


Fig. S4 The potential energy surface of V-shaped isomer N_5^+(**01**) at the CBS-QB3 level. The energy information in brackets is calculated at the B3LYP/6-311G (2d, d, p) level.

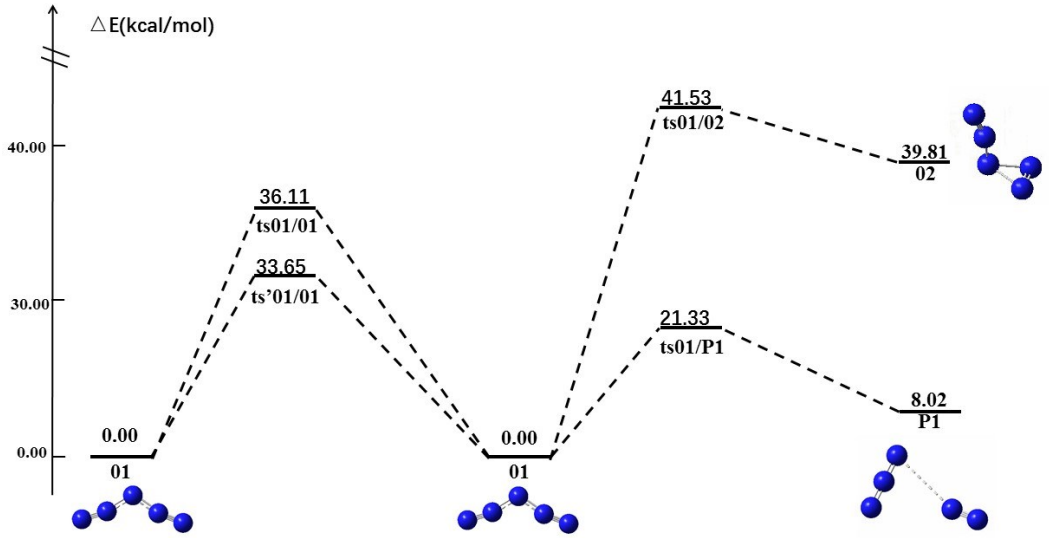
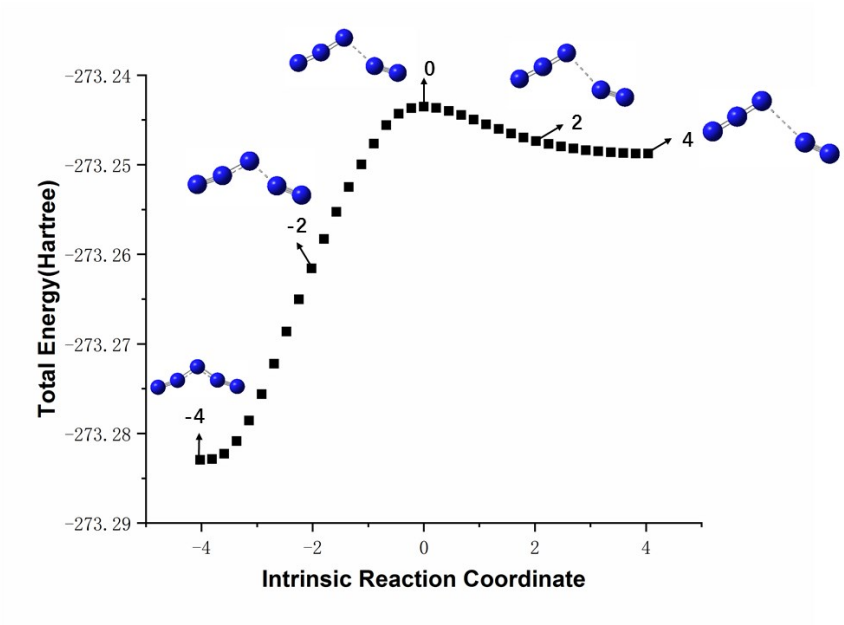
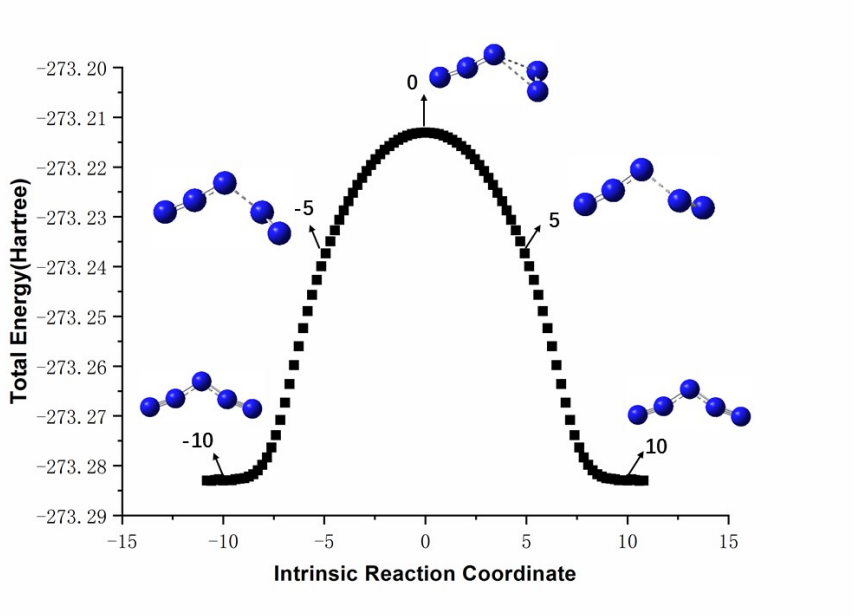


