
Supplementary information

Preparation of a neutral nitrogen allotrope hexanitrogen C_{2h} -N₆

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Supplementary Information

Preparation of a Neutral Nitrogen Allotrope Hexanitrogen $C_{2h}-N_6$

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Table of Contents

Note for the Synthesis	2
Fig. S1	2
Fig. S2	3
Fig. S3	4
Fig. S4	5
Fig. S5	5
Fig. S6	6
Fig. S7	6
Fig. S8	7
Fig. S9	7
Fig. S10	8
Fig. S11	9
Fig. S12	9
Fig. S13	10
Fig. S14	10
Fig. S15	10
Table S1.....	11
Table S2.....	12
Table S3.....	13
Table S4.....	14
Coordinates (Ångstrom) and Energies (Hartree)	15

Note for the Synthesis

The gas-phase reaction is very sensitive to the apparatus setup. We have tried many configurations and succeeded with either a directly connected U-trap or a straight tube with a flying distance of approximately 15 mm from the front side of the quartz tube to the matrix window (Fig. S1). Quartz wool must not be used. The Young valves should be open completely when conducting reactions in a U-trap. The entire setup was covered by aluminium foil to avoid light exposure during the reactions.

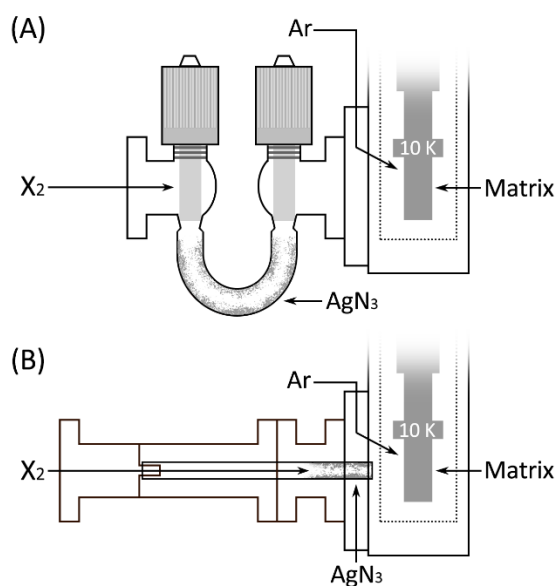


Fig. S1. Instrument setup: (A) U-trap; (B) quartz tube.

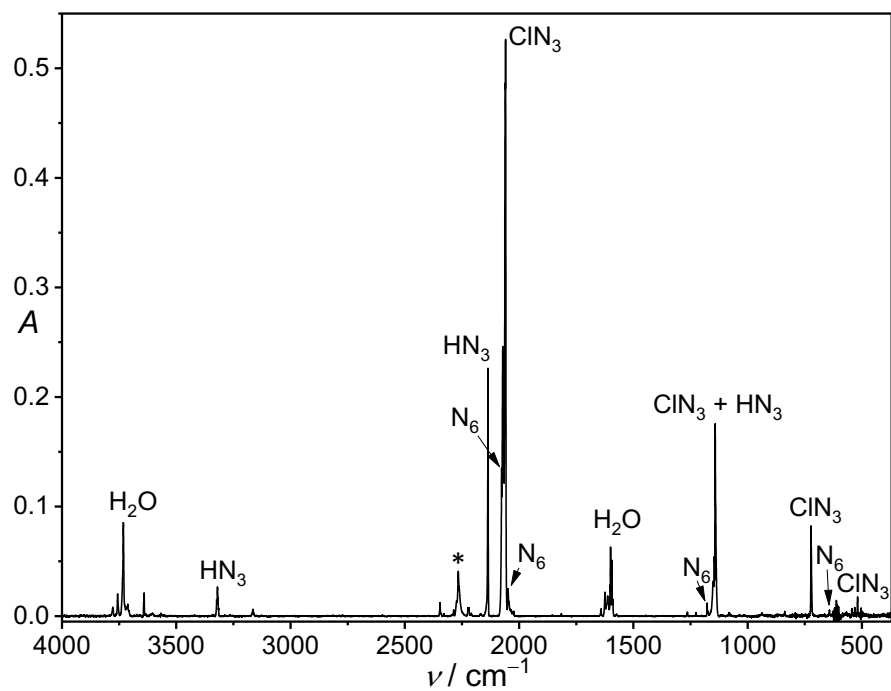


Fig. S2. Infrared spectrum of the deposition products of the reaction of Cl_2 and AgN_3 .

