

Detection of the elusive *cyclo*–1,2-dihydrotetrazete (N_4H_2) in the gas phase

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Nitrogen hydrides (N_nH_m) have attracted significant interest for their potential in developing high-energy-density materials. The synthesis of cyclic nitrogen hydrides is particularly challenging due to their inherently high strain energies. Here we report the preparation of the hitherto elusive *trans*- and *cis*-*cyclo*–1,2-dihydrotetrazete (**2a** and **2b**, *cyclo*- N_4H_2) along with its open chain isomer azidamide (**5a**, $N=N=N-NH_2$) by exposing low temperature (5 K) ice of ammonia (NH_3) to high-energy electrons. These compounds were detected and discriminated in the gas phase during the temperature programmed desorption phase exploiting isomer selectivity soft photoionization reflectron time-of-flight mass spectrometry. The *cyclo*–1,2-dihydrotetrazete signifies a free gas phase species containing a tetranitrogen ring existing without recourse to high-pressure conditions or conjugative stabilization. Our approach may provide feasible strategies for designing higher-order nitrogen ring systems and for elucidating their chemical bonding and stability.

For the last century, nitrogen hydrides (N_nH_m) have received substantial attention across the communities of theoretical chemistry, synthetic chemistry, and materials science^{1–8} from fundamental perspectives on chemical bonding and exceptional energetic properties for developing explosive, fuel, and propellant. At least nine open-chain nitrogen hydrides, including diimide (N_2H_2), hydrazine (N_2H_4), hydrogen azide (HN_3), triazene (N_3H_3), triazane (N_3H_5), ammonium azide (NH_4N_3), tetrazene ($H_2N-N=N-NH_2$), tetrazane (N_4H_6), and the hydrazinium azide salt ($N_2H_5^+N_3^-$) have been synthesized and isolated^{7–11}.

However, the pursuit of cyclic nitrogen hydrides presents a considerably greater challenge due to the substantial strain energy associated with the pure nitrogen ring. Kim et al. identified cyclotriazane (*cyclo*- N_3H_3) in crystals of zeolite A absorbed with ammonia (NH_3), wherein the *cyclo*- N_3H_3 is stabilized through coordination to silver ions, forming $Ag(cyclo-N_3H_3)^+$ complexes^{1,12}. Although theoretical calculations predicted that tetrazene (N_4H_4) and tetrazadiene (N_4H_2) containing four-membered nitrogen ring (*cyclo*- N_4) are kinetically

stable toward decomposition, no studies reported their experimental identification^{13–15}. The *cyclo*- N_4 moiety was initially prepared via benzyl and specific alkoxy carbonyl substitution of the ring (Fig. 1), as illustrated in tetrabenzyltetrazetidine and tetraalkyl tetrazetidinetetra-carboxylate radical cation^{16,17}. Electron paramagnetic resonance (EPR) spectroscopy has revealed the presence of an N_4^- molecular ion in single crystals of KN_3 or RbN_3 irradiated with UV or γ rays at 77 K¹⁸. Zheng et al. deposited nitrogen plasma on a cold window and found a weak infrared absorption at 936.7 cm^{-1} . The peak shifted to 900.0 cm^{-1} upon ^{15}N substitution and was assigned to tetrahedral N_4 species¹⁹. Bittererová et al. calculated the ground-state and excited-state properties of the rectangular N_4 molecule with D_{2h} symmetry. They discovered that its dissociation into two N_2 molecules proceeds via a new C_{2v} transition state with an effective barrier of approximately 27.2 kJ mol^{-1} , suggesting that the molecule may be stable at low temperatures²⁰. Li et al. predicted that the nitrogen-rich compound MnN_4 with a planar N_4 ring structure under high pressure exhibits both superconductivity and high hardness²¹. Y. Sajeev revealed through

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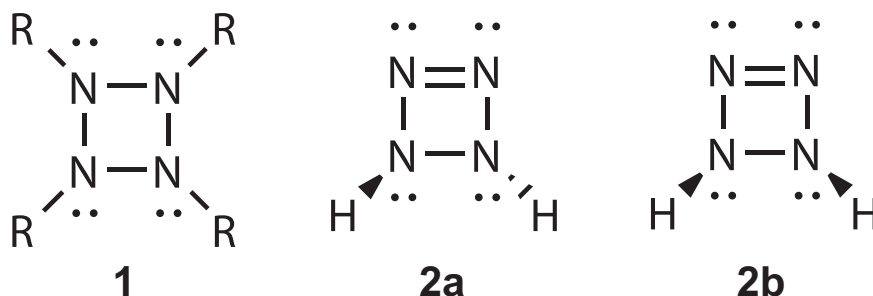


Fig. 1 | Molecules containing a tetranitrogen ring (cyclo- N_4). **1**, R substituted tetrazetidine, R = benzyl or alkyl carboxylate ester group; **2a**, trans-cyclo-1,2-dihydrotetrazete; **2b**, cis-cyclo-1,2-dihydrotetrazete. The short dashes on the nitrogen atoms denote lone pairs.

