Supporting Information for

Theoretical prediction of pressure-stabilized all-nitrogen N_{12} molecular crystal with π-π stacking

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Table S1. Structural parameters including the space group, lattice constants, and atomic positions of predicted N_{12} crystal at 0 GPa.

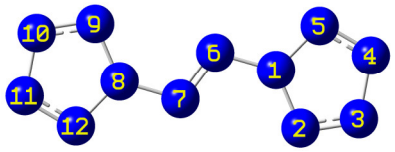
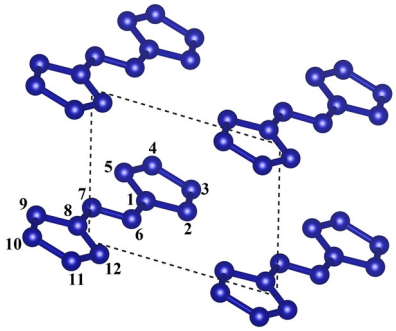
Space group	Lattice parameters	Wyckoff positions			
$P\bar{1}$	a = 4.86960 Å	2i	-0.95168	1.05881	-0.25366
	b = 5.75300 Å	2i	-0.73668	0.20806	-0.36727
	c = 5.99200 Å	2i	-0.85002	0.42199	-0.33588
	α = 105.9756	2i	0.86510	0.40412	-1.20257
	β = 66.1524	2i	0.80150	0.18119	-1.15149
	γ = 102.0559	2i	0.51155	1.10829	-1.00804
P1	a = 4.44600 Å	1a	0.81710	0.71178	0.28116
	b = 5.30643 Å	1a	0.24864	0.68788	0.49593
	c = 6.89640 Å	1a	0.25415	0.91310	0.37584
	α = 77.8501	1a	-0.01115	-0.07078	0.24756
	β = 99.0162	1a	0.97620	0.56519	0.43438
	γ = 97.4007	1a	0.86141	0.31063	0.50237
		1a	0.03708	0.22472	0.65727
		1a	0.93975	0.97548	0.74664
		1a	0.18362	0.87888	0.84066
		1a	0.11237	0.63080	0.93450
		1a	0.34333	0.50296	0.96830
		1a	0.51156	0.35077	-0.00077
$P\bar{6}2m$	a = 7.49320 Å	3f	0.18025	0.00000	0.00000
	c = 3.36100 Å	3f	0.65286	0.00000	0.00000
		6j	0.82644	0.17907	0.00000

Table S2. Harmonic vibrational analysis of N_{12} molecule.

Mode	Frequency	Infrared	Mode	Frequency	Infrared
1	38.88	0.0671	16	808.99	0.0002
2	81.58	3.7899	17	875.19	0.0000

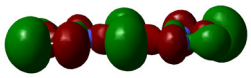
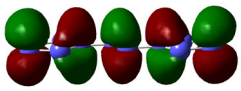
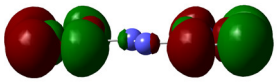
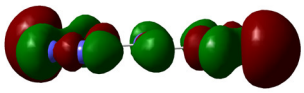
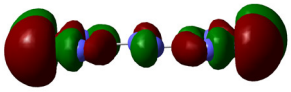
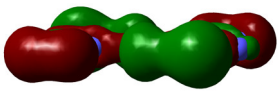
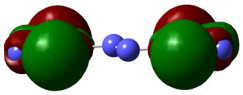
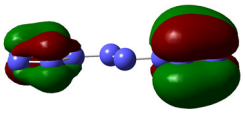
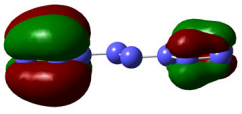
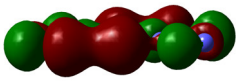
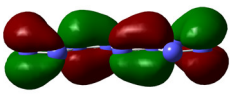
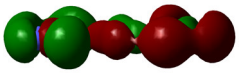
3	107.01	3.3787	18	1024.84	61.6352
4	145.16	0.0000	19	1059.72	0.0000
5	245.96	0.0000	20	1065.61	65.2366
6	266.62	0.0000	21	1079.32	0.0000
7	372.39	0.0000	22	1125.85	2.5366
8	433.01	0.0191	23	1186.45	0.0000
9	537.57	64.3590	24	1242.75	0.0001
10	672.61	0.0005	25	1259.49	200.7659
11	689.08	0.0153	26	1360.94	0.0000
12	741.48	0.0176	27	1391.45	37.6633
13	741.55	0.0010	28	1453.03	0.0004
14	748.83	129.1706	29	1455.86	11.4283
15	765.14	318.6450	30	1595.81	0.0000