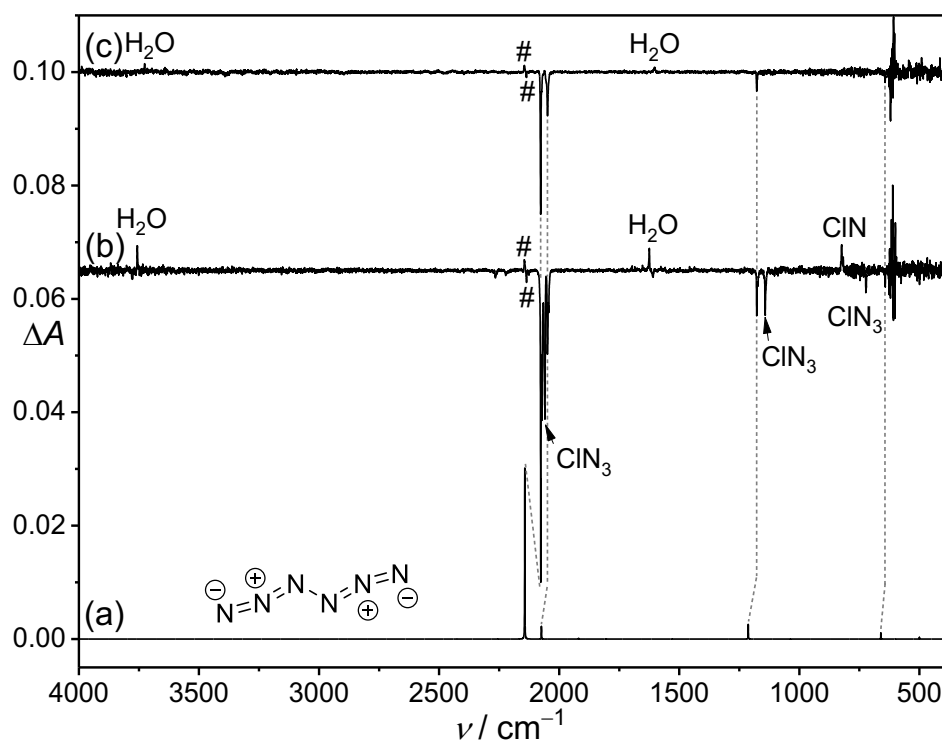


Fig. S3. Full-range version of Figure 1 in the main text. (a) Computed DVPT2 anharmonic infrared spectrum for $\text{C}_{2\text{h}}\text{-N}_6$ at B3LYP/def2-TZVP, including the combination $\nu_8 + \nu_9$. (b) Difference spectrum shows the changes after 8 min 436 nm irradiation of Cl_2 and AgN_3 reaction products. (c) Difference spectrum shows the changes after 6 min 436 nm irradiation of Br_2 and AgN_3 reaction products. Matrix sites from HN_3 (#) and H_2O are marked.

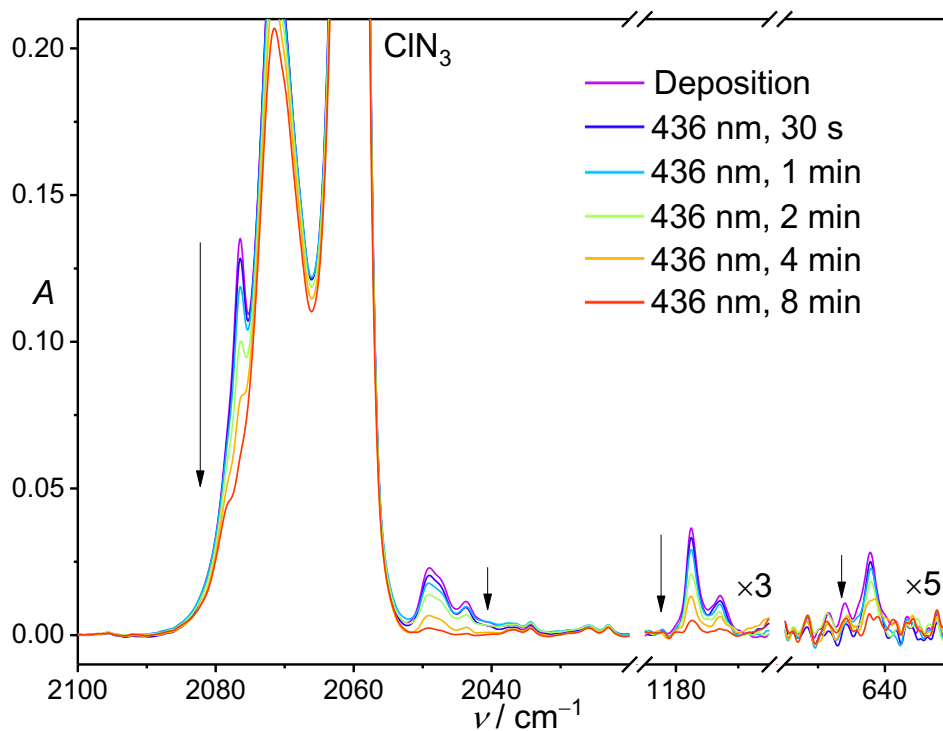


Fig. S4. Time-dependent infrared spectra upon 436 nm irradiation of Cl_2 and AgN_3 reaction products in an Ar-matrix (10 K).