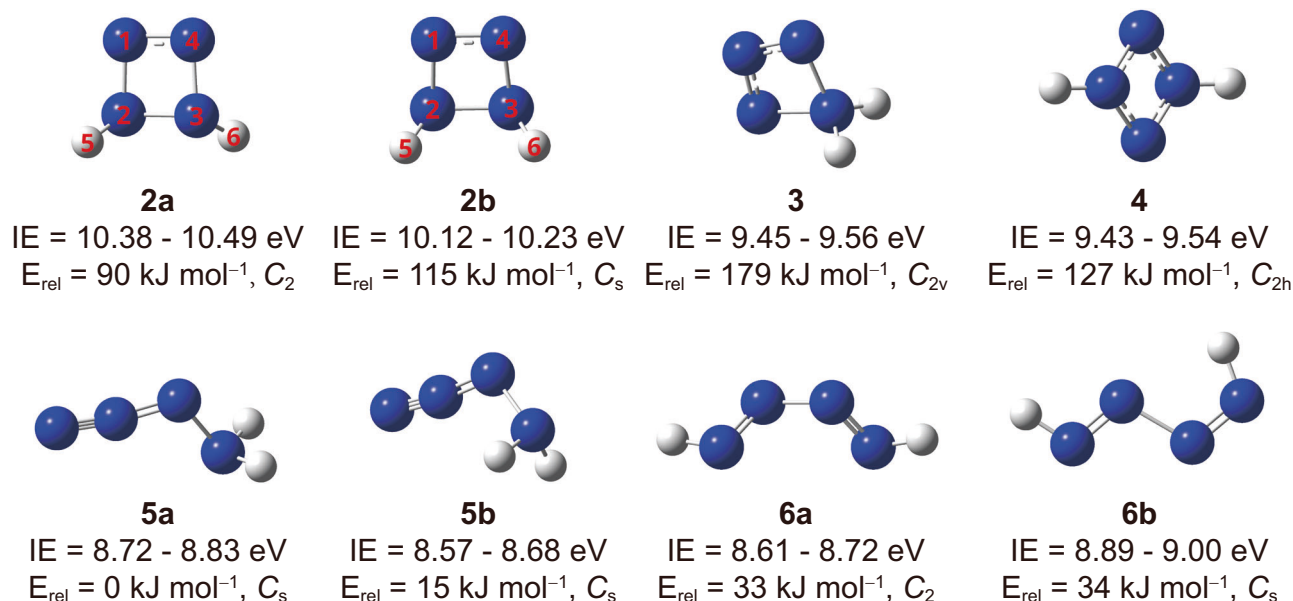


Fig. 2 | Molecular structures of distinct N_4H_2 isomers. The structures were computed at the CCSD(T)/cc-pVTZ level of theory. Relative energies (E_{rel}), adiabatic ionization energies (IE), and point groups were computed at the CCSD(T)/CBS//

CCSD(T)/cc-pVTZ + zero-point vibrational energy (ZPVE) level of theory. The atoms are color-coded in blue (nitrogen) and white (hydrogen).

calculations that the resonant attachment of an about 12 eV electron to a dinitrogen dimer (N_2)₂ can excite it into a $2p1h$ resonance state, thereby triggering a barrier-free cycloaddition reaction to generate a cyclic N_4^- anion²². Nevertheless, in the absence of additional stabilization mechanisms like coordination, complexation, and high pressure exploited in the preparation of $Ag(\text{cyclo-}N_3H_3)^+{}^{1,12}$, pentazole anion ($\text{cyclo-}N_5^-$)²³, and hexazine anions (N_6^{2-} and N_6^{4-})^{24,25}, whether free cyclic nitrogen hydrides can survive remains unclear.

In this work, we report the preparation and detection of the hitherto elusive trans- and cis-cyclo-1,2-dihydrotetrazete (**2a** and **2b**, cyclo- N_4H_2) as well as its thermodynamically most stable, open chain isomer azidamide (**5a**, $N=N-NH_2$) in the gas phase (Fig. 2). The experiments were conducted by irradiating ammonia (NH_3) or deuterated ammonia (ND_3) ices with energetic electrons at 5 K (Supplementary Tables 1 and 2) followed by heating the sample to 300 K at a rate of 1 K min⁻¹ to sublime the ices (Supplementary Fig. 1). During this temperature-programmed desorption (TPD) stage, N_4H_2 isomers were identified by employing vacuum ultraviolet (VUV) Photoionization Reflectron Time-of-Flight Mass Spectrometry (PI-ReTOF-MS) in conjunction with electronic structure computations^{26,27}. Previous studies detected solely lithium-ion-adducts $N_4H_2(N_4H_2Li^+)$ of an unknown structure generated by microwave discharge of nitrogen (N_2) and hydrogen (H_2) mixtures⁵. The present identification of cyclo-1,2-

dihydrotetrazete provides fundamental insights into unconventional synthetic pathway and photoionization properties of cyclic nitrogen hydrides along with their kinetic stabilities toward unimolecular decomposition in the gas phase thus enhancing our knowledge of highly strained cyclic molecules of fundamental interest to chemical bonding and electronic structure.

Results

Infrared spectroscopy

The chemical evolution of ammonia ices during electron irradiation was monitored by Fourier transform infrared spectroscopy (FTIR) (Fig. 3, Supplementary Tables 3 and 4). The spectra of the pristine ices exhibited absorption peaks corresponding to NH_3 at 3382 cm⁻¹ (ν_3), 3298 cm⁻¹ ($2\nu_4$), 3213 cm⁻¹ (ν_1), 1626 cm⁻¹ (ν_4), and 1057 cm⁻¹ (ν_2). Electron irradiation consumed (30 ± 5)% of the NH_3 and generated increase of broad IR signal in the range of 3370–3090, 2780, 2090, 1515, and 1153 cm⁻¹. The broad features at 3370–3090 cm⁻¹ are assigned to the stretching vibrations of newly formed N–H groups, potentially overlapping with the overtones of NH_2 scissoring mode²⁸. The band around 2780 cm⁻¹ can be attributed to the N–H stretching modes of isodiazene ($N=NH_2$) and/or combinations of newly formed NH_2 scissoring + twisting modes^{29,30}. The 2090 cm⁻¹ band corresponds to the asymmetric stretching mode of $-N=N=N$ groups³¹. The absorption at