Fig. S5 The potential energy surface of V-shaped isomer N_5^+(**01**) at the CCSD/cc-pVTZ level.



(A) **TS01/P1**



(B) **TS01/01**

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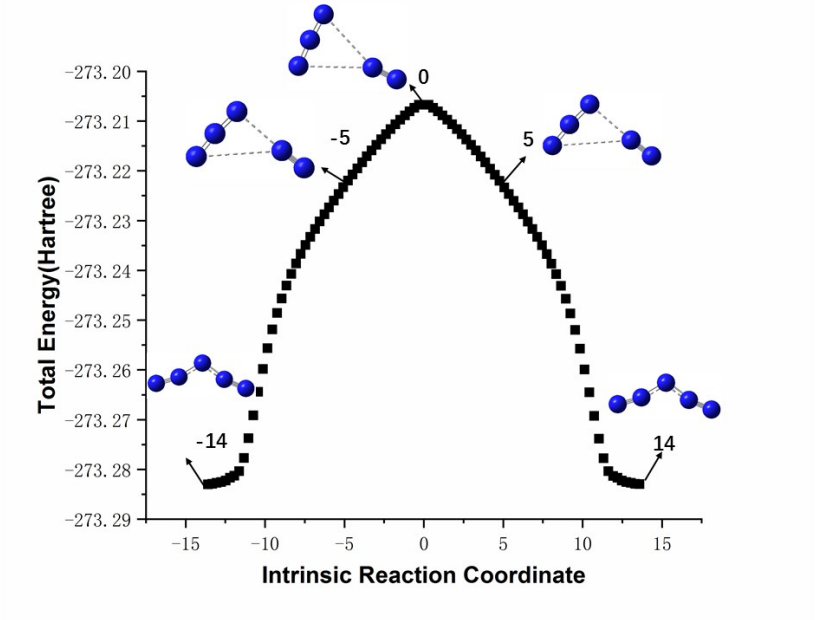
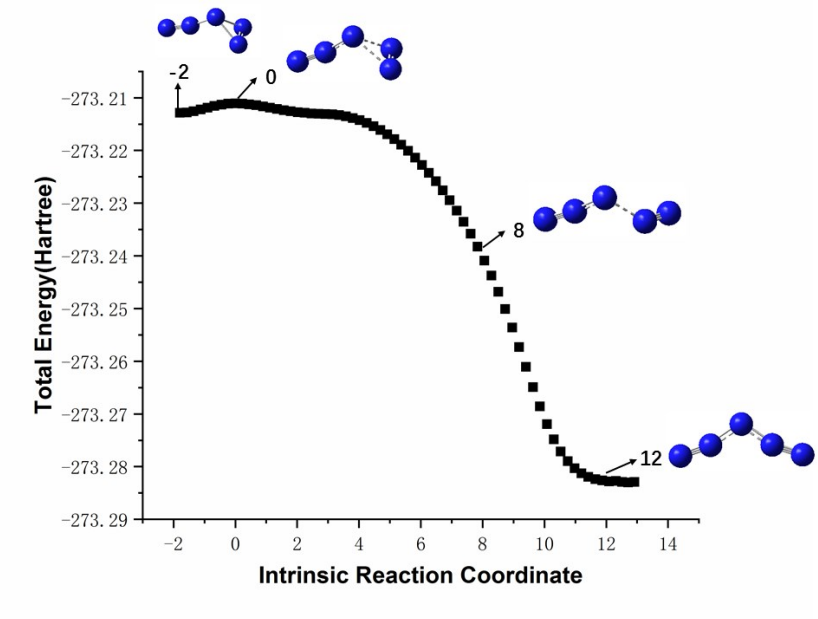