Table S3. Geometries of N_{12} in gas phase and solid state.

		Bond (Å)	Angle (°)
Gas Phase		B12 1.375	A123 104.28
		B15 1.375	A234 109.61
		B23 1.375	A345 109.23
		B34 1.383	A451 104.75
		B45 1.281	A512 112.13
		B16 1.370	A516 118.87
		B67 1.247	A216 129.00
			A167 111.20
Solid State		B12 1.345	A123 104.92
		B15 1.354	A234 109.11
		B23 1.288	A345 109.50
		B34 1.387	A451 104.36
		B45 1.289	A512 112.11

	B16 1.367	A516 128.95
	B67 1.254	A216 118.93
		A167 110.65

Table S4. The energy level of 34 delocalized electrons.

Orbital number	Energy/au	Energy/eV	Type	Molecular Orbital
42	-0.34232	-9.315	LP	
41	-0.35392	-9.631	π	
40	-0.36246	-9.863	LP	
39	-0.36538	-9.942	LP	
38	-0.36717	-9.991	LP	
37	-0.38932	-10.594	LP	
36	-0.39737	-10.813	LP	
35	-0.40108	-10.914	π	
34	-0.40127	-10.919	π	
33	-0.40948	-11.142	LP	
32	-0.41760	-11.363	π	
31	-0.48497	-13.197	LP	

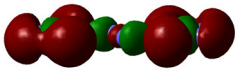
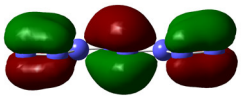
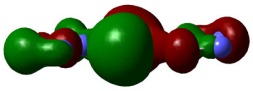
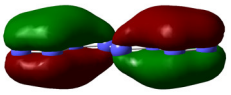
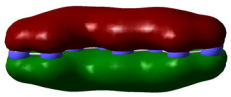
30	-0.48588	-13.221	LP	
29	-0.50673	-13.789	π	
28	-0.54922	-14.945	LP	
27	-0.58408	-15.894	π	
26	-0.61030	-16.607	π	

Table S5. Formation enthalpy of N_{12} crystal under different pressures, where the N_2 crystal was chosen as precursor.

Pressure (GPa)	Formation enthalpy (eV/atom)
0	0.80
20	0.39
40	0.18
60	0.03
80	-0.09
100	-0.19

Table S6. The enthalpy of N_{10} and N_{12} under different pressures, unit is eV atom^{-1}.

	0 GPa	20 GPa	40 GPa	60 GPa	80 GPa	100 GPa
N_{10}-VIP	-7.580	-6.365	-5.400	-4.534	-3.734	-2.986
N_{10}-P2$_1$	-7.605	-6.379	-5.355	-4.477	-3.670	-2.917
N_{12}	-7.578	-6.367	-5.403	-4.537	-3.735	-2.982