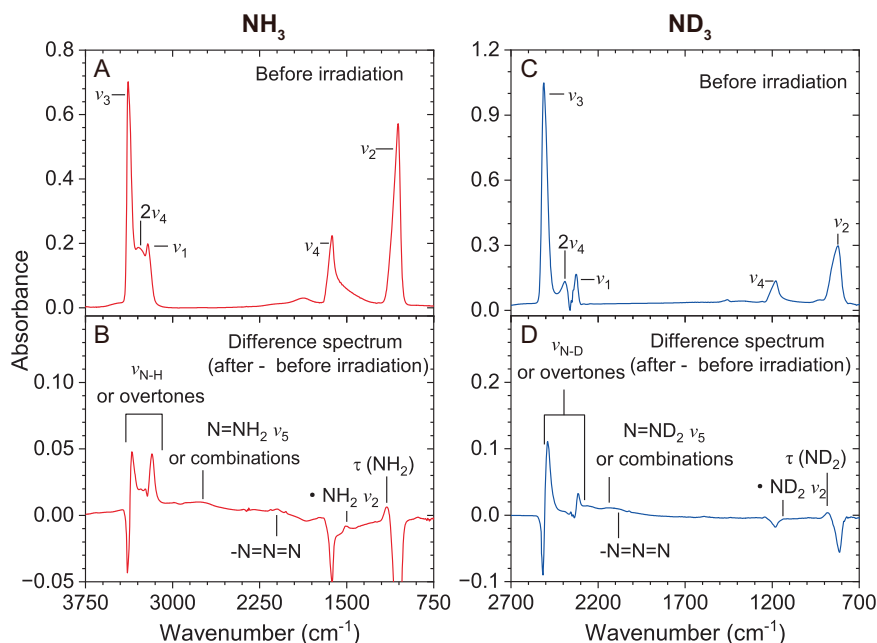


Fig. 3 | FTIR spectra of the ammonia (NH₃, left) and deuterated ammonia (ND₃, right) ices. **A NH₃, spectrum before electron irradiation; **B** NH₃, difference spectrum after electron irradiation; **C** ND₃, spectrum before electron irradiation; **D** ND₃, difference spectrum after electron irradiation.**

1515 cm⁻¹ can be associated with the bending mode of amino radicals ($\cdot\text{NH}_2$) (ν_2)³⁰ and/or NH₂ scissoring mode²⁸. The band near 1153 cm⁻¹ is assigned to the NH₂ twisting mode²⁸. The intensities of these peaks increase with irradiation time, indicating that they originate from the products of the irradiation process (Supplementary Fig. 2). The substitution of NH₃ by ND₃ induced red-shifted of the hydrogen-related absorptions and further supported the previous assignments (Supplementary Table 4). However, electron irradiation could generate a series of amines, imines, and azide homologs. Each homolog has similar functional groups and hence exhibits overlapping, non-unique IR absorptions. Therefore, an alternative approach is utilized to selectively probe discrete isomers.

Photon-ionization reflectron time-of-flight mass spectrometry

During the TPD phase, we characterized the sublimated molecules exploiting single VUV Photon-Ionization Reflectron Time-of-Flight Mass Spectrometry (PI-ReTOF-MS)^{26,27} (Supplementary Table 5). This approach can accurately distinguish isomers by tuning the photon energy (PE) based on the adiabatic ionization energies of the target products, thereby selectively ionizing the molecules or leaving them neutral, and distinguishing isomers through comparison of the resulting mass spectrometric signals. Guided by the quantum chemical calculations of N₄H₂ isomers (Fig. 2, Supplementary Table 6, and Source data), four photon energies were selected, namely 10.49 eV, 9.90 eV, 9.20 eV and 8.74 eV (Supplementary Table 1). Photons at 10.49 eV can ionize all isomers if produced since this energy exceeds the IE of each distinct isomer. Photons at 10.49 eV can ionize all isomers if produced, since this energy exceeds the IE of each distinct isomer; 9.90 eV photons can ionize only isomers **3** to **6b**; 9.20 eV ionization is limited to species **5a** to **6b**; 8.74 eV photons are able to ionize **5b** to **6b**. Although 8.74 eV is slightly higher than the computed lower ionization threshold of **5a**, this does not affect the findings of this study, as elaborated in the subsequent sections. Figure 4 presents the PI-ReTOF-MS results. Since NH₃ ices contain only two different atoms, the molecular recognition and analysis relying on the mass-to-charge ratio (m/z) of the ionized species is unambiguous and well-defined (Supplementary Table 5). We focus on the signal at $m/z = 58$ (Fig. 5), which can be attributed to N₄H₂⁺ ions. At PE = 10.49 eV, three

sublimation events at 224 K (peak **I**), 235 K (peak **II**) and 257 K (peak **III**) are detected (Fig. 5A). In a separate experiment, substitution of NH₃ with ND₃ shifts this signal from $m/z = 58$ to $m/z = 62$ (Fig. 5B). This result confirms that the species responsible for the signal at $m/z = 58$ contains two hydrogen atoms (H) and therefore can only be N₄H₂⁺. When the PE is reduced to 9.90 eV, the peak **II** at 235 K vanishes, while the 224 K (peak **I**) and 257 K (peak **III**) features are still present (Fig. 5C). This suggests the peak **II** (235 K) can be linked to **2a** (10.38–10.49 eV) and/or **2b** (IE = 10.12–10.23 eV) since only their IEs are between 10.49 eV and 9.90 eV. Further lowering the PE to 9.20 eV eliminates the sublimation event at 257 K (peak **III**) (Fig. 5D), indicating that this peak is associated with **3** (IE = 9.45–9.56 eV) and/or **4** (IE = 9.43–9.54 eV). The peak **I** at 224 K remaining at PE = 9.20 eV is attributed to **5a** since it disappears when the PE is decreased to 8.74 eV (Fig. 5E). It should be noted that in a blank control experiment conducted under the same experimental conditions but without irradiating the NH₃ ice, the $m/z = 58$ ion signal was not detected (Fig. 5F). This confirms that the identified N₄H₂ isomers **2a/2b**, **3/4**, and **5a** are generated by the electron irradiation of the ice samples. To further confirm the identification of isomer **2**, we measured its photoionization efficiency (PIE) curve. As shown in Fig. 6, there are two onsets of the ion counts at 10.17–10.21 eV and 10.45–10.49 eV, which fall within the range of the computed IEs of **2b** (10.12–10.23 eV) and **2a** (10.38–10.49 eV), respectively.

