Supplementary Methods

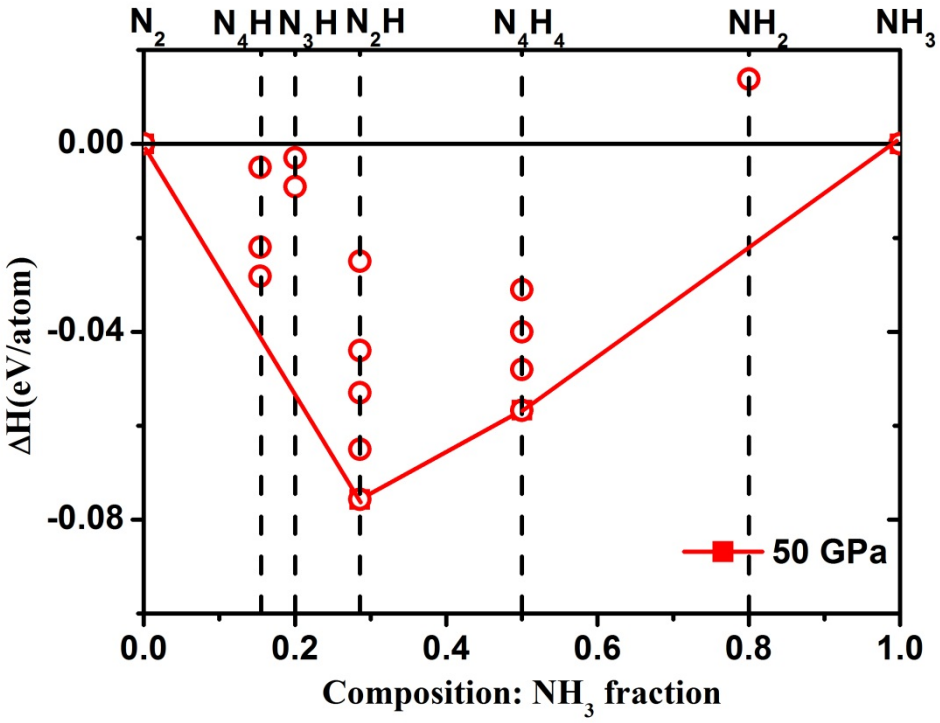
To seek for energetically stable hydronitrogens, we perform a global minimization of the energy landscape of N-H system at high pressures by combining *ab initio* density functional theory (DFT) total-energy calculations with a particle swarm optimization (PSO) algorithm as implemented in the CALYPSO code. Structure searches are performed at 50, 100, and 200 GPa with up to eight formula units for the hydronitrogens with varied H and N contents. Firstly, a population of random structures with certain crystallographic symmetry are constructed (as the first generation), in which the internal atomic positions are generated by symmetry operations of randomly selected space groups. Then the structures are optimized to the free energy local minima with DFT calculations. By evaluating the enthalpies of these structures, 60% of them with the lower enthalpies, together with the 40% newly generated structures, are used to produce the structures of next generation by the structure operators of PSO. In this step, a structure fingerprinting technique of bond characterization matrix is applied to generate new structures, so that identical (or extremely similar) structures are strictly forbidden. These significantly enhance the diversity of the generated structures, which is crucial for final convergence of the global structure search. The local structure optimizations are performed by using the conjugate gradients method. For most of the cases, the structure searches reach the convergence (*i.e.*, no new structure with the lower energy emerging) after 50 generations, at which more than thousand structures are evaluated.

