SUPPORTING INFORMATION

For

A new allotrope of nitrogen as high-energy density material

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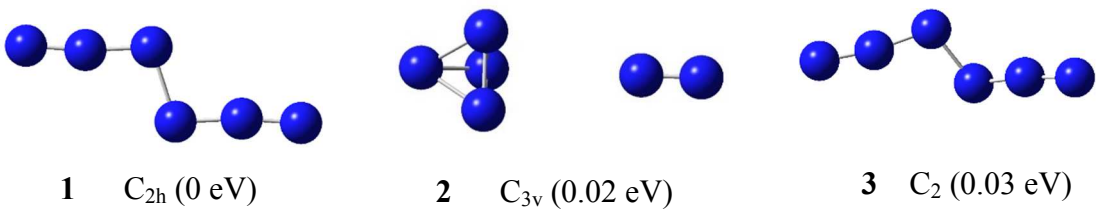
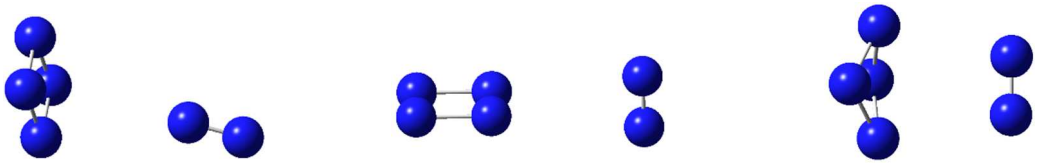
1. Optimized geometries of the gas-phase N_6 isomers.

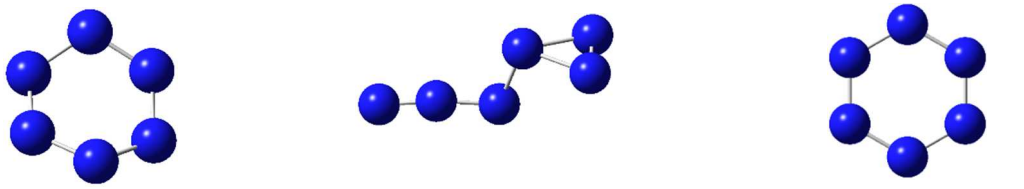
Figure S1. The optimized N_6 isomers at MP2/cc-PVDZ level. Numbers in brackets are the energies relative to that of the C_{2h} geometry. Molecular symmetries are determined with a tolerance of 0.01 Å.



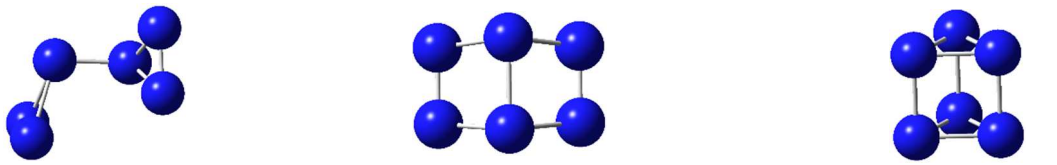
1 C_{2h} (0 eV) **2** C_{3v} (0.02 eV) **3** C_2 (0.03 eV)



4 C_1 (0.15 **5** C_s (0.17 eV) **6** C_{2v} (1.17 eV)



7 C_2 (1.19 eV) **8** C_s (1.23 **9** D_{6h} (1.30 eV)



10 C_2 (2.52 eV) **11** C_2 (2.80 eV) **12** D_{3h} (6.38 eV)

Table S1. Optimized coordinates of the N_6 isomers at the MP2/cc-PVDZ level. Isomers are listed in the same order as in Fig. S1. Numbers are in the unit of Å.

Isomer 1

N1	-2.76118700	-0.15650800	0.00118800
N2	0.46096900	-0.56895700	-0.00131400
N3	1.63515100	-0.10360400	0.00012800

N4	-0.46098800	0.56909800	-0.00131100
N5	-1.63518400	0.10371200	0.00012400
N6	2.76124000	0.15625800	0.00118500

Isomer 2

N1	0.96405600	0.50768800	0.68434500
N2	0.96034600	0.33799400	-0.78098200
N3	-3.09522700	0.00086400	-0.00269600
N4	-1.96523600	-0.00114000	0.00354500
N5	0.96364200	-0.84629300	0.09861600
N6	2.17241900	0.00088600	-0.00282800

Isomer 3

N1	-0.47845200	0.55584900	-0.34781000
N2	-1.59667200	0.10047700	0.03319600
N3	-2.68759200	-0.15875800	0.31477700
N4	2.68763600	0.15852900	0.31485400
N5	1.59674600	-0.10062100	0.03313200
N6	0.47833400	-0.55547500	-0.34814900

Isomer 4

N1	-2.98616000	0.00001300	0.09555400
N2	-1.85628800	0.00014200	0.09379200
N3	1.51363300	-0.76930200	0.52028900
N4	1.51410300	0.76888800	0.52049600
N5	0.90714200	-0.77341100	-0.61519600
N6	0.90757100	0.77367100	-0.61493500