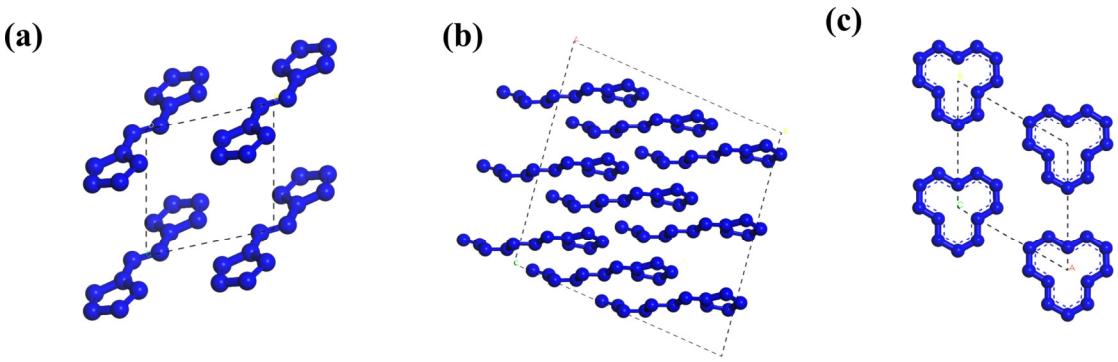


Figure S1. Crystal structures of predicted N_{12} crystal with (a) $P\bar{1}$, (b) P1 and (c) $P\bar{6}2m$ symmetry.

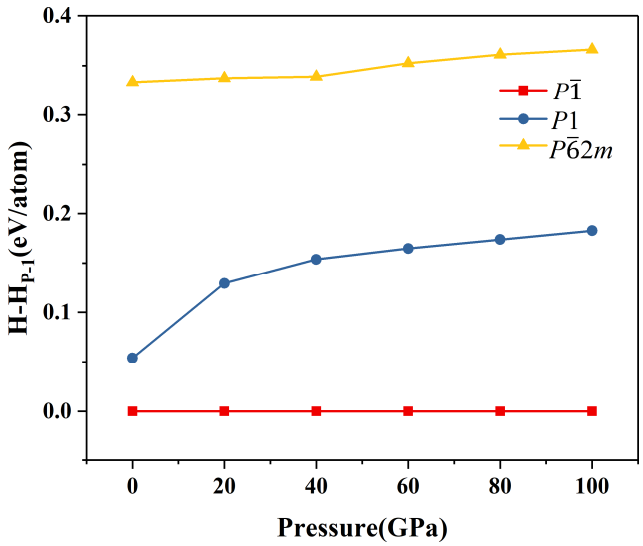


Figure S2. The enthalpy changes of different crystalline N_{12} with increasing of pressure.

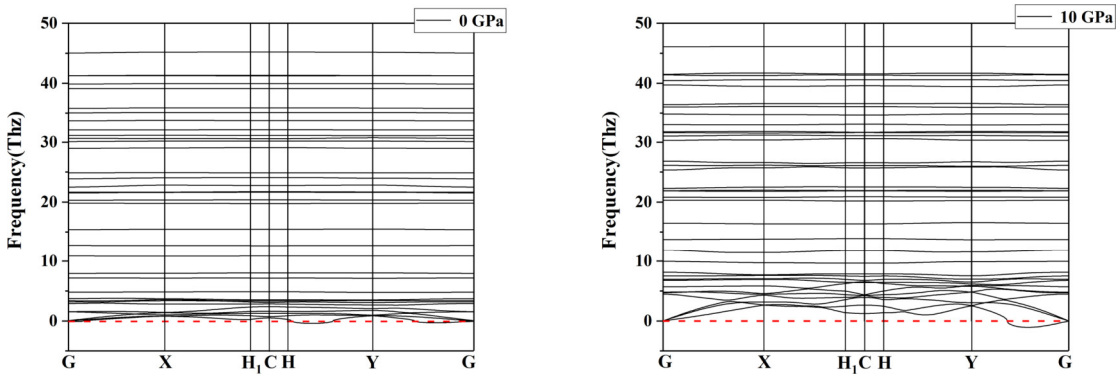


Figure S3. Phonon dispersion calculation for crystalline N_{12} crystal at 0 and 10 GPa.