After providing convincing evidence for the preparation and identification of trans- and cis-cyclo-1,2-dihydro-tetrazete (**2a** and **2b**, cyclo-N₄H₂), now we turn our attention to their computed geometric structures at the CCSD(T)/cc-pVTZ level of theory. Both isomers **2a** and **2b** feature four-nitrogen rings with one N(1)=N(4) double bond and three single N-N bonds. The computed bond angles of the nitrogen ring in **2a** are $\angle\text{N}(1)=\text{N}(4)-\text{N}(3) = \angle\text{N}(4)=\text{N}(1)-\text{N}(2) = 93.1^\circ$ and $\angle\text{N}(1)-\text{N}(2)-\text{N}(3) = \angle\text{N}(2)-\text{N}(3)-\text{N}(4) = 86^\circ$, which are similar to that in **2b** $\angle\text{N}(1)=\text{N}(4)-\text{N}(3) = \angle\text{N}(4)=\text{N}(1)-\text{N}(2) = 93.7^\circ$ and $\angle\text{N}(1)-\text{N}(2)-\text{N}(3) = \angle\text{N}(2)-\text{N}(3)-\text{N}(4) = 86.3^\circ$. These bond angles are also close to the bond angles of $\angle\text{C}=\text{C}-\text{C}$ (94.2°) and $\angle\text{C}-\text{C}-\text{C}$ (85.8°) in cyclobutene (**7**, cyclo-C₄H₆) – an isoelectronic species of **2a** and **2b**. The bond length of the N(1)=N(4) double bond is 1.282 Å for **2a** and 1.278 Å for **2b**; these values are slightly larger than the N=N bond length of trans-diazene (HN=NH, 1.252 Å)³². Meanwhile, the bond lengths of the two

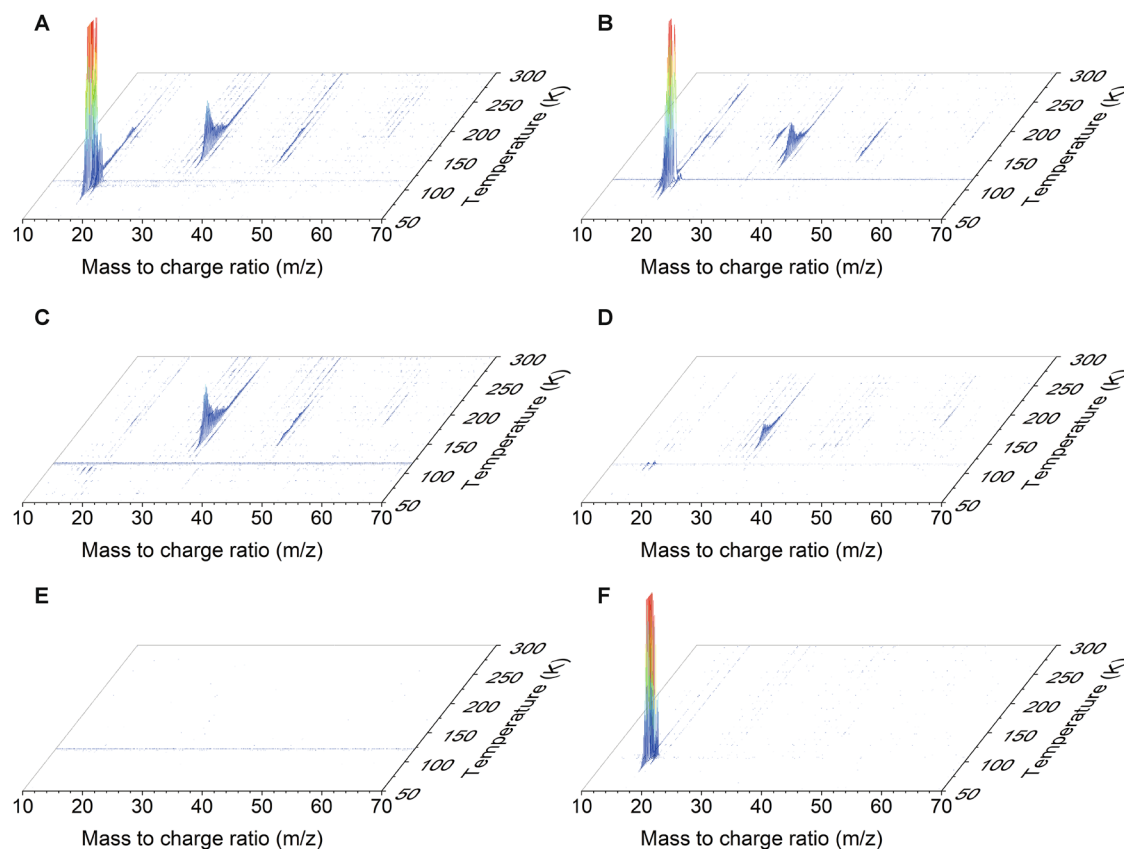


Fig. 4 | ReTOF-MS data during the TPD phase of the irradiated ammonia (NH_3) and deuterated ammonia (ND_3) ices. **A** NH_3 , PE = 10.49 eV; **B** ND_3 , PE = 10.49 eV; **C** NH_3 , PE = 9.9 eV; **D** NH_3 , PE = 9.2 eV; **E** NH_3 , PE = 8.74 eV; **F** NH_3 , PE = 10.49 eV, no irradiation.