Supplementary Tables

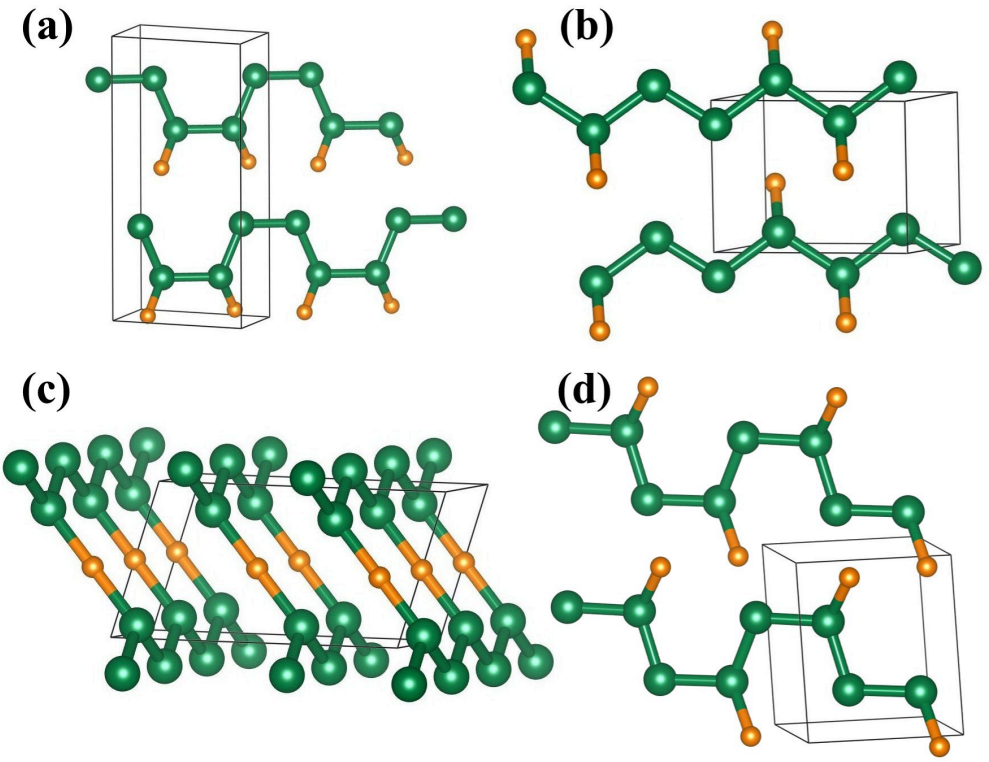
Supplementary Table S1. Detailed structural information for the energetically stable phases of hydronitrogen identified in our structure search.

Chemical composition	Space group	Pressure (GPa)	Lattice parameters (Å)	Atomic coordinates (Fractional)
N_2H	*P*-1	50	a=3.689 b=3.547 c=2.677 α=71.35 β=78.67 γ=66.44	N1 2i 0.6750 0.3692 0.1068 N2 2i 0.6745 0.9942 0.4148 H1 2i 0.0775 0.6700 0.1662
N_2H	$P2_1/c$	200	a=2.354 b=6.093 c=3.137 α=90.00 β=104.66 γ=90.00	N1 4e 0.5982 0.5963 0.0536 N2 4e 0.9291 0.9036 0.9438 H1 4e 0.7119 0.2340 0.5011
N_4H_4	*C*2	100	a=3.396 b=3.977 c= 4.498 α=90.00 β=93.82 γ=90.00	N1 2c 0.7495 0.6545 0.6737 N1 2c 0.9473 0.6605 0.1288 H1 2c 0.9853 0.1611 0.7797 H2 2c 0.2590 0.3656 0.5227
N_4H_4	*P*-1	200	a=4.276 b=2.469 c=2.424 α=98.55 β=87.52γ=95.62	N1 2i 0.8289 0.2375 0.7746 N2 2i 0.3712 0.0906 0.5132 H1 1a 0.0000 0.0000 0.0000 H2 2i 0.2852 0.4832 0.9316 H3 1g 0.0000 0.5000 0.5000
NH_2	*CC*	200	a=3.437 b=8.056 c=2.527 α=90.00 β=116.84 γ=90.00	N1 2a 0.0930 0.8654 0.1244 N2 2a 0.9876 0.6334 0.6464 H1 2a 0.0205 0.4607 0.9160 H2 2a 0.5590 0.4579 0.3583 H3 2a 0.0338 0.7420 0.4041 H4 2a 0.3153 0.6353 0.1721

