Supporting Information for

A novel all-nitrogen molecular crystal N_{16} as promising high-energy density material

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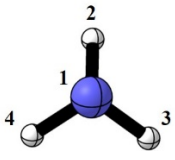
Table S1. Harmonic vibrational analysis of N_{16} molecule.

Mode	Frequency	Infrared	Mode	Frequency	Infrared
1	41.68	0.0001	22	834.35	0.1864
2	57.49	1.3169	23	916.95	27.6215
3	57.68	1.3276	24	917.14	27.5905
4	74.12	0.2877	25	1041.28	1.4787
5	74.26	0.2769	26	1041.46	1.5181
6	91.12	1.8537	27	1045.05	1.2268
7	187.03	0.0000	28	1071.04	42.2564
8	326.10	0.3131	29	1071.21	42.1406
9	326.15	0.3138	30	1084.04	0.1509
10	363.01	0.1206	31	1125.69	0.1101
11	401.83	3.7782	32	1125.89	0.1087
12	401.90	3.7920	33	1131.49	6.3023
13	601.83	4.0438	34	1250.76	16.4274
14	649.19	0.0000	35	1251.03	16.4709
15	678.41	3.4005	36	1275.72	0.0193
16	678.43	3.4278	37	1389.00	0.5344
17	750.04	0.7745	38	1407.93	0.6561
18	750.08	0.7843	39	1408.29	0.6637
19	752.33	0.0000	40	1458.46	1.9723
20	800.03	66.7973	41	1458.66	1.9936
21	800.44	66.8810	42	1462.31	16.1381

Table S2. Geometries of NH_3 and N_{16} in gas phase and N_{16} in solid state.

		Bond (Å)	Angle (°)	Dihedral (°)
NH_3		B12 1.019	A213 105.76	D2431 40.29
Gas Phase		B13 1.019	A314 105.76	
		B14 1.019	A412 105.76	

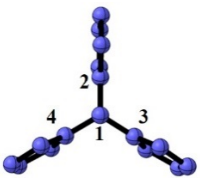
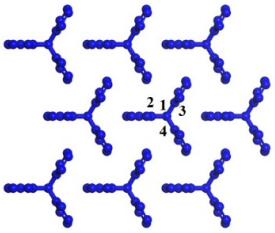
N_{16} Gas Phase		B12 1.375 B13 1.375 B14 1.375	A213 115.27 A314 115.28 A412 115.27	D2431 24.35
N_{16} Solid State		B12 1.380 B13 1.378 B14 1.378	A213 114.69 A314 114.65 A412 114.69	D2431 25.75

Table S3. Structural parameters including the space groups, lattice constants, and atomic positions for predicted N_{16} and N_8 cubic crystals. Previous reported crystalline N_8 molecule is also listed for comparison.

	Space group	Lattice parameters	Wyckoff positions			
N_{16}[a]	Cm	a = 6.79045 Å	4b	0.13958	0.87311	0.29248
		b = 11.95041 Å	4b	0.22408	0.77699	0.29251
		c = 5.21160 Å	4b	0.20641	0.74759	0.02699
		β = 108.1848	4b	0.11188	0.82580	0.86536
			4b	0.07242	0.90326	0.02966
			2a	0.96365	0.00000	0.93150
			2a	0.76449	0.00000	0.94936
			2a	0.59795	0.00000	0.72697
			2a	0.44305	0.00000	0.81987
			2a	0.51551	0.00000	0.09995
			2a	0.71547	0.00000	0.18015
N_8-cubic[a]	R-3	a = 6.55631 Å	18f	0.00391	0.19270	0.43283
		c = 6.61140 Å	6c	0.00000	0.00000	0.29792
N_8[b]	P1	a = 10.68587 Å	1a	0.76023	0.18969	0.00696
		b = 4.48237 Å	1a	0.64516	0.17816	0.03418
		c = 6.75541 Å	1a	0.56465	0.27353	0.86156

	α = 90.9501	1a	0.86600	0.19162	0.01120
	β = 83.3467	1a	0.00853	0.83059	0.47863
	γ = 45.6150	1a	0.11972	0.71651	0.61687
		1a	0.81238	0.86403	0.39450
		1a	0.91869	0.75063	0.53785
		1a	0.40343	0.20654	0.06804
		1a	0.28267	0.21933	0.06239
		1a	0.31823	0.79038	0.51711
		1a	0.21811	0.76835	0.55340
		1a	0.71261	0.80945	0.43763
		1a	0.61123	0.78967	0.44381
		1a	0.44330	0.28690	0.87645
		1a	0.17529	0.21887	0.07765

[a] predicted in this work.

[b] from reference[1].

Table S4. Formation energy of N_{16} in the gas phase and solid state.