nitrogen bonds N(1)–N(2) and N(3)–N(4) connected to the N(1)=N(4) double bond are in the range of 1.410–1.420 Å, which are shorter than that in hydrazine ($\text{H}_2\text{N}-\text{NH}_2$, 1.446 Å). The observed shortening of the single bonds and elongation of the double bonds may be attributed to the hyperconjugative coupling between the N(1)=N(4) π^* orbital and the lone pairs of the adjacent nitrogen atoms N(2) and N(3)³³. The remaining N(2)–N(3) bond lies considerably distant from the double bond and exhibits a bond length of 1.446 Å for **2a** and 1.446 Å for **2b**, closely matching that in $\text{H}_2\text{N}-\text{NH}_2$ (1.446 Å). In **2a**, the two nitrogen bonds N(1)–N(2) and N(3)–N(4) have the same bond lengths of 1.413 Å. With two hydrogens (H(5) and H(6)) located on opposite sides of the nitrogen ring, **2a** possesses only a single twofold rotation axis and therefore belongs to the C_2 point group. The isomer **2b** is characterized by a C_s point group symmetry with two hydrogens situated on the same side of the tetranitrogen ring. Strain energy is an important property of these cyclic molecules. Constructed homodesmotic equations evaluate this characteristic of **2a**, **2b**, and *cyclo*- C_4H_6 (**7**) (Fig. 7). The strain energy of **2a** (78 kJ mol^{−1}) and **2b** (106 kJ mol^{−1}) is lower than that of *cyclo*- C_4H_6 (**7**) (138 kJ mol^{−1}). Note that according to a natural bond analysis (NBO), the lowest unoccupied molecular orbital (LUMO) and highest occupied molecular orbital (HOMO) of these species exhibit distinct features^{34–36}. The HOMO and LUMO of *cyclo*- C_4H_6 (**7**) are mainly contributed by the $\text{C}_1=\text{C}_2$ π -bonding orbital and the associated π^* anti-bonding orbital, respectively. In the cases of **2a** and **2b**, the HOMO exhibits two-fold degeneracy with contributions primarily from four nitrogen atoms: N_1 , N_2 , N_3 , N_4 account for 19%, 28%, 28%, 19% of the HOMO, respectively. The LUMO is dominated by the p orbitals of N_1 and N_4 (>90%). The HOMO–LUMO gaps of **2a** (15.25 eV) and **2b** (14.86 eV) are comparable, whereas **7** exhibits a somewhat lower gap of 13.63 eV, suggesting slightly higher chemical reactivity.

Discussion

It is worth discussing the potential generation mechanisms of the identified N_4H_2 isomers. Previous studies have shown that low-dose electron irradiation of NH_3 ices can lead to the formation of the amino radical ($\cdot\text{NH}_2$), HN_3 , azide radical ($\text{N}_3\cdot$), nitrogen molecule (N_2), and $\text{HN}=\text{NH}$ ^{7,8,30}. Prolonged irradiation may promote $\text{N}_3\cdot$ and $\cdot\text{NH}_2$ radicals accumulation and therefore their recombination to produce **5a** barrierlessly (Fig. 8). Isomer **5a** could undergo intramolecular cyclization to **3**, followed by a hydrogen transfer to afford **2a**. Further hydrogen transfer to the same side of the tetranitrogen ring of **2a** can lead to the formation of **2b**. The barriers for these isomerization reactions are 216 kJ mol^{−1} (**TS1**), 118 kJ mol^{−1} (**TS2**), and 48 kJ mol^{−1} (**TS3**), which could be overcome by the energy delivered to the reactants via incident electrons (2000 eV or 1.9×10^5 kJ mol^{−1}). Alternatively, N_2 and $\text{HN}=\text{NH}$ may undergo one-step cyclization to produce **2b** overcoming a 474 kJ mol^{−1} energy barrier (**TS4**) upon electron irradiation. To further assess the energetic feasibility of the bimolecular association between N_2 and N_2H_2 , we computed the interaction energy³⁷ at the CCSD(T)/cc-pVTZ level. The interaction energy, $E_{\text{int}} = E_{\text{N}_2 \cdots \text{N}_2\text{H}_2} - (E_{\text{N}_2} + E_{\text{N}_2\text{H}_2})$, was found to be -5.97 kJ mol^{−1}. The negative value indicates a weak but stabilizing interaction, consistent with a physically reasonable pre-reactive encounter complex. Such stabilization supports the plausibility of the bimolecular association step. These reaction pathways are likely routes for the formation of the identified N_4H_2 isomers.

In summary, we prepared the previously elusive *cis-cyclo*-1,2-dihydrotetrazete (**2b**, *cyclo*- N_4H_2) along with open-chain azidamide (**5a**, $\text{N}=\text{N}=\text{N}-\text{NH}_2$) via energetic electron exposure of pure NH_3 ices and discriminated the isomers exploiting vacuum ultraviolet (VUV) PI-ReTOF-MS to analyze the sublimed molecules from the irradiated samples during the temperature programmed desorption (TPD) stage. The isotopic experiment employing deuterated ammonia (ND_3)