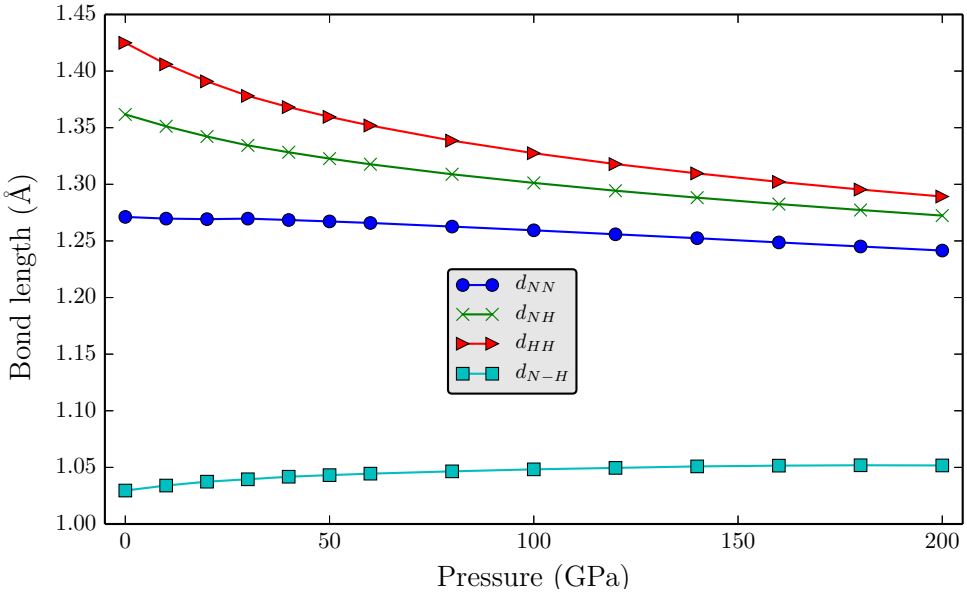
Supplementary Figures



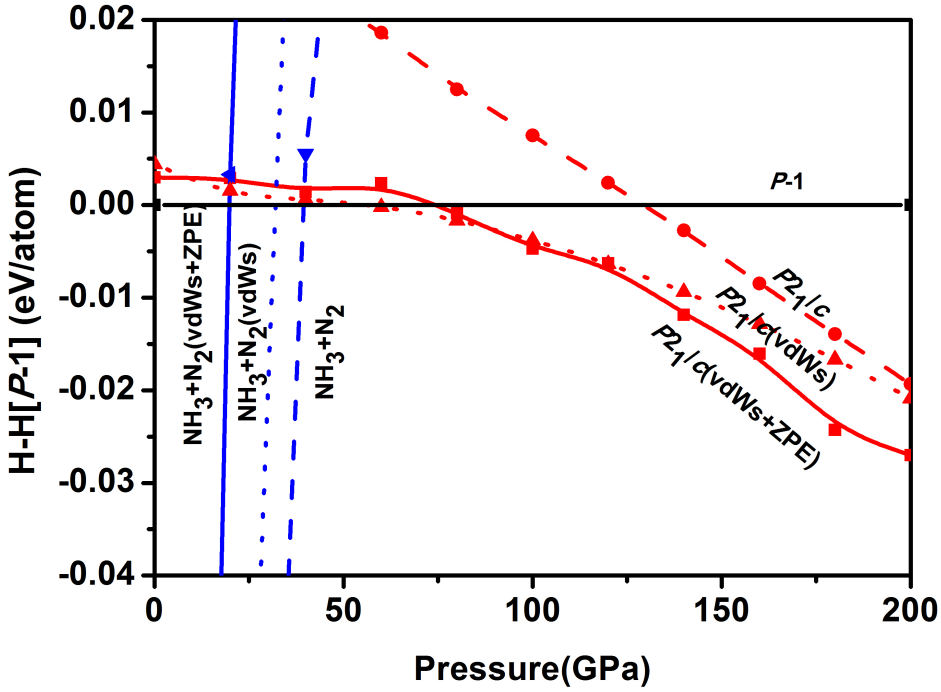
Supplementary Figure S1. The convex hull of the N-H system with respect to NH_3 and N_2 as the binary variables at 50 GPa.