(C) **TS'01/01**



(D) **TS01/02**

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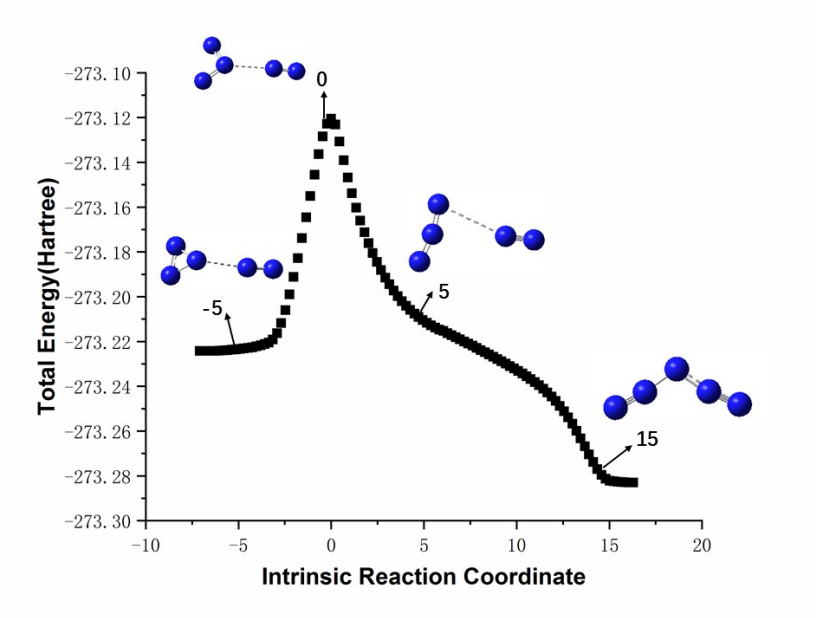
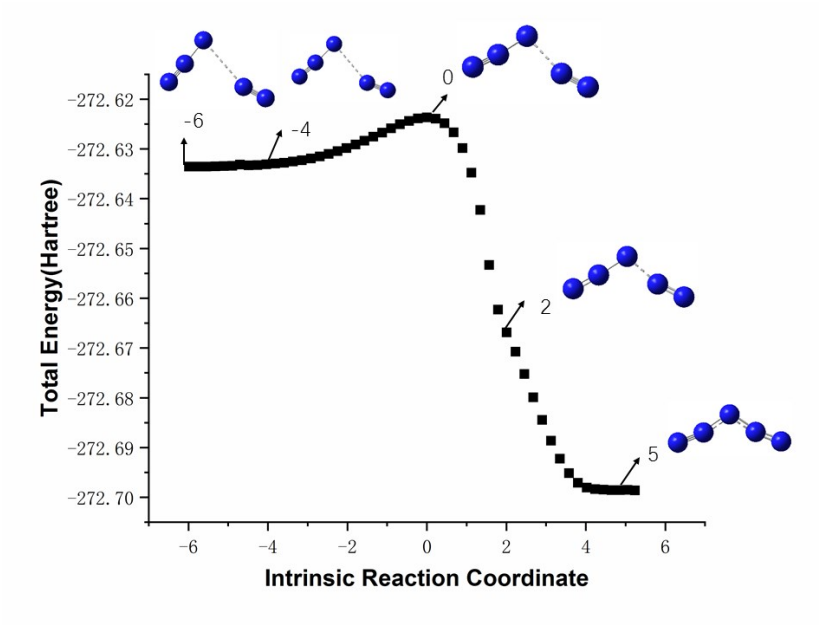
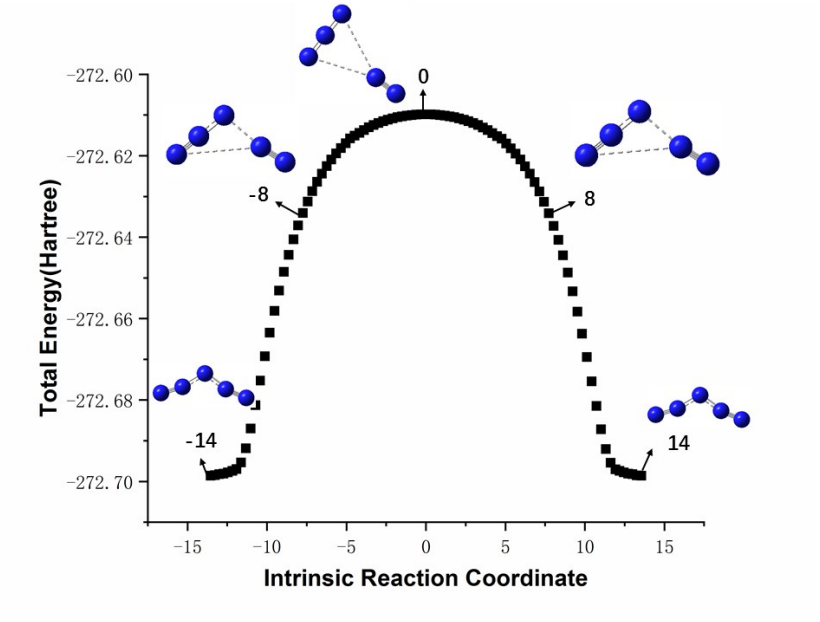


(E) **TS01/P2**

Fig. S6 The intrinsic reaction coordinate (IRC) connection of transition states (A) **TS01/P1**, (B)**TS01/01**, (C)**TS'01/01**, (D) **TS01/02** and (E)**TS01/P2** at the B3LYP/6-31G(d) level.