Isomer 5

N1	-0.52492300	-0.64404100	-0.00059900
N2	-2.06942200	-0.64341300	0.00148600
N3	-2.06943900	0.64339900	0.00113500
N4	-0.52493300	0.64405800	-0.00094200
N5	2.58779200	-0.00039700	-0.56547100
N6	2.60092600	0.00039400	0.56439100

Isomer 6

N1	0.78004300	1.09084800	0.00024500
N2	0.78010400	-1.09103000	-0.00013400
N3	1.12864600	-0.00028700	0.79270400
N4	-1.90964300	-0.56607700	0.00006900

N5	-1.90780100	0.56642000	-0.00008300
N6	1.12865000	0.00012600	-0.79280200

Isomer 7

N1	1.14383600	-0.64511900	0.21807800
N2	-1.14884500	-0.63627000	-0.21869200
N3	0.00548300	1.28135700	0.00079200
N4	-1.14372000	0.64543500	0.21792300
N5	1.14899200	0.63598700	-0.21884100
N6	-0.00574600	-1.28139000	0.00074100

Isomer 8

N1	0.62969800	0.01531300	0.55036400
N2	-1.47884300	-0.00348900	-0.09494700
N3	1.87625200	0.62351700	-0.05742700
N4	-0.31262200	-0.02367600	-0.58300400
N5	1.87966400	-0.62113300	-0.01822500
N6	-2.59414800	0.00946700	0.20323900

Isomer 9

N1	0.00000000	-1.33732300	0.00000000
N2	-1.15845300	-0.66871100	0.00000000
N3	-1.15842900	0.66875500	0.00000000
N4	0.00002000	1.33737400	0.00000000
N5	1.15839500	0.66870600	0.00000000
N6	1.15846600	-0.66880000	0.00000000

Isomer 10

N1	1.78197300	-0.20765300	-0.34580600
N2	1.33889900	0.76314300	0.26657100
N3	0.52597500	-0.55548400	0.49300600
N4	-1.33894100	0.76313700	-0.26655900
N5	-1.78194900	-0.20768100	0.34581300
N6	-0.52595700	-0.55546300	-0.49302500

Isomer 11

N1	0.00102400	0.76651900	0.56728800
N2	0.00162600	-0.76646200	0.56745100
N3	1.19020800	0.63960900	-0.28420500
N4	1.19079500	-0.63905500	-0.28411100
N5	-1.19139600	-0.63890400	-0.28331900