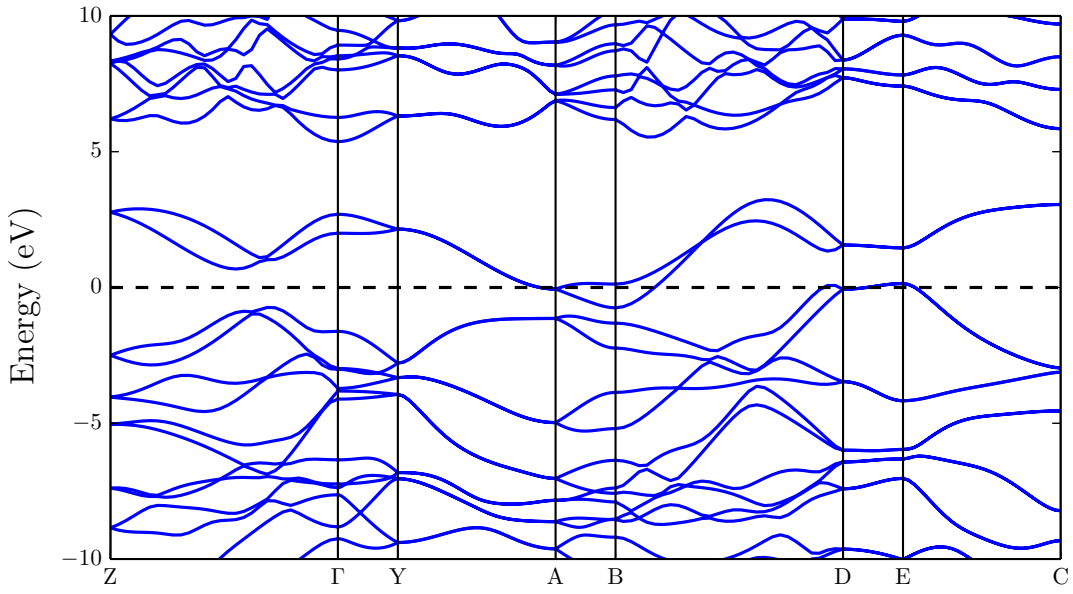
Supplementary Figure S2. Crystal structures of the N_2H polymeric phase with (a) the *C*2 space group, (b) the *C*2/m space group, (c) *C*mcm space group, and (d) *C*c space group.



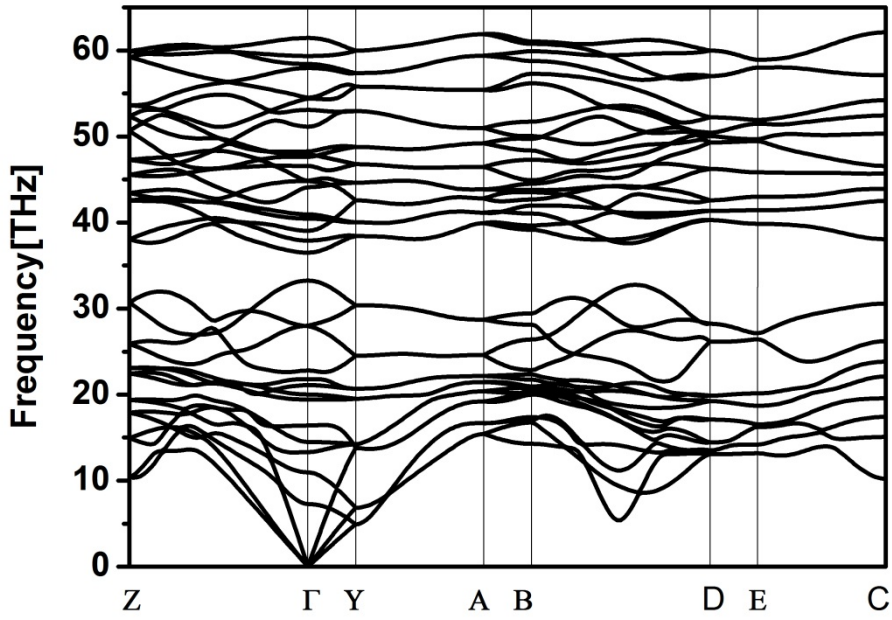
Supplementary Figure S3. Pressure dependence of bond lengths of the bond between N_H (denoted as d_{HH}), the one between N_N (denoted as d_{NN}), the one between N_H and N_N (denoted as d_{NH}), and the one between N and H (denoted as $d_{N\text{-}H}$) for the low-pressure *P*-1 phase of N_2H.



Supplementary Figure S4. Comparison of the enthalpy-pressure relationship by using different levels of approach (DFT, DFT+vdWs, DFT+vdWs+ZPE) for the stable low-pressure *P*-1 phase, high-pressure $P2_1/c$ phase, as well as dissociation into NH_3+N_2. The energy is in eV per atom and relative to the *P*-1 phase.



Supplementary Figure S5. Calculated band structure (with DFT) for the high-pressure $P2_1/c$ phase of N_2H at 50 GPa.



Supplementary Figure S6. Calculated phonon band dispersion for the high-pressure $P2_1/c$ phase of N_2H at 200 GPa.