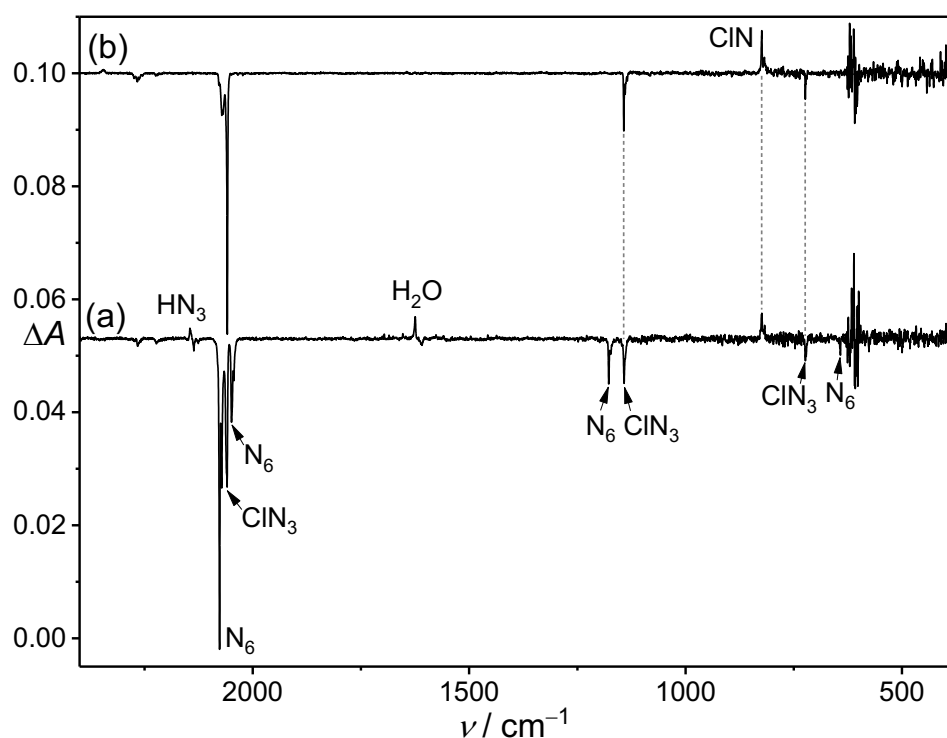


Fig. S5. (a) Difference spectrum showing the changes after 8 min 436 nm irradiation of Cl_2 and AgN_3 reaction products. (b) Difference spectrum showing the changes after 5 min 365 nm irradiation (peaks from N_6 had completely vanished in previous irradiation). Matrix sites from HN_3 (#) and H_2O are marked.

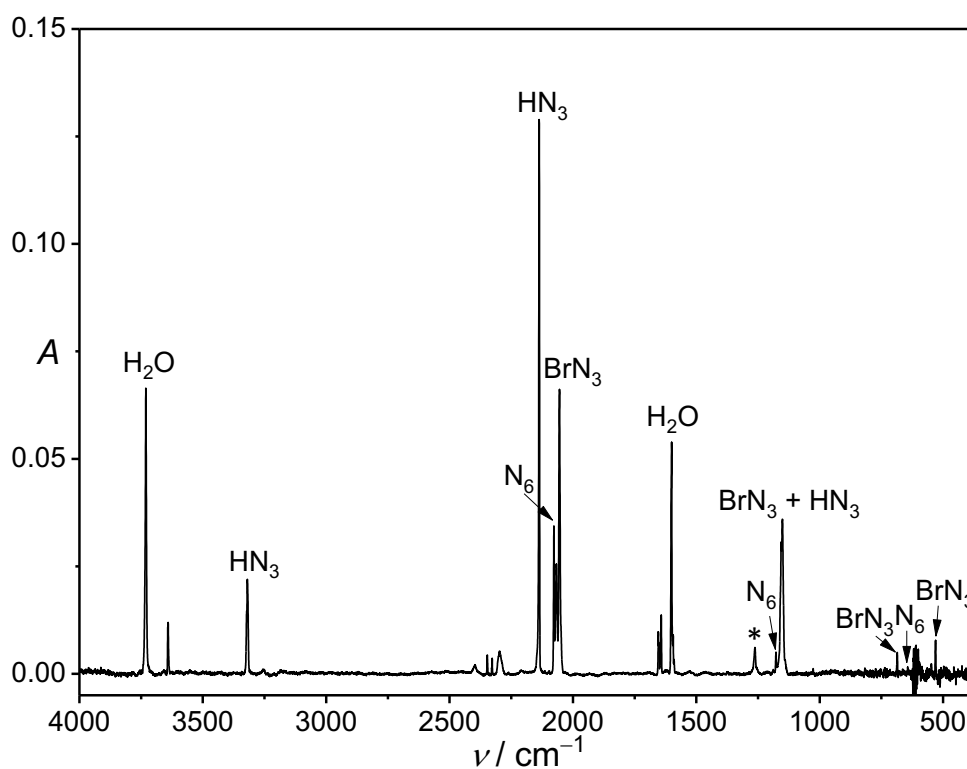


Fig. S6. Infrared spectrum of the deposition products of the reaction of Br_2 and AgN_3 .

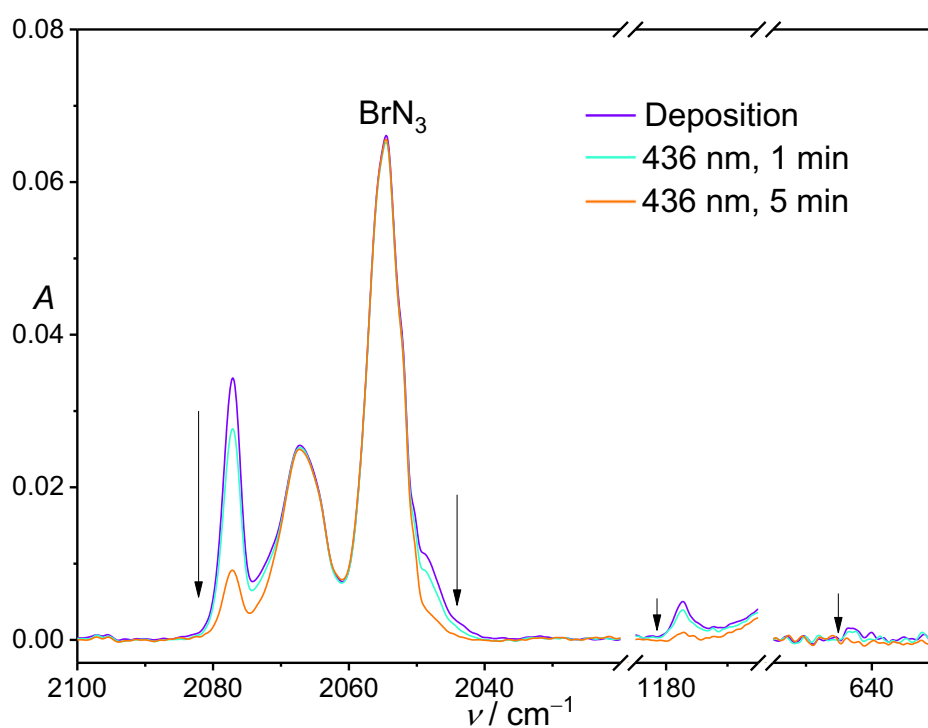


Fig. S7. Time-dependent infrared spectra upon 436 nm irradiation of Br_2 and AgN_3 reaction products in an Ar-matrix (10 K).