N6	-1.19225700	0.63829400	-0.28310300

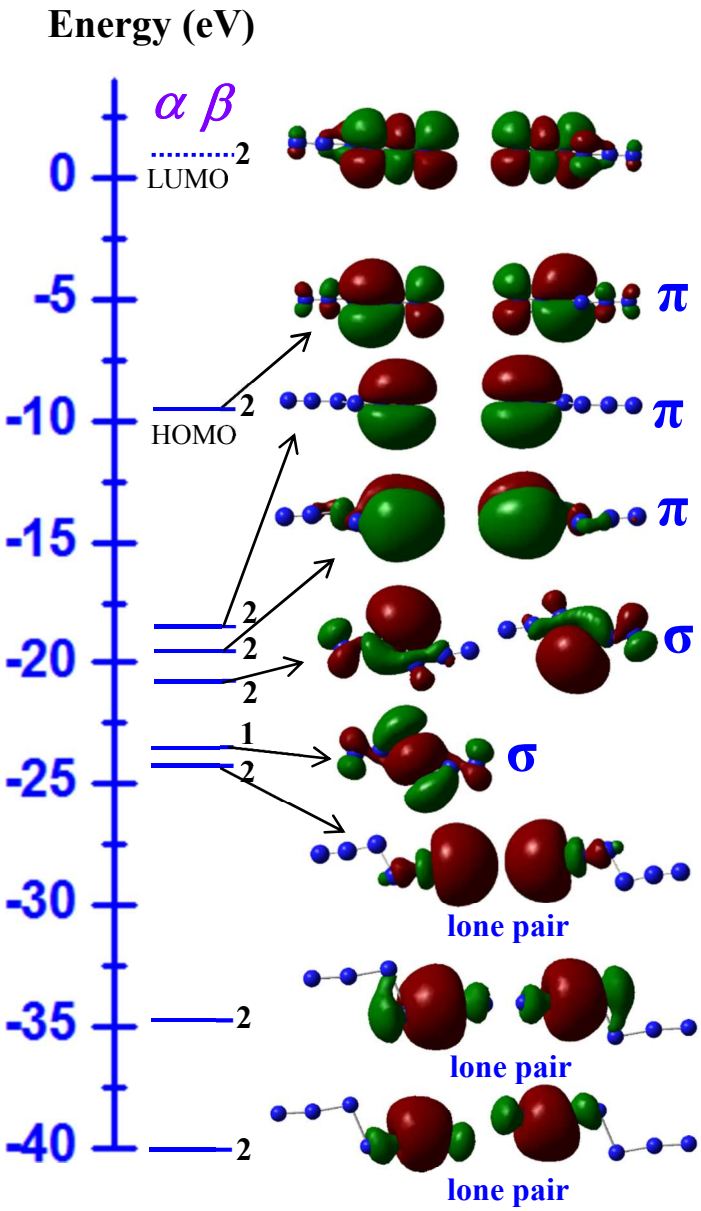
Isomer 12

N1	0.76687100	0.85900400	-0.11553000
N2	-0.76686900	-0.52913500	-0.68642200
N3	-0.76683500	0.85915500	-0.11501500
N4	-0.76677000	-0.32997900	0.80151700
N5	0.76683900	-0.32944000	0.80170400
N6	0.76676500	-0.52960500	-0.68625400

2. Molecular orbitals of the C_{2h} isomer.

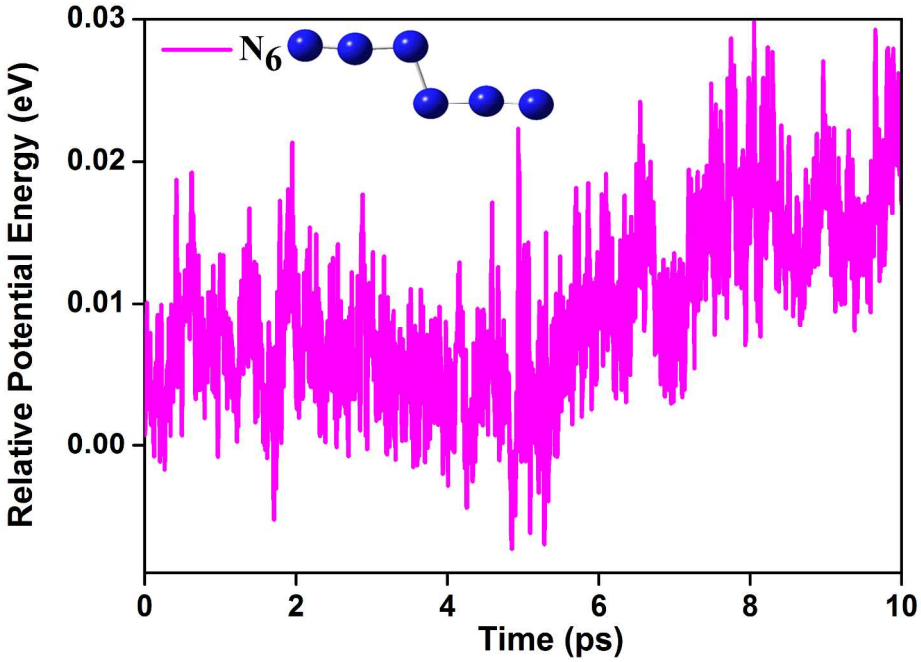
Figure S2. Molecular orbitals (MO) and MO energy level correlation diagram of the C_{2h} isomer calculated at the MP2/cc-pVDZ level. Presented in the diagram are 9 bonding orbitals and 6 lone pairs which adopt 30 outer-shell electrons of the isomer. The occupied and unoccupied levels are marked by solid and dotted lines, respectively. The number next to each energy level indicates

the level degeneracy. The orbitals were plotted using the isovalue of 0.01 $e^-/Å^3$.



3. Thermodynamic stability of the C_{2h} isomer. Thermodynamic stability of the global minimum N_6 molecule was examined by using the Born−Oppenheimer molecular dynamics simulation with an NVT thermodynamic ensemble implemented in the DMoL[3] code[1] at room temperature (T=300 K). The figure below shows the relative potential energy of the isomer during the simulation, which remains unchanged.

Figure S3. Evolution of the relative potential energy (eV) of the C_{2h} isomer in MD simulation during a 10 ps period of simulation time. A time step of 1 fs was employed.