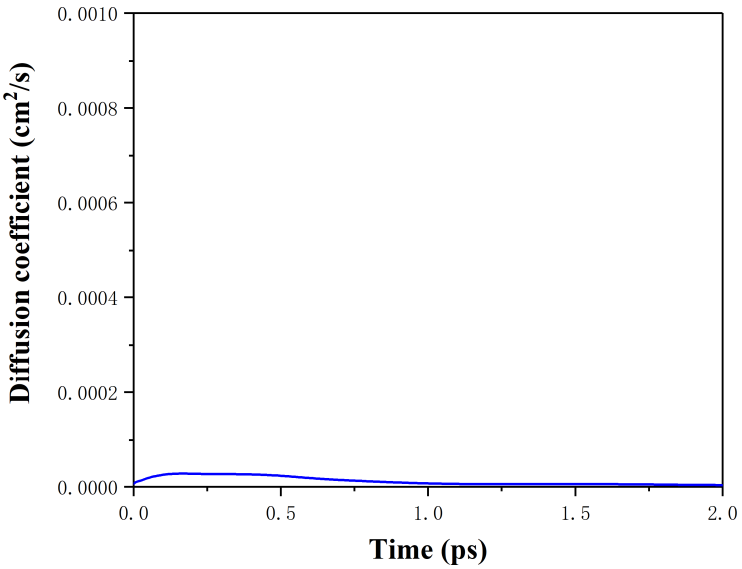


Figure S4. The calculated diffusion coefficient of the N atom in N_{12} crystal at the temperatures of 300 K.

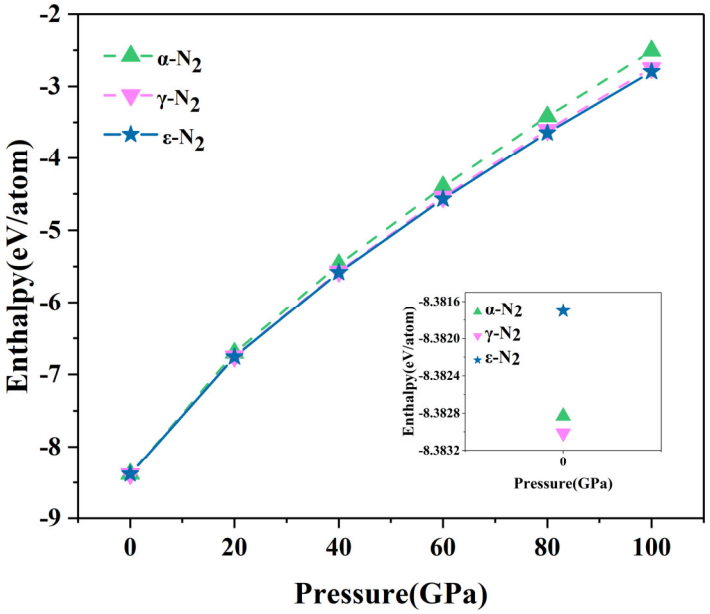


Figure S5. The enthalpy changes of nitrogen with α-, γ- and ε- phase under different pressures.

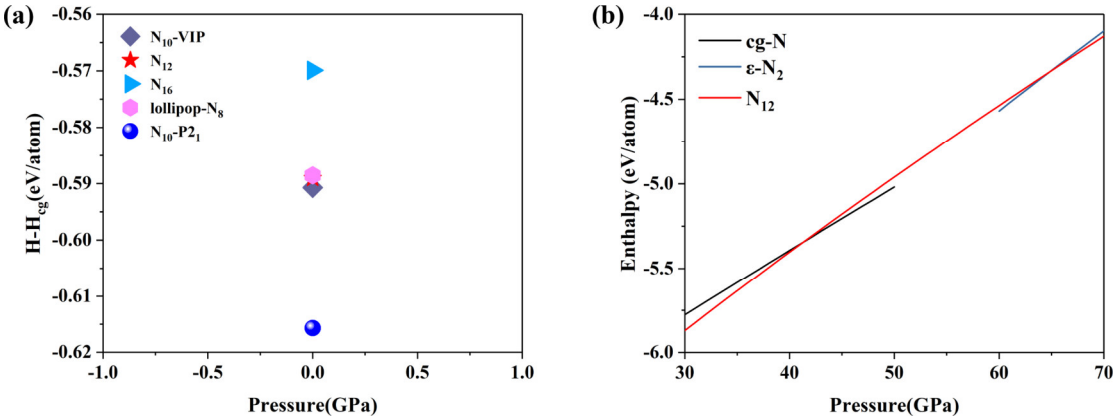


Figure S6. (a) The energy of N_{10}, N_{12}, N_{16} and lollipop-N_8 at 0 GPa; (b) the energy changes of N_{12} compared with cg-N and ε-N_2.