	N_2(a.u.)	N_{16}(a.u.)	Formation Energy(eV)
Gas Phase	-109.519	-875.517	17.178
Solid State	ε-N_2(eV)	N_{16}(eV)	
0 GPa	-374.020	-111.874	12.799
20 GPa	-299.139	-92.659	7.054
40 GPa	-243.291	-77.344	3.753
60 GPa	-194.838	-63.597	1.349
80 GPa	-150.943	-50.852	-0.537
100 GPa	-110.329	-38.836	-2.059

We carefully analyzed the symmetry of N_{16} molecular crystal and found that it can be assigned to either the Cm or P1 symmetry group (see the figure S1 below) depending on the symmetry operation criteria parameter. However, the structural relaxation enthalpies from imposing either symmetry group result in practically the same results. We therefore assigned the higher symmetry of Cm to this structure. Majority solid-state compounds show much higher symmetry. However, this trend can be interrupted in molecular crystals, especially for those consisting of large molecules. The Cm structure may seem to have higher symmetry as both the molecule and the lattice are highly ordered. However, the combination of the large molecule and the translational symmetry of the lattice impose a large constraint on the overall symmetry. Considering the unit cell contains only two N_{16} molecules, the translational symmetry of this molecular crystal is quite "high".

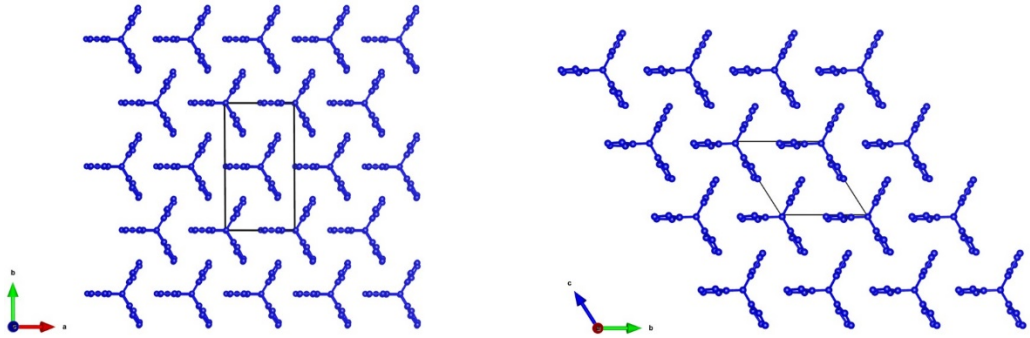


Figure S1. Structures of N_{16} molecular crystal with Cm and P1 symmetry.

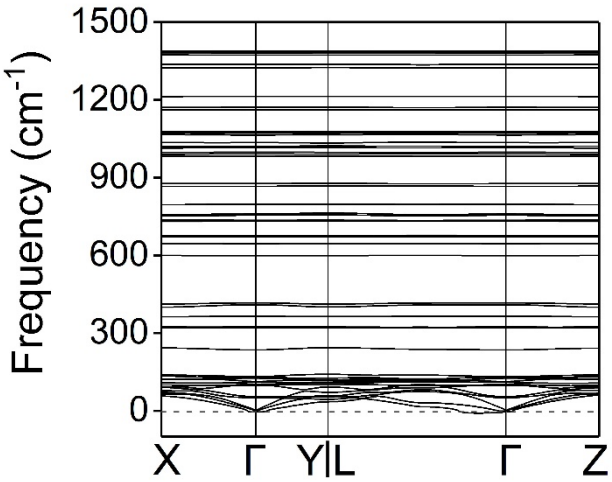


Figure S2. The phonon spectra of N_{16} solid structure.

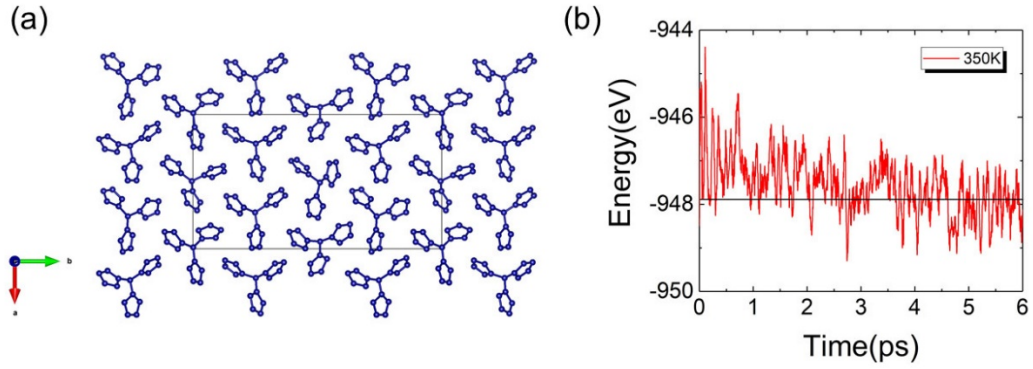


Figure S3. (a) Snapshots of the final configurations and (b) energy change for molecular dynamic simulation at 350K.

Reference

1 Hirshberg, B., Gerber, R. B. & Krylov, A. I. Calculations predict a stable molecular crystal of N_8. *Nat Chem* **6**, 52 (2014).