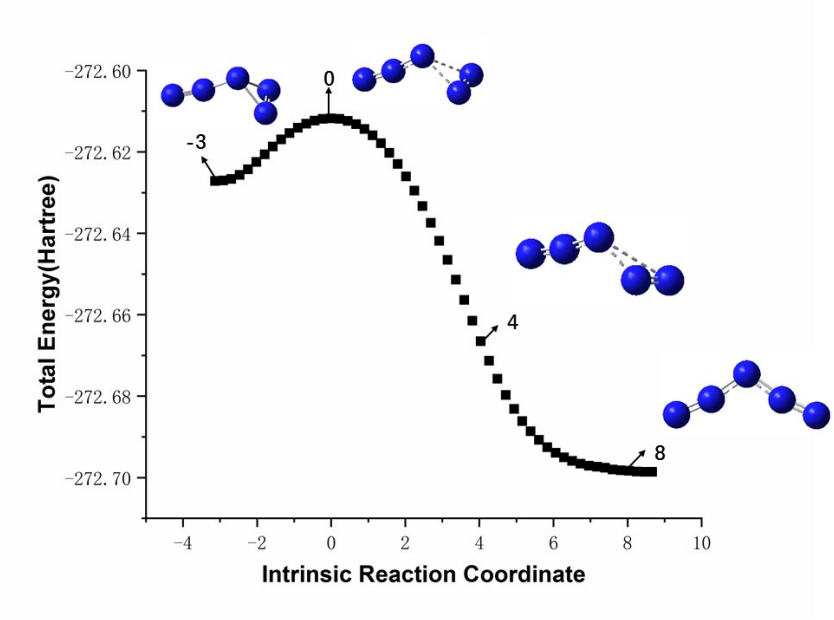


(A) **TS01/P1**



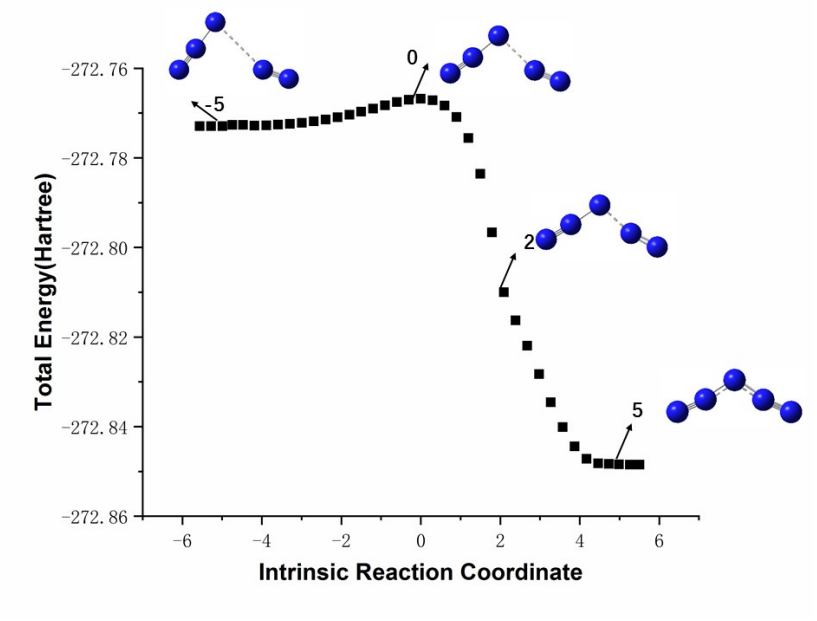
(B) **TS'01/01**

Continued



(C)**TS01/02**

Fig. S7 The intrinsic reaction coordinate (IRC) connection of transition states (A) **TS01/P1**, (B)**TS'01/01**, (C)**TS01/02** at the MP2/6-311+G(d) level.



TS01/P1

Fig. S8 The intrinsic reaction coordinate (IRC) connection of transition states **TS01/P1** at the MP2/cc-pVTZ level.

Table S3 The energy barrier (ΔE^b) (kcal/mol) of N_2-extrusion for the N_3^-, N_5^-, N_5^+ at the CBS-QB3 level and the average decomposition temperature of the corresponding salt has been reported (ΔT) (°C). We have not found the transition state of N_3^- decomposition into N_2 and N^- (the open-shell singlet state), but because the decomposition process endothermics 66.68 kcal/mol, the energy barrier should be at least greater than 66.68 kcal/mol. a , b and c are respectively from the *Ref*. 2, 3 and 4.

	ΔE^b	ΔT
N_3^-	>66.68	(~300)[a]
N_5^-	25.24	(~100)[b]
N_5^+	22.01	(<70)[c]

References

1. M. T. Nguyen and T.-K. Ha, *Chem. Phys. Lett*., 2001, **335**, 311-320.
2. P. Atkins and T. Overton, *Shriver and Atkins' inorganic chemistry*, Oxford University Press, USA, 2010.
3. P. Wang, Y. Xu, Q. Lin and M. Lu, *Chem. Soc. Rev.*, 2018, **47**, 7522-7538.
4. K. O. Christe, *Propellants, Explos., Pyrotech.*, 2007, **32**, 194–204.