4. Natural bond orbital analysis of the C_{2h} isomer.

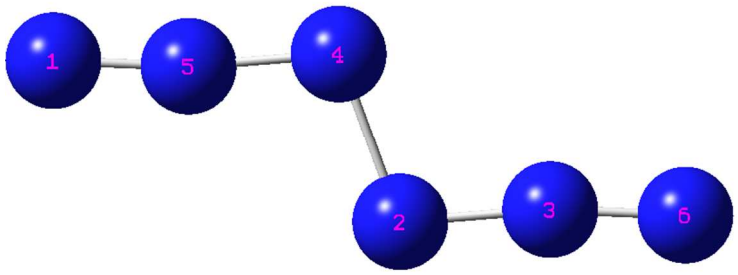


Table S2

(Occupancy)	Bond orbital/ Coefficients/ Hybrids		
1. (1.99873)	BD (1) N	1 - N 5	
	(43.45%)	0.6592* N	1 s(29.19%)p 2.43(70.81%)
			0.0000 0.5347 0.0773 -0.0002 0.6896
			-0.0304 -0.4809 0.0189 0.0000 0.0000
	(56.55%)	0.7520* N	5 s(47.57%)p 1.10(52.43%)
			0.0001 0.6891 0.0282 -0.0006 -0.7170
			0.0410 0.0904 -0.0203 0.0000 0.0000
2. (1.99507)	BD (2) N	1 - N 5	
	(55.80%)	0.7470* N	1 s(0.00%)p 1.00(100.00%)
			0.0000 0.0000 0.0000 0.0000 0.0000
			0.0000 0.0000 0.0000 1.0000 -0.0049
	(44.20%)	0.6649* N	5 s(0.00%)p 1.00(100.00%)
			0.0000 0.0000 0.0000 0.0000 0.0000
			0.0000 0.0000 0.0000 1.0000 0.0019
3. (1.97728)	BD (3) N	1 - N 5	
	(35.81%)	0.5984* N	1 s(1.18%)p83.97(98.82%)
			0.0000 0.1061 0.0225 0.0001 0.5095
			-0.0241 0.8528 -0.0271 0.0000 0.0000
	(64.19%)	0.8012* N	5 s(1.10%)p89.87(98.90%)
			-0.0002 0.1031 0.0193 0.0003 0.2216
			0.0085 0.9689 0.0307 0.0000 0.0000
4. (1.99222)	BD (1) N	2 - N 3	
	(39.84%)	0.6312* N	2 s(20.71%)p 3.83(79.29%)
			0.0000 0.4517 0.0555 0.0000 0.8653
			-0.0276 -0.2062 0.0308 0.0000 0.0000
	(60.16%)	0.7757* N	3 s(51.43%)p 0.94(48.57%)
			0.0001 0.7167 -0.0250 0.0000 -0.6590
			0.0139 0.2260 0.0135 0.0000 0.0000