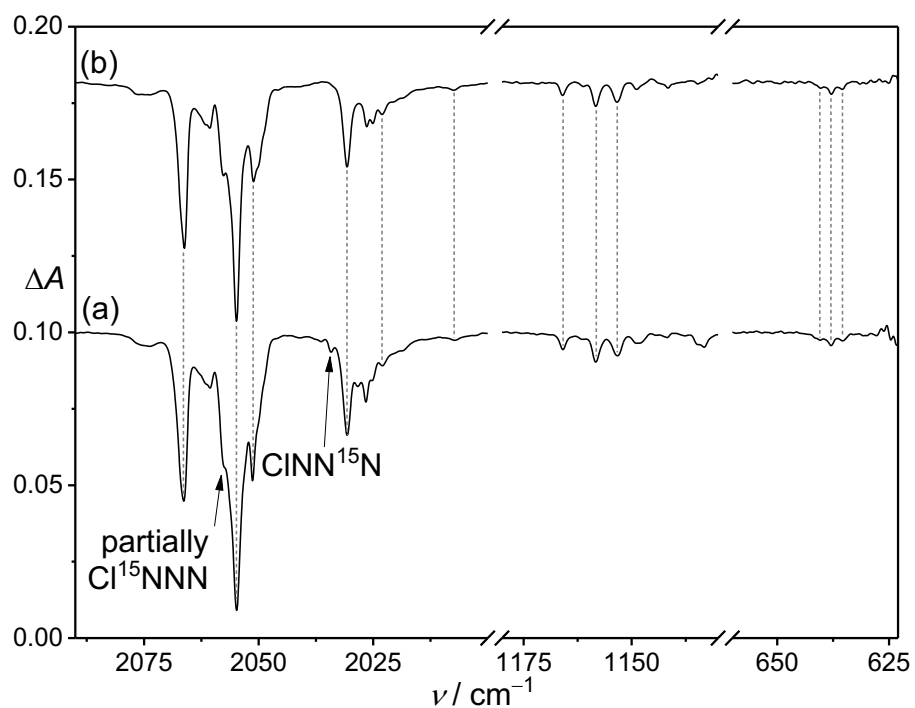


Fig. S8. (a) Difference spectrum showing the changes after 8 min 436 nm irradiation of Cl_2 and AgNN^{15}N reaction products. (b) Difference spectrum shows the changes after 6 min 436 nm irradiation of Br_2 and AgNN^{15}N reaction products.

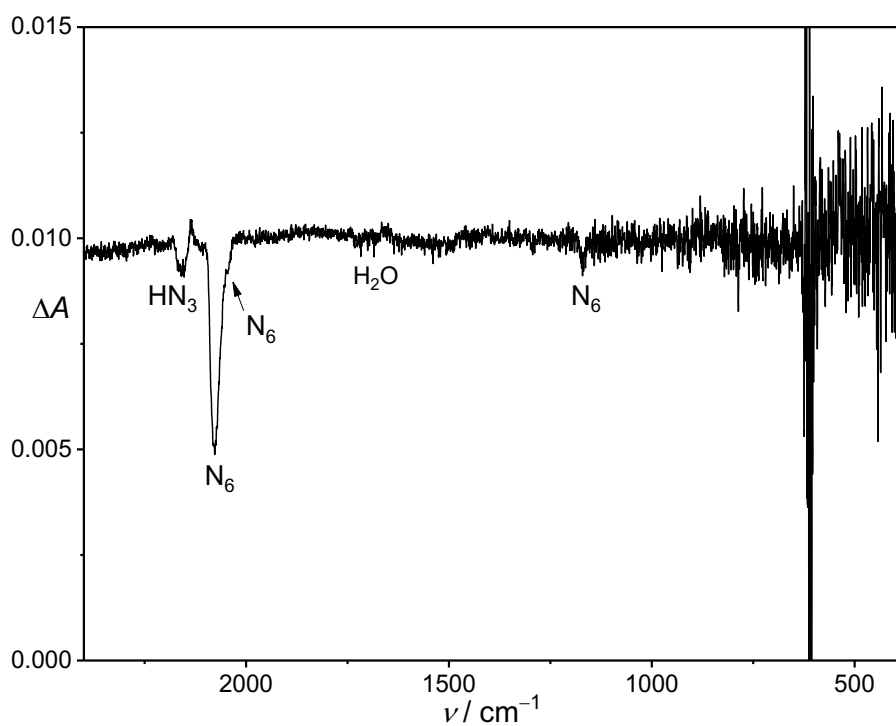


Fig. S9. Difference spectrum of $\text{C}_{2\text{h}}\text{-N}_6$ showing the changes after 8 min 436 nm irradiation of Br_2 and AgN_3 reaction products film at 77 K. Matrix sites from HN_3 and H_2O are marked.