Table S4 Cartesian coordinates of the optimized isomeric structures and transitional structures at MP2/cc-pVTZ, CBS-QB3 and CCSD/cc-pVTZ level.

"mol"----"Stoichiometry"

"lf"----"lowest frequency(cm^{-1})"

"te_zpe"----"total energy with zero-point energy (a.u.)"

"te_gfe"----"total energy with Gibbs free energy (a.u.)"

##

01 charge=1 spin=1 mol=N5(1+) RMP2-FC/CC-pVTZ

lf=186.4 te_zpe=-272.828613 te_gfe=-272.854966

7	-0.000000	2.111253	-0.409924
7	-0.000000	1.070346	0.026953
7	0.000000	0.000000	0.765943
7	-0.000000	-1.070346	0.026953
7	-0.000000	-2.111253	-0.409924

TS01/P1 charge=1 spin=1 mol=N5(1+) UMP2-FC/CC-pVTZ

lf=-395.4 te_zpe=-272.750095 te_gfe=-272.778398

7	2.156073	-0.020063	0.000000
7	1.162125	0.448361	0.000000
7	0.000000	1.130836	0.000000
7	-1.191644	-0.476371	0.000000
7	-2.126554	-1.082763	0.000000

TS'01/01 charge=1 spin=1 mol=N5(1+) RMP2-FC/CC-pVTZ

lf=-108.8 te_zpe=-272.738002 te_gfe=-272.767706

7 1.374575 -0.000002 0.000185

7 -2.610709 0.000056 -0.000015

7 -1.497198 -0.000033 0.000021

7 1.366721 1.179235 -0.000096

7 1.366611 -1.179256 -0.000096

TS01/02 charge=1 spin=1 mol=N5(1+) RMP2-FC/CC-pVTZ

lf=-427.5 te_zpe=-272.744645 te_gfe=-272.772289

7 1.612591 -0.474566 -0.425724

7 1.300658 -0.044956 0.583488

7 0.046130 0.871479 -0.174206

7 -0.980314 0.087116 -0.031864

7 -1.979065 -0.439073 0.048306

P1 charge=1 spin=1 mol=N5(1+) UMP2-FC/CC-pVTZ

lf=70.0 te_zpe=-272.757466 te_gfe=-272.788264

7 -1.034351 1.735131 0.000000

7 0.000000 1.369669 0.000000

7 1.286181 0.944409 0.000000

7 -0.055639 -1.472331 -0.000000

7 -0.196191 -2.576878 -0.000000

02 charge=1 spin=1 mol=N5(1+) RMP2-FC/CC-pVTZ

lf=222.9 te_zpe=-272.759427 te_gfe=-272.786509

7 -1.558050 1.277834 0.000000

7 -0.584552 0.710950 0.000000

7 0.714201 0.306306 0.000000

7 0.714201 -1.147545 0.602932

7 0.714201 -1.147545 -0.602932

P2 charge=1 spin=1 mol=N5(1+) RMP2-FC/CC-pVTZ

lf=58.8 te_zpe=-272.775912 te_gfe=-272.807042

7 1.351836 0.668249 0.000000

7 -1.233434 -0.998038 0.666123

7 -1.233434 -0.998038 -0.666123

7 -1.233434 0.162850 -0.000000

7 2.348464 1.164977 0.000000

"mol"----"Stoichiometry"

"lf"----"lowest frequency(cm-1)"

"te_zpe"----"total energy with zero-point energy (a.u.) at B3LYP/6-311G(2d,d,p) "

"te_gfe"----"total energy with Gibbs free energy (a.u.) at B3LYP/6-311G(2d,d,p) "