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 5. (1.91419)      BD ( 1) N    2 - N     4
                   ( 50.00%)    0.7071* N    2 s( 15.13%)p 5.61( 84.87%)
                                 0.0000    0.3887    0.0138 -0.0009    0.0166
                                 0.0194    0.9208 -0.0103    0.0000    0.0000
                   ( 50.00%)    0.7071* N    4 s( 15.13%)p 5.61( 84.87%)
                                 0.0000    0.3887    0.0138 -0.0009 -0.0166
                                -0.0194 -0.9208    0.0103    0.0000    0.0000
 6. (1.99873)      BD ( 1) N    3 - N     6
                   ( 56.55%)    0.7520* N    3 s( 47.57%)p 1.10( 52.43%)
                                 0.0001    0.6891    0.0282 -0.0006    0.7170
                                -0.0410 -0.0904    0.0203    0.0000    0.0000
                   ( 43.45%)    0.6592* N    6 s( 29.19%)p 2.43( 70.81%)
                                 0.0000    0.5347    0.0773 -0.0002 -0.6896
                                 0.0304    0.4809 -0.0189    0.0000    0.0000
 7. (1.99507)      BD ( 2) N    3 - N     6
                   ( 44.20%)    0.6649* N    3 s(  0.00%)p 1.00(100.00%)
                                 0.0000    0.0000    0.0000    0.0000    0.0000
                                 0.0000    0.0000    0.0000    1.0000    0.0019
                   ( 55.80%)    0.7470* N    6 s(  0.00%)p 1.00(100.00%)
                                 0.0000    0.0000    0.0000    0.0000    0.0000
                                 0.0000    0.0000    0.0000    1.0000 -0.0049
 8. (1.97728)      BD ( 3) N    3 - N     6
                   ( 64.19%)    0.8012* N    3 s(  1.10%)p89.87( 98.90%)
                                 0.0002 -0.1031 -0.0193 -0.0003    0.2216
                                 0.0085    0.9689    0.0307    0.0000    0.0000
                   ( 35.81%)    0.5984* N    6 s(  1.18%)p83.97( 98.82%)
                                 0.0000 -0.1061 -0.0225 -0.0001    0.5095
                                -0.0241    0.8528 -0.0271    0.0000    0.0000
 9. (1.99222)      BD ( 1) N    4 - N     5
                   ( 39.84%)    0.6312* N    4 s( 20.71%)p 3.83( 79.29%)
                                 0.0000    0.4517    0.0555    0.0000 -0.8653
                                 0.0276    0.2062 -0.0308    0.0000    0.0000
                   ( 60.16%)    0.7756* N    5 s( 51.43%)p 0.94( 48.57%)
                                 0.0001    0.7167 -0.0250    0.0000    0.6590
                                -0.0139 -0.2260 -0.0135    0.0000    0.0000
10. (1.99969)      CR ( 1) N    1            s(100.00%)p 0.00(  0.00%)
                                 1.0000    0.0005    0.0000    0.0000 -0.0003
                                 0.0000    0.0001    0.0000    0.0000    0.0000
11. (1.99961)      CR ( 1) N    2            s(100.00%)p 0.00(  0.00%)
                                 1.0000    0.0002    0.0000    0.0000 -0.0001
                                 0.0000 -0.0001    0.0000    0.0000    0.0000
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12. (1.99958)       CR ( 1) N     3       s(100.00%)p 0.00(    0.00%)
                                          1.0000 -0.0001    0.0000    0.0000    0.0000
                                          0.0000 -0.0002    0.0000    0.0000    0.0000
13. (1.99961)       CR ( 1) N     4       s(100.00%)p 0.00(    0.00%)
                                          1.0000    0.0002    0.0000    0.0000    0.0001
                                          0.0000    0.0001    0.0000    0.0000    0.0000
14. (1.99958)       CR ( 1) N     5       s(100.00%)p 0.00(    0.00%)
                                          1.0000 -0.0001    0.0000    0.0000    0.0000
                                          0.0000    0.0002    0.0000    0.0000    0.0000
15. (1.99969)       CR ( 1) N     6       s(100.00%)p 0.00(    0.00%)
                                          1.0000    0.0005    0.0000    0.0000    0.0003
                                          0.0000 -0.0001    0.0000    0.0000    0.0000
16. (1.97565)       LP ( 1) N     1       s( 70.21%)p 0.42( 29.79%)
                                         -0.0006    0.8376 -0.0235    0.0000 -0.5079
                                         -0.0074    0.1998    0.0038    0.0000    0.0000
17. (1.93712)       LP ( 1) N     2       s( 64.46%)p 0.55( 35.54%)
                                         -0.0003    0.8027 -0.0159    0.0003 -0.4967
                                         -0.0127 -0.3295 -0.0056    0.0000    0.0000
18. (1.53299)       LP ( 2) N     2       s(    0.00%)p 1.00(100.00%)
                                          0.0000    0.0000    0.0000    0.0000    0.0000
                                          0.0000    0.0000    0.0000    0.9999    0.0128
19. (1.93712)       LP ( 1) N     4       s( 64.46%)p 0.55( 35.54%)
                                         -0.0003    0.8027 -0.0159    0.0003    0.4967
                                          0.0127    0.3295    0.0056    0.0000    0.0000
20. (1.53299)       LP ( 2) N     4       s(    0.00%)p 1.00(100.00%)
                                          0.0000    0.0000    0.0000    0.0000    0.0000
                                          0.0000    0.0000    0.0000    0.9999    0.0128
21. (1.97565)       LP ( 1) N     6       s( 70.21%)p 0.42( 29.79%)
                                         -0.0006    0.8376 -0.0235    0.0000    0.5079
                                          0.0074 -0.1998 -0.0038    0.0000    0.0000
22. (0.00863)       RY*( 1) N     1       s(    0.00%)p 1.00(100.00%)
                                          0.0000    0.0000    0.0000    0.0000    0.0000
                                          0.0000    0.0000    0.0000    0.0049    1.0000
23. (0.00180)       RY*( 2) N     1       s(    2.12%)p46.20( 97.88%)
                                          0.0000 -0.0126    0.1447    0.0087 -0.0071
                                          0.0493    0.0348    0.9875    0.0000    0.0000
24. (0.00033)       RY*( 3) N     1       s( 91.67%)p 0.09(    8.33%)
                                          0.0000 -0.0158    0.9571    0.0182 -0.0675
                                          0.2342    0.0188 -0.1535    0.0000    0.0000
25. (0.00018)       RY*( 4) N     1       s(    5.66%)p16.66( 94.34%)
                                          0.0000 -0.0302    0.2354    0.0173 -0.0471
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-0.9701 -0.0014 0.0131 0.0000 0.0000

26. (0.00000) RY*(5) N 1 s(99.98%)p 0.00(0.02%)

27. (0.00584) RY*(1) N 2 s(0.00%)p 1.00(100.00%)
0.0000 0.0000 0.0000 0.0000 0.0000
0.0000 0.0000 0.0000 -0.0128 0.9999

28. (0.00462) RY*(2) N 2 s(0.14%)p99.99(99.86%)
0.0000 -0.0104 0.0352 0.0032 -0.0352
-0.3003 0.0215 0.9522 0.0000 0.0000

29. (0.00371) RY*(3) N 2 s(29.90%)p 2.34(70.10%)
0.0000 0.0012 0.5468 0.0052 -0.0238
0.8036 -0.0226 0.2329 0.0000 0.0000

30. (0.00055) RY*(4) N 2 s(69.68%)p 0.44(30.32%)
0.0000 -0.0215 0.8341 0.0256 -0.0502
-0.5125 0.0061 -0.1948 0.0000 0.0000

31. (0.00000) RY*(5) N 2 s(99.99%)p 0.00(0.01%)

32. (0.00995) RY*(1) N 3 s(3.41%)p28.32(96.59%)
0.0000 -0.0274 0.1821 0.0144 -0.0429
-0.8272 0.0011 0.5289 0.0000 0.0000

33. (0.00736) RY*(2) N 3 s(28.60%)p 2.50(71.40%)
0.0000 0.0066 0.5348 0.0040 -0.0214
-0.3669 0.0435 -0.7596 0.0000 0.0000