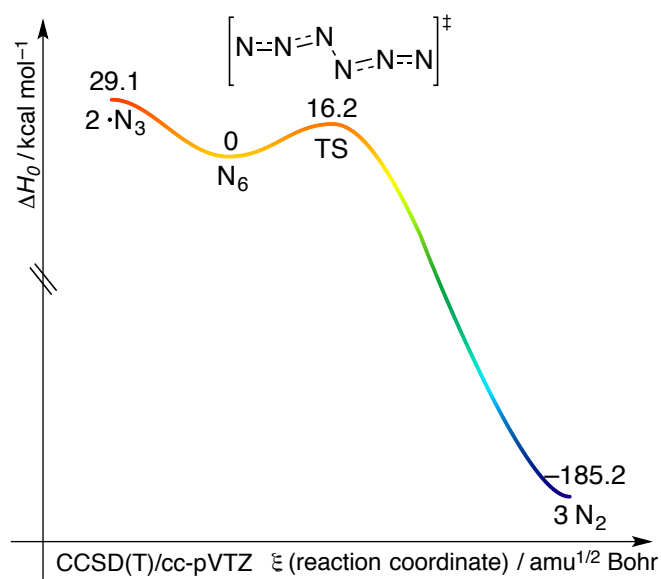


Fig. S10. Potential energy profile (ΔH_0 , kcal mol^{-1}) for N_6 at CCSD(T)/cc-pVTZ + ZPVE.

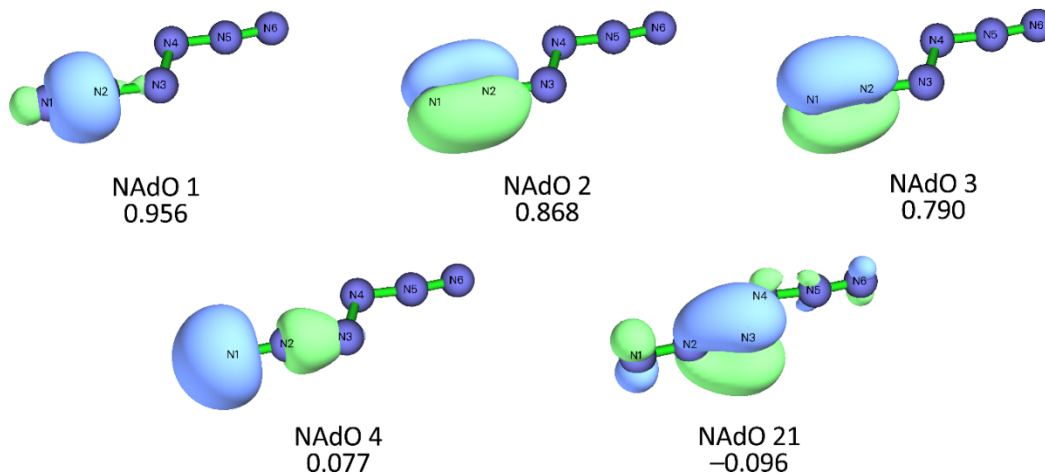


Fig. S11. Natural adaptive orbitals (NAdOs) of C_{2h} -N₆ from bond order density (BOD) analysis of bond N1-N2 (isovalue = 0.064), eigenvalues of NAdOs are given.

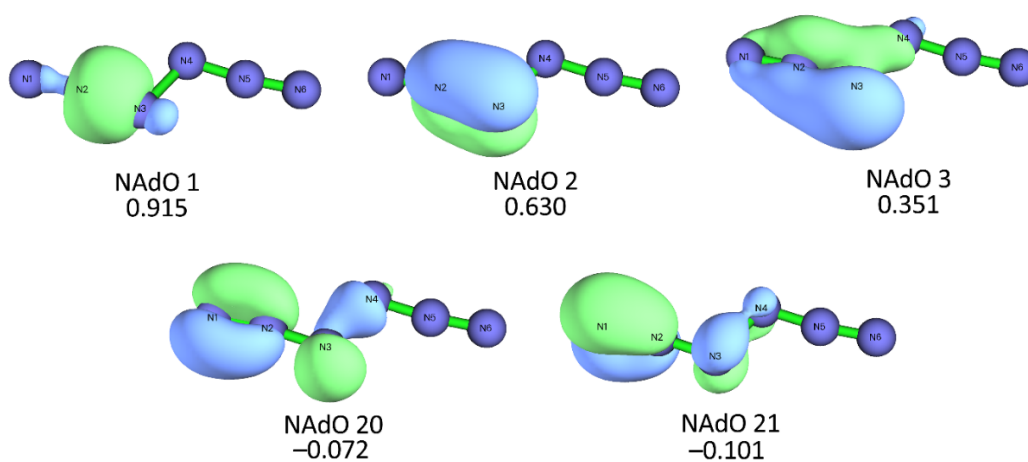


Fig. S12. Natural adaptive orbitals (NAdOs) of C_{2h} -N₆ from bond order density (BOD) analysis of bond N2-N3 (isovalue = 0.064), eigenvalues of NAdOs are given.