"te_ms_zpe"----"total energy with zero-point energy (a.u.) at CBS-QB3"

"te_ms_gfe"----"total energy with Gibbs free energy (a.u.) at CBS-QB3"

##

01 charge=1 spin=1 mol=N5(1+) CBS-QB3

lf=195.2 te_zpe=-273.333023 te_gfe=-273.359307 te_ms_zpe=-272.938166 te_ms_gfe= -272.964465

7 -0.000000 1.082950 0.005931

7 -0.000000 2.128453 -0.370308

7 0.000000 0.000000 0.728754

7 -0.000000 -1.082950 0.005931

7 -0.000000 -2.128453 -0.370308

TS01/P1 charge=1 spin=1 mol=N5(1+) UCBS-QB3

lf=-423.5 te_zpe=-273.299415 te_gfe=-273.327751 te_ms_zpe=-272.901034 te_ms_gfe= -272.929393

7 2.231453 0.117739 -0.000000

7 1.142700 0.437737 -0.000000

7 0.000000 0.951768 -0.000000

7 -1.188935 -0.522744 0.000000

7 -2.185219 -0.984500 0.000000

TS01/01 charge=1 spin=1 mol=N5(1+) CBS-QB3

lf=-213.8 te_zpe=-273.268456 te_gfe=-273.297539 te_ms_zpe=-272.870386 te_ms_gfe= -272.899495

7 -0.677915 -1.593162 0.553824

7 -0.677915 -1.593162 -0.553824

7 -0.677915 0.673709 0.000000

7 0.490506 1.020988 0.000000

7 1.543239 1.491627 0.000000

TS'01/01 charge=1 spin=1 mol=N5(1+) CBS-QB3

lf=-515.6 te_zpe=-273.265344 te_gfe=-273.295065 te_ms_zpe=-272.875819 te_ms_gfe= -272.905568

7 1.370839 0.000004 -0.000038

7 -2.567912 0.000004 0.000007

7 -1.470700 -0.000015 -0.000010

7 1.333876 1.179507 0.000021

7 1.333897 -1.179500 0.000021

TS01/02 charge=1 spin=1 mol=N5(1+) CBS-QB3

lf=-241.2 te_zpe=-273.262869 te_gfe=-273.290304 te_ms_zpe=-272.872675 te_ms_gfe= -272.900130

7 1.424844 -0.260732 -0.569368

7 1.424212 -0.259019 0.570020

7 0.108948 0.816571 -0.000880

7 -0.959294 0.055975 -0.000018

7 -1.998710 -0.352795 0.000245

TS01/P2 charge=1 spin=1 mol=N5(1+) CBS-QB3

lf=-1591.8 te_zpe=-273.177871 te_gfe=-273.208404 te_ms_zpe=-272.782603 te_ms_gfe= -272.813170

7 2.638659 -0.073060 -0.047098

7 -0.942825 -0.112463 0.320665

7 1.544321 -0.018808 -0.010631

7 -1.366610 0.983590 -0.097838

7 -1.873545 -0.779259 -0.165098

P1 charge=1 spin=1 mol=N5(1+) UCBS-QB3

lf=78.5 te_zpe=-273.306662 te_gfe=-273.336874 te_ms_zpe=-272.917992 te_ms_gfe= -272.948238

7 2.253346 0.485903 0.000000

7 1.139342 0.833384 0.000000

7 0.000000 1.210485 0.000000

7 -1.279203 -0.909359 -0.000000

7 -2.113486 -1.620413 -0.000000

02 charge=1 spin=1 mol=N5(1+) CBS-QB3

lf=222.7 te_zpe=-273.262358 te_gfe=-273.289624 te_ms_zpe=-272.875270 te_ms_gfe= -272.902557

7 -1.506413 1.353007 -0.000000

7 -0.585613 0.734842 -0.000000

7 0.697342 0.317638 -0.000000

7 0.697342 -1.202744 0.583102

7 0.697342 -1.202744 -0.583102

P2 charge=1 spin=1 mol=N5(1+) CBS-QB3

lf=109.4 te_zpe=-273.276968 te_gfe=-273.306641 te_ms_zpe=-272.890667 te_ms_gfe= -272.920371

7 1.167741 0.860981 0.000000

7 -1.073655 -1.176963 0.648113

7 -1.073655 -1.176963 -0.648113

7 -1.073655 -0.013411 -0.000000

7 2.053224 1.506357 0.000000

"mol"----"Stoichiometry"

"lf"----"lowest frequency(cm-1)"

"te_zpe"----"total energy with zero-point energy (a.u.)"