34. (0.00079) RY*(3) N 3 s(0.00%)p 1.00(100.00%)
0.0000 0.0000 0.0000 0.0000 0.0000
0.0000 0.0000 0.0000 -0.0019 1.0000

35. (0.00036) RY*(4) N 3 s(68.24%)p 0.47(31.76%)
0.0000 -0.0026 0.8211 -0.0908 -0.0160
0.4200 0.0042 0.3754 0.0000 0.0000

36. (0.00001) RY*(5) N 3 s(99.64%)p 0.00(0.36%)

37. (0.00584) RY*(1) N 4 s(0.00%)p 1.00(100.00%)
0.0000 0.0000 0.0000 0.0000 0.0000
0.0000 0.0000 0.0000 -0.0128 0.9999

38. (0.00462) RY*(2) N 4 s(0.14%)p99.99(99.86%)
0.0000 -0.0104 0.0352 0.0032 0.0352
0.3003 -0.0215 -0.9522 0.0000 0.0000

39. (0.00371) RY*(3) N 4 s(29.90%)p 2.34(70.10%)
0.0000 0.0012 0.5468 0.0052 0.0238
-0.8036 0.0226 -0.2328 0.0000 0.0000

40. (0.00055) RY*(4) N 4 s(69.68%)p 0.44(30.32%)
0.0000 -0.0215 0.8341 0.0256 0.0502
0.5125 -0.0061 0.1948 0.0000 0.0000

41. (0.00000) RY*(5) N 4 s(99.99%)p 0.00(0.01%)

42. (0.00995) RY*(1) N 5 s(3.41%)p28.32(96.59%)
0.0000 -0.0274 0.1821 0.0144 0.0429
0.8272 -0.0011 -0.5289 0.0000 0.0000
43. (0.00736) RY*(2) N 5 s(28.61%)p 2.50(71.39%)
0.0000 0.0066 0.5348 0.0040 0.0214
0.3669 -0.0435 0.7596 0.0000 0.0000
44. (0.00079) RY*(3) N 5 s(0.00%)p 1.00(100.00%)
0.0000 0.0000 0.0000 0.0000 0.0000
0.0000 0.0000 0.0000 -0.0019 1.0000
45. (0.00036) RY*(4) N 5 s(68.24%)p 0.47(31.76%)
0.0000 -0.0026 0.8211 -0.0908 0.0160
-0.4200 -0.0042 -0.3754 0.0000 0.0000
46. (0.00001) RY*(5) N 5 s(99.64%)p 0.00(0.36%)
47. (0.00863) RY*(1) N 6 s(0.00%)p 1.00(100.00%)
0.0000 0.0000 0.0000 0.0000 0.0000
0.0000 0.0000 0.0000 0.0049 1.0000
48. (0.00180) RY*(2) N 6 s(2.12%)p46.20(97.88%)
0.0000 -0.0126 0.1447 0.0087 0.0071
-0.0493 -0.0348 -0.9875 0.0000 0.0000
49. (0.00033) RY*(3) N 6 s(91.67%)p 0.09(8.33%)
0.0000 -0.0158 0.9571 0.0182 0.0675
-0.2342 -0.0188 0.1535 0.0000 0.0000
50. (0.00018) RY*(4) N 6 s(5.66%)p16.67(94.34%)
0.0000 -0.0302 0.2354 0.0173 0.0471
0.9701 0.0014 -0.0131 0.0000 0.0000
51. (0.00000) RY*(5) N 6 s(99.98%)p 0.00(0.02%)
52. (0.02335) BD*(1) N 1 - N 5
(56.55%) 0.7520* N 1 s(29.19%)p 2.43(70.81%)
0.0000 0.5347 0.0773 -0.0002 0.6896
-0.0304 -0.4809 0.0189 0.0000 0.0000
(43.45%) -0.6592* N 5 s(47.57%)p 1.10(52.43%)
0.0001 0.6891 0.0282 -0.0006 -0.7170
0.0410 0.0904 -0.0203 0.0000 0.0000
53. (0.45669) BD*(2) N 1 - N 5
(44.20%) 0.6649* N 1 s(0.00%)p 1.00(100.00%)
0.0000 0.0000 0.0000 0.0000 0.0000
0.0000 0.0000 0.0000 -1.0000 0.0049
(55.80%) -0.7470* N 5 s(0.00%)p 1.00(100.00%)
0.0000 0.0000 0.0000 0.0000 0.0000
0.0000 0.0000 0.0000 -1.0000 -0.0019
54. (0.07311) BD*(3) N 1 - N 5

(64.19%) 0.8012* N 1 s(1.18%)p83.97(98.82%)
0.0000 0.1061 0.0225 0.0001 0.5095
-0.0241 0.8528 -0.0271 0.0000 0.0000
(35.81%) -0.5984* N 5 s(1.10%)p89.87(98.90%)
-0.0002 0.1031 0.0193 0.0003 0.2216
0.0085 0.9689 0.0307 0.0000 0.0000