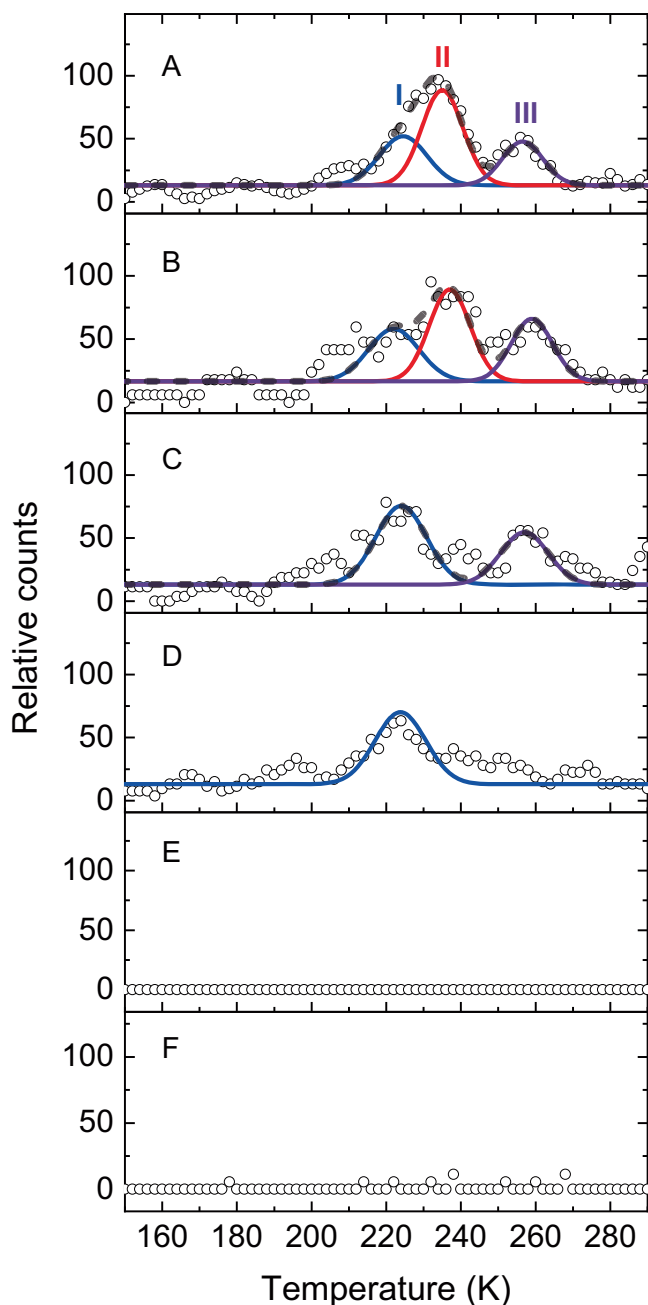


Fig. 5 | PIMS data at $m/z = 58$ ($N_4H_2^+$) during the TPD phase of the electron irradiated ammonia (NH_3) and deuterated ammonia (ND_3) ices. A PE = 10.49 eV; B PE = 10.49 eV, N_4D_2 ; C PE = 9.9 eV; D PE = 9.2 eV; E PE = 8.74 eV; F PE = 10.49 eV, no electron irradiation.

shifted the detected molecular ions of these isomers from $m/z = 58$ to $m/z = 62$, thereby further corroborating the assignments. The isomers sublimes at temperatures from 220 K to 260 K, which corresponds to average velocities close to 300 m s^{-1} . Given a $2.0 \pm 0.2 \text{ mm}$ separation between the sample surface and the ionization region, the lifetimes of the detected N_4H_2 isomers must exceed $6.5 \mu\text{s}$ to ensure their survival over this flight distance. In addition, our calculations show that overcoming an energy barrier of 131 kJ mol^{-1} is required for the decomposition of **2b** through **TS4**, which is higher than the decomposition barrier for N_6 (61 kJ mol^{-1})³⁸. The substantial decomposition barrier of 131 kJ mol^{-1} translates to a mean lifetime of more than 400 years at room temperature, indicating that the molecule is persistent under standard conditions. This work represents the gas-phase identification

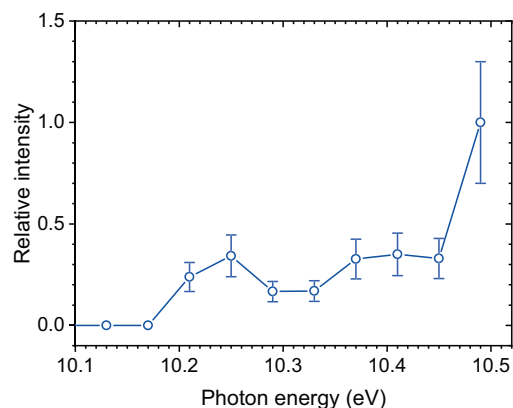


Fig. 6 | Photoionization efficiency (PIE) curves of isomers **2a and **2b** ($N_4H_2^+$). The error bars correspond to the statistical uncertainty of the machine.**

of a molecule comprising a four-membered ring composed exclusively of nitrogen atoms, achieved without recourse to high-pressure conditions or conjugative stabilization. Compared to the gas-phase pyrolysis and high-pressure routes, the strategy of electron irradiation of low temperature ices has a few features: energetic electrons can generate radicals and deliver energy to reactant to overcome high reaction barriers; the irradiation-generated radicals are formed in close proximity, facilitating their subsequent reactions; the formed species can be protected at cryogenic temperatures, preventing their decomposition that might otherwise occur under high-temperature or high-pressure conditions. Our approach may offer feasible conceptual pathways for the construction of higher-order nitrogen ring systems, with potential applicability as high-energy-density materials.

Methods

Experimental

The experimental setup involves preparing pure ammonia (NH_3) ice and its isotope-substituted counterpart (ND_3) on a silver wafer at a low temperature (5 K) within an ultrahigh-pressure chamber (base pressure: 10^{-11} Torr) (Supplementary information, Supplementary Fig. 1) with the design of the setup merged from references 26 and 27^{26,27}.