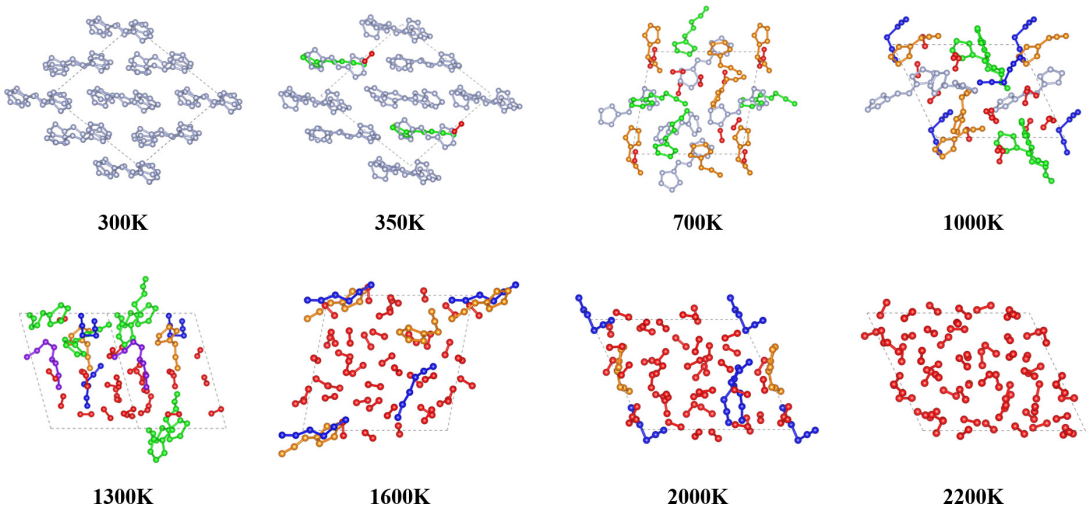


Figure S7. MD snapshots of the final configurations under different temperatures.

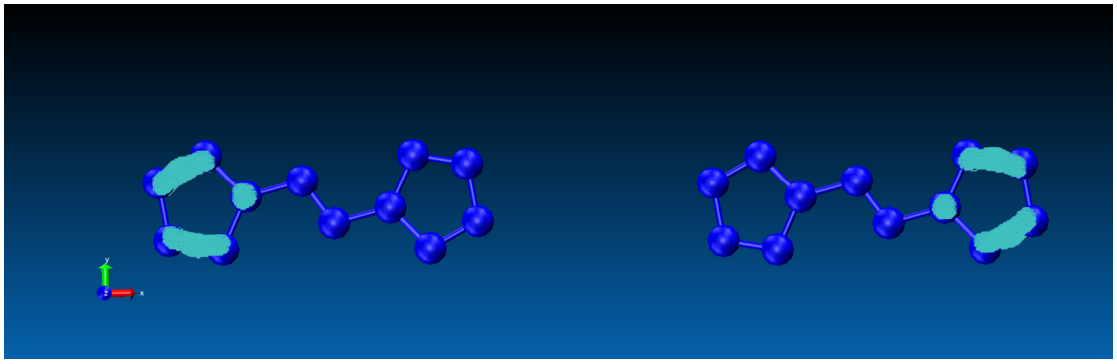


Figure S8. LOLIPOP interface of two pentazole rings in N_{12} molecule. The definite integral of LOL-π from a distance of 0.5 Å away from the molecular plane, and integration radius is 1.94 Å.