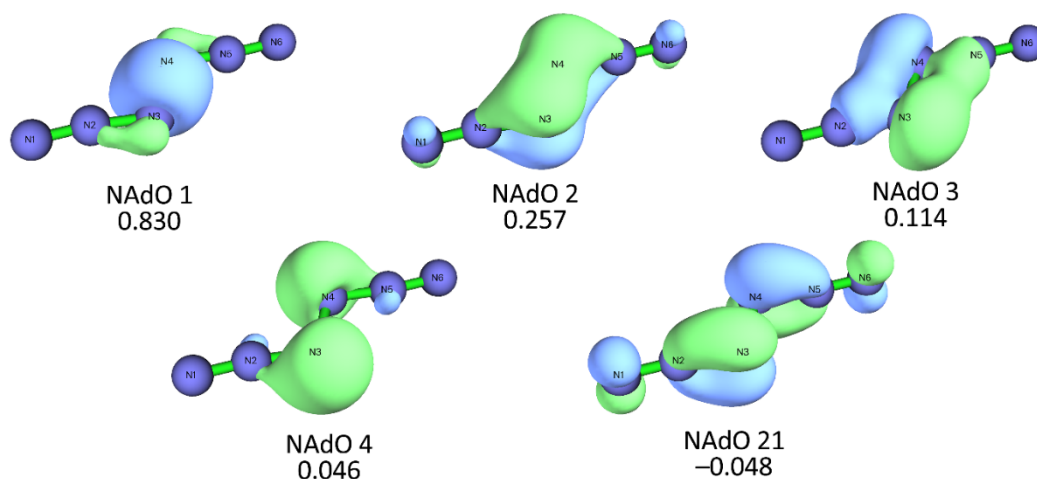


Fig. S13. Natural adaptive orbitals (NAdOs) of C_{2h} - N_6 from bond order density (BOD) analysis of bond N3-N4 (isovalue = 0.064), eigenvalues of NAdOs are given.

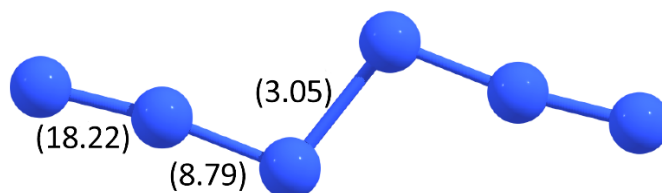


Fig. S14. The computed bond force constants ($\text{aJ } \text{\AA}^{-2}$) of C_{2h} - N_6 .

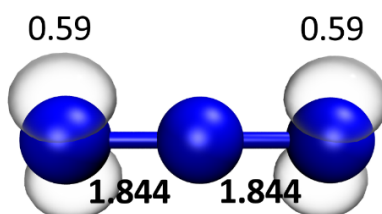


Fig. S15. Computed spin density of azide radical. Mulliken spin population (in regular) and natural bond order (in bold) are shown.

Table S1. Experimental and computed IR frequencies ($> 400\text{ cm}^{-1}$) and intensities (km mol^{-1}) for $\text{C}_{2\text{h}}\text{-N}_6$.

$\nu_{\text{cal.}}$		$\nu_{\text{exp.}}$	$\Delta\nu_{\text{cal.}}(^{15}\text{N}/^{14}\text{N})^{\text{c}}$			$\Delta\nu_{\text{exp.}}(^{15}\text{N}/^{14}\text{N})$			assignment
B3LYP/DVPT2 ^a	CCSD(T)/harm ^b	Ar-matrix	1a	1b	1c				
2198.1 (0)	2185.0 (0)	n.o.	24.5	11.6	10.0	n.o.	n.o.	n.o.	$\nu_{12}, A_g, \nu_{\text{sym}} \text{N1N2N3}$
2143.5 (1095)	2125.0 (1180)	2076.6 (s)	24.4	16.7	4.8	25.9	22.2	10.9	$\nu_{11}, B_u, \nu_{\text{asym}} \text{N1N2N3}$
2074.0 (80) ^d	2102.5	2049.0 (m)	12.2	29.5	44.0	17.6	27.8	41.2	$\nu_8 + \nu_9$
1259.6 (0)	1265.3 (0)	n.o.	8.1	19.3	30.2	n.o.	n.o.	n.o.	$\nu_{10}, A_g, \nu_{\text{sym}} \text{N3N2N1}$
1212.6 (95)	1202.4 (120)	1177.6 (m)	11.3	18.7	23.6	11.6	19.3	24.3	$\nu_9, B_u, \nu_{\text{asym}} \text{N3N2N1}$
869.1 (0)	900.0 (0)	871.4 ^e	0.6	11.4	22.4	8.3 ^e	8.5 ^e	16.9 ^e	$\nu_8, A_g, \nu \text{N3N4}$
660.5 (41)	648.5 (31)	642.1 (w)	1.5	4.0	6.5	1.4	4.3	7.3	$\nu_7, B_u, \delta_{\text{asym}} \text{N1N2N3}$
598.0 (0)	599.2 (0)	n.o.	5.7	4.4	4.1	n.o.	n.o.	n.o.	$\nu_6, A_g, \delta_{\text{sym}} \text{N1N2N3}$
537.0 (0)	531.4 (0)	n.o.	3.7	2.6	2.5	n.o.	n.o.	n.o.	$\nu_5, B_g, \omega_{\text{sym}} \text{N1N2N3}$
500.2 (11)	496.0 (10)	n.o.	3.4	2.8	3.1	n.o.	n.o.	n.o.	$\nu_4, A_u, \omega_{\text{asym}} \text{N1N2N3}$

^aAnharmonic frequencies computed at B3LYP/def2-TZVP using the DVPT2 method.

^bUnscaled harmonic frequencies computed at CCSD(T)/cc-pVTZ.

^cAnharmonic isotope shifts computed at B3LYP/def2-TZVP using the DVPT2 method.

^dB3LYP/def2-TZVP computation suggests there is Fermi resonance with ν_{11} .

^eDerived from a combination band.

Table S2. Experimental and computed IR frequencies ($> 400\text{ cm}^{-1}$) and intensities (km mol^{-1}) with different methods for $\text{C}_{2\text{h}}\text{-N}_6$.