55. (0.02308) BD*(1) N 2 - N 3
(60.16%) 0.7757* N 2 s(20.71%)p 3.83(79.29%)
0.0000 0.4517 0.0555 0.0000 0.8653
-0.0276 -0.2062 0.0308 0.0000 0.0000
(39.84%) -0.6312* N 3 s(51.43%)p 0.94(48.57%)
0.0001 0.7167 -0.0250 0.0000 -0.6590
0.0139 0.2260 0.0135 0.0000 0.0000

56. (0.02923) BD*(1) N 2 - N 4
(50.00%) 0.7071* N 2 s(15.13%)p 5.61(84.87%)
0.0000 0.3887 0.0138 -0.0009 0.0166
0.0194 0.9208 -0.0103 0.0000 0.0000
(50.00%) -0.7071* N 4 s(15.13%)p 5.61(84.87%)
0.0000 0.3887 0.0138 -0.0009 -0.0166
-0.0194 -0.9208 0.0103 0.0000 0.0000

57. (0.02335) BD*(1) N 3 - N 6
(43.45%) 0.6592* N 3 s(47.57%)p 1.10(52.43%)
-0.0001 -0.6891 -0.0282 0.0006 -0.7170
0.0410 0.0904 -0.0203 0.0000 0.0000
(56.55%) -0.7520* N 6 s(29.19%)p 2.43(70.81%)
0.0000 -0.5347 -0.0773 0.0002 0.6896
-0.0304 -0.4809 0.0189 0.0000 0.0000

58. (0.45669) BD*(2) N 3 - N 6
(55.80%) 0.7470* N 3 s(0.00%)p 1.00(100.00%)
0.0000 0.0000 0.0000 0.0000 0.0000
0.0000 0.0000 0.0000 1.0000 0.0019
(44.20%) -0.6649* N 6 s(0.00%)p 1.00(100.00%)
0.0000 0.0000 0.0000 0.0000 0.0000
0.0000 0.0000 0.0000 1.0000 -0.0049

59. (0.07311) BD*(3) N 3 - N 6
(35.81%) 0.5984* N 3 s(1.10%)p89.87(98.90%)
-0.0002 0.1031 0.0193 0.0003 -0.2216
-0.0085 -0.9689 -0.0307 0.0000 0.0000
(64.19%) -0.8012* N 6 s(1.18%)p83.97(98.82%)
0.0000 0.1061 0.0225 0.0001 -0.5095
0.0241 -0.8528 0.0271 0.0000 0.0000

60. (0.02308) BD*(1) N 4 - N 5
(60.16%) 0.7756* N 4 s(20.71%)p 3.83(79.29%)
0.0000 0.4517 0.0555 0.0000 -0.8653
0.0276 0.2062 -0.0308 0.0000 0.0000
(39.84%) -0.6312* N 5 s(51.43%)p 0.94(48.57%)
0.0001 0.7167 -0.0250 0.0000 0.6590
-0.0139 -0.2260 -0.0135 0.0000 0.0000

5. Optimized structure parameters of the predicted crystalline N_6 phase.

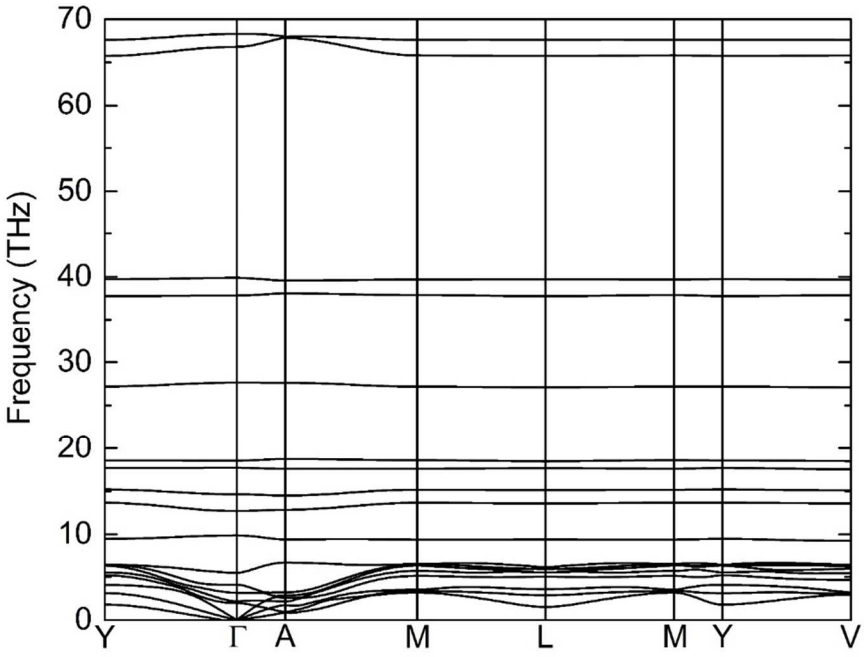
Table S3

Structure	P (GPa)	Lattice parameters (Å, º)	Atomic coordinates (fractional)		
*C*2/*m*	0	a = 5.74, b = 3.29, c = 8.33	4i	0.0802	0.0000 0.3523
		β = 114.7	4i	0.1147	0.0000 0.0784
			4i	0.0716	0.0000 0.2128