Energetic electrons are used to irradiate the ice to trigger the chemical-bond cleavage processes and non-equilibrium reactions. Following irradiation, the ice was heated to 300 K with a 1 K min^{-1} rate (temperature-programmed desorption (TPD)) to sublime solid-phase species (Supplementary Table 5). During the irradiation and TPD stages, the ice and the sublimed species were monitored using Fourier transform infrared spectroscopy (FTIR) and vacuum ultraviolet (VUV) PI-ReTOF-MS, respectively (Fig. 3 and Supplementary Table 4). This photoionization process utilizes four-wave mixing to produce vacuum ultraviolet light ($\omega_{\text{vuv}} = 2\omega_1 - \omega_2$). Here, ω_1 is obtained by frequency doubling of the output of a dye laser (LIOP-TEC, Liopstar-E) pumped by an Nd:YAG laser, while ω_2 is produced by a nanosecond tunable optical parametric oscillator laser (INNOLAS, SpitLight 600 OPO).

Theoretical

The N_4H_2 isomers and ions, transition states, azide radical ($N_3\cdot$), and amino radical ($\cdot NH_2$), nitrogen molecules, trans-diazene ($HN=NH$) were all computed at the CCSD(T)/cc-pVTZ level of theory generating zero-point vibrational energies (ZPVEs). The Cartesian coordinates (Å) and vibrational frequencies are provided as a Source Data file. With the previous optimized structures of the N_4H_2 isomers and ions, their energies were computed exploiting coupled cluster singles, doubles, and perturbative triples (CCSD(T)) method³⁹ with 3-point complete

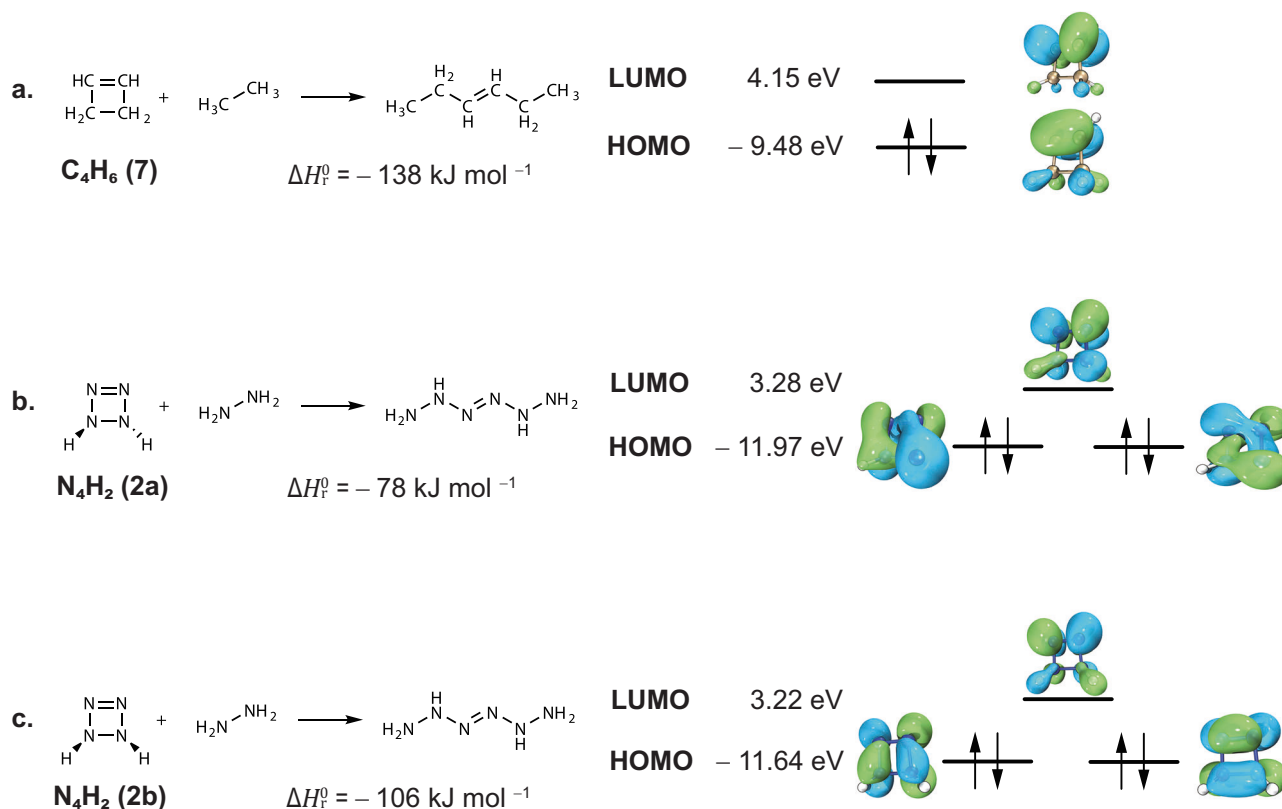


Fig. 7 | Homodesmotic equations for the determination of the strain energies of cyclobutene (C_4H_6 (7)), N_4H_2 (2a) and N_4H_2 (2b). Based on the premise that 7, 2a and 2b exhibit equal numbers of broken/formed C–C bonds and N–N bonds in their respective educts and products, their strain energies were computed at the CCSD(T)/cc-pVTZ level of theory using equations (a), (b) and (c). Computed

frontier natural bond orbitals (NBO), highest occupied molecular orbitals (HOMO), and lowest unoccupied molecular orbitals (LUMO) of 7, 2a and 2b are also shown. Blue and green colors correspond to electronically rich and deficient circumstances, respectively. The atoms on the right side of the figure are color-coded in bronze gold (carbon), white (hydrogen), and blue (nitrogen).