$V_{\text{cal.}}$			$V_{\text{exp.}}$	assignment
B3LYP/harm ^a	B3LYP/DVPT2 ^b	CCSD(T)/harm ^c	Ar-matrix	
2249.5 (0)	2198.1 (0)	2185.0 (0)	n.o.	$\nu_{12}, A_g, \nu_{\text{sym}} \text{ N1N2N3}$
2191.7 (1314)	2143.5 (1095)	2125.0 (1180)	2076.6 (s)	$\nu_{11}, B_u, \nu_{\text{asym}} \text{ N1N2N3}$
2145.1	2074.0 (80)	2102.5	2049.0 (m)	$\nu_8 + \nu_9$
1306.1 (0)	1259.6 (0)	1265.3 (0)	n.o.	$\nu_{10}, A_g, \nu_{\text{sym}} \text{ N3N2N1}$
1251.5 (121)	1212.6 (95)	1202.4 (120)	1177.6 (m)	$\nu_9, B_u, \nu_{\text{asym}} \text{ N3N2N1}$
893.6 (0)	869.1 (0)	900.0 (0)	871.4 ^d	$\nu_8, A_g, \nu \text{ N3N4}$
665.7 (42)	660.5 (41)	648.5 (31)	642.1 (w)	$\nu_7, B_u, \delta_{\text{asym}} \text{ N1N2N3}$
611.1 (0)	598.0 (0)	599.2 (0)	n.o.	$\nu_6, A_g, \delta_{\text{sym}} \text{ N1N2N3}$
545.0(0)	537.0 (0)	531.4 (0)	n.o.	$\nu_5, B_g, \omega_{\text{sym}} \text{ N1N2N3}$
510.6 (12)	500.2 (11)	496.0 (10)	n.o.	$\nu_4, A_u, \omega_{\text{asym}} \text{ N1N2N3}$

^aUnscaled harmonic frequencies computed at B3LYP/def2-TZVP.

^bAnharmonic frequencies computed at B3LYP/def2-TZVP using the DVPT2 method.

^cUnscaled harmonic frequencies computed at CCSD(T)/cc-pVTZ.

^dDerived from a combination band.

Table S3. Computed anharmonic IR frequencies (DVPT2 method at B3LYP/def2-TZVP, > 400 cm^{-1}) and intensities (km mol^{-1}) for isotopomers of $\text{C}_{2\text{h}}\text{-N}_6$.

$\nu_{\text{cal.}}$				Mode
natural	$^{15}\text{NNNNN}^{15}\text{N}$	$^{15}\text{NNN}^{15}\text{NNN}$	$\text{NN}^{15}\text{N}^{15}\text{NNN}$	
2198.1 (0)	2173.6 (0)	2186.5 (13)	2193.6 (0)	ν_{12}
2143.5 (1095)	2119.1 (1041)	2126.8 (1068)	2138.7 (1125)	ν_{11}
2074.0 (80)	2061.7 (128)	2044.4 (81)	2030.0 (35)	$\nu_8 + \nu_9$
1259.6 (0)	1251.5 (0)	1240.4 (5)	1229.4 (0)	ν_{10}
1212.6 (95)	1201.3 (92)	1193.9 (98)	1189.1 (107)	ν_9
869.1 (0)	868.6 (0)	857.8 (< 1)	846.7 (0)	ν_8
660.5 (41)	659.0 (41)	656.5 (40)	654.0 (40)	ν_7
598.0 (0)	592.3 (0)	593.5 (< 1)	594.8 (0)	ν_6
537.0 (0)	533.2 (0)	534.3 (< 1)	535.4 (0)	ν_5
500.2 (11)	496.6 (11)	497.2 (11)	498.0 (11)	ν_4

Table S4. Computed rate constants (s^{-1}) for the decomposition of $C_{2h}-N_6$ with different models included in Polyrate17C at the B3LYP/def2-TZVP level at different temperature.

T/K	TST	CVT	CVT/ZCT	CVT/SCT
2.8				
10.0				
20.0	9.09E-171	2.08E-171	5.06E-19	1.68E-14
28.0	1.12E-118	3.85E-119	3.63E-18	4.06E-14
40.0	1.47E-79	6.69E-80	1.82E-16	5.01E-13
50.0	2.81E-61	1.44E-61	2.27E-15	3.21E-12
75.0	7.72E-37	4.48E-37	2.37E-13	1.23E-10
77.3	2.40E-35	1.40E-35	3.50E-13	1.66E-10
100.0	1.46E-24	8.71E-25	1.36E-11	2.56E-09
125.0	3.72E-17	2.20E-17	8.94E-10	4.98E-08
150.0	3.45E-12	1.99E-12	6.29E-08	1.01E-06
175.0	1.28E-08	7.15E-09	3.72E-06	2.09E-05
194.7	1.92E-06	1.05E-06	7.85E-05	2.32E-04
200.0	6.29E-06	3.41E-06	1.73E-04	4.46E-04
225.0	8.04E-04	4.20E-04	5.86E-03	9.65E-03
250.0	3.98E-02	2.00E-02	1.31E-01	1.75E-01
273.1	7.95E-01	3.86E-01	1.61E+00	1.96E+00
275.0	9.88E-01	4.79E-01	1.94E+00	2.35E+00
298.1	1.21E+01	5.66E+00	1.69E+01	1.94E+01

Coordinates (Ångstrom) and Energies (Hartree)