"te_gfe"----"total energy with Gibbs free energy (a.u.)"

##

01 charge=1 spin=1 mol=N5(1+) RCCSD-FC/CC-pVTZ

lf=190.0 te_zpe=-272.810033 te_gfe=-272.836388

7 0.000000 1.071585 0.024939

7 0.000000 2.081064 -0.424595

7 -0.000000 0.000000 0.799312

7 -0.000000 -1.071585 0.024939

7 -0.000000 -2.081064 -0.424595

TS01/P1 charge=1 spin=1 mol=N5(1+) UCCSD-FC/CC-pVTZ

lf=-559.3 te_zpe=-272.774011 te_gfe=-272.802397

7 2.178288 0.041634 0.000000

7 1.131752 0.452751 0.000000

7 0.000000 1.039559 0.000000

7 -1.195953 -0.466769 -0.000000

7 -2.114086 -1.067174 -0.000000

TS01/01 charge=1 spin=1 mol=N5(1+) RCCSD-FC/CC-pVTZ

lf=-130.4 te_zpe=-272.747319 te_gfe=-272.778690

7 -0.693953 -1.762205 0.549681

7 -0.693953 -1.762205 -0.549681

7 -0.693953 0.919172 0.000000

7 0.474426 1.163004 0.000000

7 1.607433 1.442234 0.000000

TS'01/01 charge=1 spin=1 mol=N5(1+) RCCSD-FC/CC-pVTZ

lf=-92.2 te_zpe=-272.753014 te_gfe=-272.782762

7 1.389472 0.000087 0.000441

7 -2.632387 0.000475 0.004487

7 -1.536047 -0.000946 -0.006168

7 1.389845 -1.177951 0.000624

7 1.389118 1.178335 0.000617

TS01/02 charge=1 spin=1 mol=N5(1+) RCCSD-FC/CC-pVTZ

lf=-217.4 te_zpe=-272.742290 te_gfe=-272.770201

7 1.447383 -0.280303 -0.561687

7 1.447230 -0.280662 0.561631

7 0.046466 0.906570 0.000240

7 -0.982050 0.094896 -0.000211

7 -1.959029 -0.440501 0.000027

P1 charge=1 spin=1 mol=N5(1+) UCCSD-FC/CC-pVTZ

lf=41.2 te_zpe=-272.792213 te_gfe=-272.823601

7 1.181782 1.387608 -0.000000

7 -0.000000 1.396165 -0.000000

7 -1.182551 1.396137 -0.000000

7 0.000655 -1.541879 0.000000

7 0.000113 -2.638032 0.000000

02 charge=1 spin=1 mol=N5(1+) RCCSD-FC/CC-pVTZ

lf=221.5 te_zpe=-272.745829 te_gfe=-272.772947

7 -1.572790 1.256999 0.000000

7 -0.614945 0.715702 0.000000

7 0.729245 0.303305 0.000000

7 0.729245 -1.138003 0.591504

7 0.729245 -1.138003 -0.591504

P2 charge=1 spin=1 mol=N5(1+) RCCSD-FC/CC-pVTZ

lf=32.9 te_zpe=-272.771589 te_gfe=-272.803490

7 -1.299222 0.222612 -0.000000

7 -1.299222 -0.917060 0.654167

7 -1.299222 -0.917060 -0.654167

7 2.456606 1.012025 0.000000

7 1.441061 0.599483 0.000000