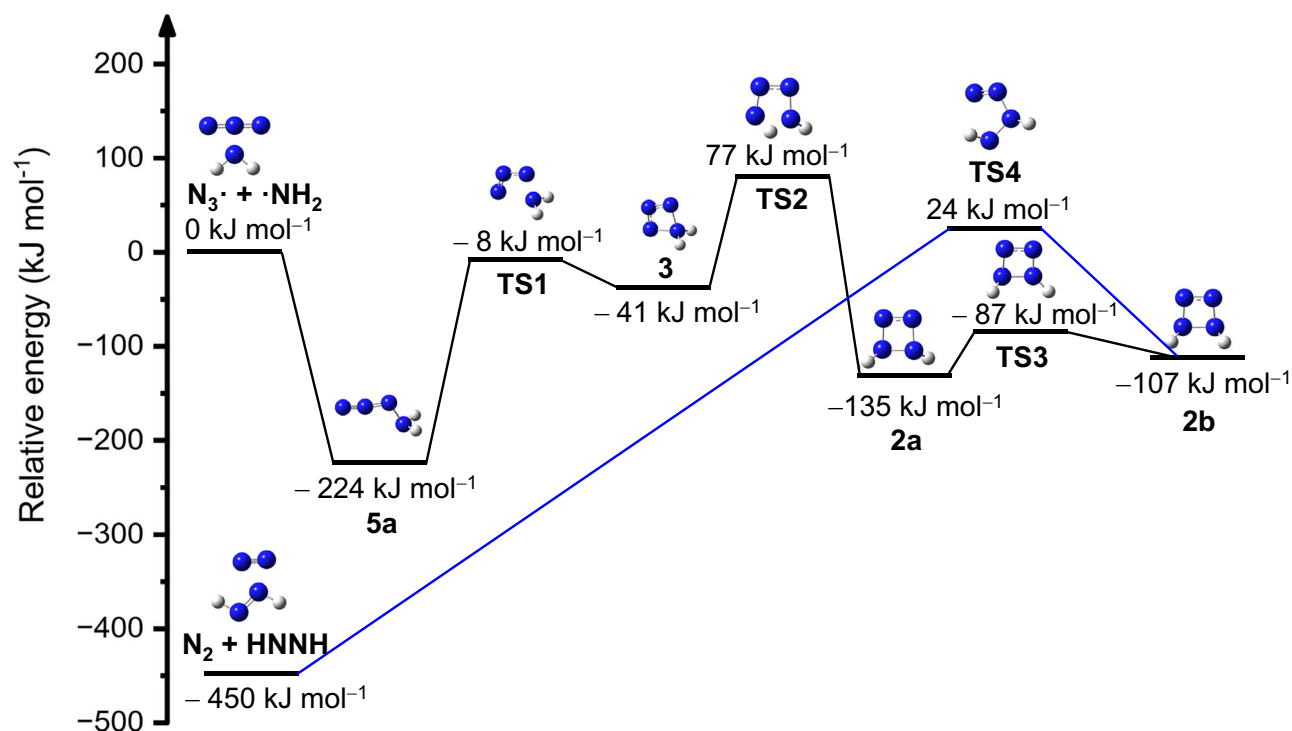


Fig. 8 | Potential energy surface (PES) for the formation of N_4H_2 isomers. The energies were computed at the M06-2X/aug-cc-pVTZ level of theory. The atoms are color-coded in blue (nitrogen) and white (hydrogen).

basis set (CBS) extrapolations⁴⁰ utilizing the cc-pVDZ, cc-pVTZ and cc-pVQZ basis sets^{41,42} (Supplementary Tables 6, Source data). The adiabatic ionization energies of the N₄H₂ isomers were obtained by calculating the energy difference between the neutral molecules and their corresponding cations at the CCSD(T)/CBS//CCSD(T)/cc-pVTZ level of theory with ZPVE corrections. Harmonic frequencies of the N₄H₂ and N₄D₂ isomers were computed at the CCSD(T)/cc-pVTZ level. Regarding anharmonic corrections, since direct CCSD(T)-level VPT2 anharmonic calculations are currently not available in the ORCA package, to address this limitation while preserving the high accuracy of the CCSD(T) harmonic frequencies, we adopted a hybrid CC/DFT correction scheme⁴³. The hybrid CC/DFT correction scheme is based on the assumption that the differences between coupled-cluster and DFT anharmonic frequencies primarily arise from the harmonic contributions. Accordingly, the corrected anharmonic frequencies were evaluated as:

$$\nu_{\text{CCSD(T)/DFT}} = \omega_{\text{CCSD(T)}} + \Delta\nu_{\text{DFT}} \quad (1)$$

where $\omega_{\text{CCSD(T)}}$ is the harmonic frequency calculated at the CCSD(T)/cc-pVTZ level, and $\Delta\nu_{\text{DFT}}$ is the anharmonic correction obtained from VPT2 calculations at the B3LYP/aug-cc-pVTZ level⁴⁴. The corrected anharmonic frequencies, the band positions of the N₄H₂ and N₄D₂ isomers, along with the calculated isotopic shifts, are shown in the Source Data file. The ionization energies were corrected for the Stark effect by 0.03 eV^{45,46}. All computations were employed the ORCA software package⁴⁷. Note that the computational uncertainty in the ionization energies was estimated to be −0.02 to +0.09 (Supplementary Table 6)⁴⁸.

Data availability

All data generated in this study are provided in the article, Supplementary Information, and Source Data file. Data supporting the findings of this manuscript are also available from the corresponding author upon request. Source data are provided with this paper.

Code availability

The authors did not use any previously unreported custom computer code or algorithm.

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Author contributions

J.Y., Z.L., and Y.W. performed the experiments. C.Z. organized the experiments. X.G. and C.Q.Z. carried out the theoretical calculations. X.L., W.Z., R.I.K., and C.Z. contributed to the discussion of the data analysis and the scientific findings. J.Y., R.I.K., and C.Z. wrote the manuscript, which was read, revised, and approved by all co-authors.

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Competing interests

The authors declare no competing interests.

Additional information

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