C_{2h}-N₆

B3LYP/Def2-TZVP

N	0.12299000	-1.62281000	0.00000000
N	-0.55232000	0.46173000	0.00000000
N	-0.12299000	1.62281000	0.00000000
N	-0.12299000	-2.72347000	0.00000000
N	0.12299000	2.72347000	0.00000000
N	0.55232000	-0.46173000	0.00000000

Zero-point correction=	0.024497
Thermal correction to Energy=	0.029944
Thermal correction to Enthalpy=	0.030888
Thermal correction to Gibbs Free Energy=	-0.004602
Sum of electronic and zero-point Energies=	-328.437429
Sum of electronic and thermal Energies=	-328.431982
Sum of electronic and thermal Enthalpies=	-328.431038
Sum of electronic and thermal Free Energies=	-328.466528

C_{2h}-N₆

CCSD(T)/cc-pVTZ (internal coordinates)

N	0	0	0	0.000000000000	0.00000000	0.00000000
N	1	0	0	2.183250347540	0.00000000	0.00000000
N	2	1	0	1.251470563090	140.26056724	0.00000000
N	1	2	3	1.138174076326	147.74187273	179.99999791
N	3	2	1	1.138173914125	172.51870278	180.00000121
N	1	2	3	1.251470292364	39.73940168	0.00000000

CCSD(T)/cc-pVTZ electronic energy= -327.83100190

CCSD(T)/cc-pVTZ enthalpy= -327.80072255

ZPVE (CCSD(T)/cc-pVTZ) = 0.02376194

CCSD(T)/cc-pVTZ free energy= -327.83552055

N₃ radical (for bond dissociation energy, optimized)

CCSD(T)/cc-pVTZ (internal coordinates)

N	0	0	0	0.000000000000	0.00000000	0.00000000
N	1	0	0	1.183096393309	0.00000000	0.00000000
N	2	1	0	1.183097047958	179.99201228	0.00000000

CCSD(T)/cc-pVTZ electronic energy= -163.88936302

CCSD(T)/cc-pVTZ enthalpy= -163.87719650

ZPVE (CCSD(T)/cc-pVTZ) = 0.00815819

CCSD(T)/cc-pVTZ free energy= -163.89696460

N₂

CCSD(T)/cc-pVTZ (internal coordinates)

N	0	0	0	0.000000000000	0.00000000	0.00000000
N	1	0	0	1.103764945364	0.00000000	0.00000000

CCSD(T)/cc-pVTZ electronic energy= -109.37393684

CCSD(T)/cc-pVTZ enthalpy= -109.36528827

ZPVE (CCSD(T)/cc-pVTZ) = 0.00534378

CCSD(T)/cc-pVTZ free energy= -109.38704037

TS for dissociation into 3 N₂

B3LYP/Def2-TZVP

N	-1.65648200	-0.18493100	0.04565900
N	0.50636600	0.53652100	0.40348600
N	1.65642700	-0.18484500	-0.04558600
N	-2.75997100	-0.35164900	0.04658100
N	2.75990400	-0.35171800	-0.04668600
N	-0.50624400	0.53662100	-0.40345400

Zero-point correction= 0.019154
 Thermal correction to Energy= 0.025313
 Thermal correction to Enthalpy= 0.026258
 Thermal correction to Gibbs Free Energy= -0.011009
 Sum of electronic and zero-point Energies= -328.410897
 Sum of electronic and thermal Energies= -328.404737
 Sum of electronic and thermal Enthalpies= -328.403793
 Sum of electronic and thermal Free Energies= -328.441059
 Imaginary frequency = 1064.2i cm⁻¹

HN₃

CCSD(T)/cc-pVTZ (internal coordinates)

N	0	0	0	0.000000000000	0.00000000	0.00000000
H	1	0	0	1.018084387995	0.00000000	0.00000000
N	1	2	0	1.247654099142	108.30841720	0.00000000
N	3	1	2	1.136185843383	171.65256383	179.94322536

CCSD(T) energy = -164.538676947267

N₂H₄

CCSD(T)/cc-pVTZ (internal coordinates)

N	0	0	0	0.000000000000	0.00000000	0.00000000
H	1	0	0	1.015363736070	0.00000000	0.00000000
H	1	2	0	1.011963693700	106.58076088	0.00000000
N	1	2	3	1.444844072999	110.78254425	244.88663846
H	4	1	2	1.011963733466	106.20306068	270.12547224
H	4	1	2	1.015363973025	110.78242868	25.47448396

CCSD(T) energy = -111.698718776961

trans-HNNH

CCSD(T)/cc-pVTZ (internal coordinates)

N	0	0	0	0.000000000000	0.00000000	0.00000000
H	1	0	0	1.030943064633	0.00000000	0.00000000
N	1	2	0	1.253583342219	105.72863279	0.00000000
H	3	1	2	1.030943064632	105.72863280	180.00000000

CCSD(T) energy = -110.478027131268

TS for dissociation into 3 N₂

CCSD(T)/cc-pVTZ (internal coordinates)

N	0	0	0	0.000000000000	0.00000000	0.00000000
N	1	0	0	2.241861029835	0.00000000	0.00000000
N	2	1	0	1.569830117585	114.04432242	0.00000000
N	1	2	3	1.126410511898	161.64725208	105.40114534
N	3	2	1	1.118386052358	152.04470148	194.40036918
N	2	1	3	1.339279152996	33.55891178	91.74769990

CCSD(T)/cc-pVTZ electronic energy= -327.80072402

CCSD(T)/cc-pVTZ enthalpy= -327.77487147

ZPVE (CCSD(T)/cc-pVTZ) = 0.01873790

CCSD(T)/cc-pVTZ free energy= -327.81200831

Imaginary frequency = 966.3i cm⁻¹