6. Phonon dispersion relations for the crystalline N_6 structure.

Figure S4. Phonon dispersion of the predicted *C*2/*m* crystalline structure, calculated at ambient

pressure using the finite displacement method.[2]



7. The effects of the van der Waals interactions in nitrogen crystals.

Van der Waals (vdW) non-local interaction represents the interaction between the charge densities in different parts of an atomic system. These interactions originate from the instantaneous fluctuations of the electron distributions, and can contribute to the phase stability of rare-gas solids, molecular crystals, and many other systems. Also known as London dispersion interactions, the vdW interactions are not treated within the standard exchange-correlation functionals. To correct for the vdW interactions, Dion et al.[3] proposed an approach by separating the exchange correlation (xc) energy functional $E_{xc}[n]$ into three components,

$$E_{xc}[n] = E_x^{GGA}[n] + E_c^{LDA}[n] + E_c^{nl}[n], \quad \text{(S1)}$$

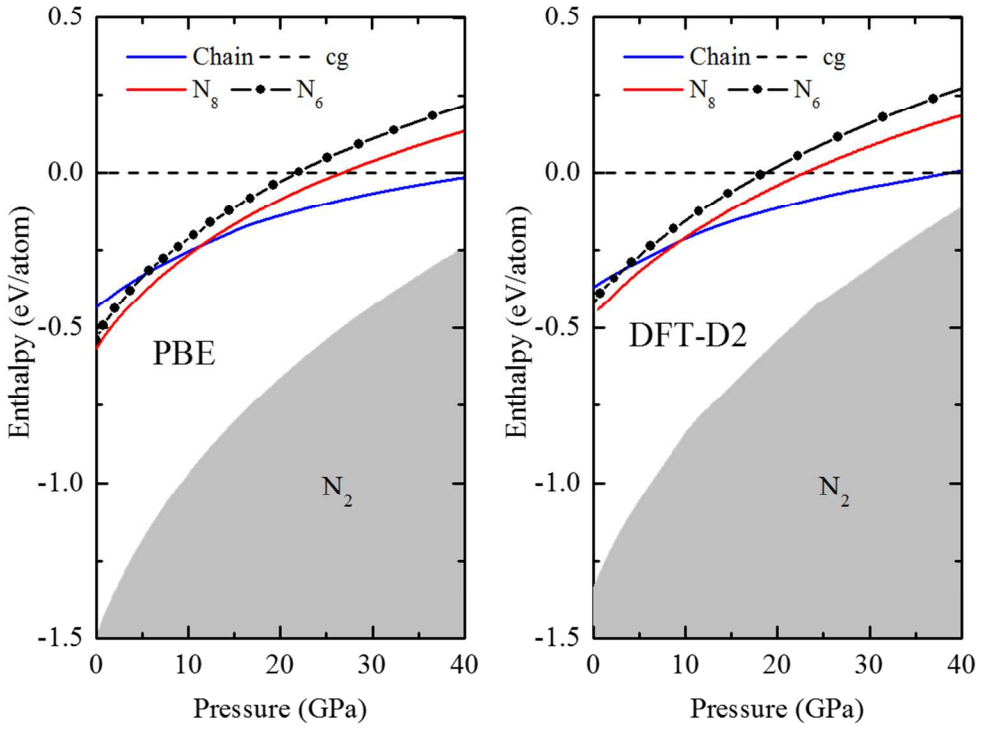
where the three terms are the GGA exchange energy, the LDA correlation energy, and the non-local correlation energy term which represent the vdW interaction. This method has been termed the van der Waals density functional (vdW-DF).

We determined the equation of state of the nitrogen crystals using a well-established van der Waals density functional, optPBE-vdW,[4] and compared the results with a semi-empirical approach for vdW corrections, DFT-D2,[5] and the standard Purdew-Burke-Ernzerhof (PBE) functional.[6] These results are presented in Fig. 2c of the paper and Fig. S6.The three approaches turned out to be consistent with each other as the enthalpies of structures we obtained were very close in all the schemes. As expected, the crystal made of N_2 is the most stable one as it contains triple bonds. The crystals of N_6 and N_8, both with similar bonding patterns, have similar enthalpy characteristics, *i.e.*, they are energetically more favorable than the cubic gauche structure at ambient pressure and are less favorable after approximately 25 GPa. With regards to the enthalpy per atom, the values obtained from the DFT-D2 scheme was 5-10 % less than the values obtained using the optPBE-vdW functional.

The crystal structures were fully optimized using the Vienna Ab initio Simulation package (VASP).[7] An energy cut-off of 400 Ry was used for the planewave basis set and to sample the Brillouin zone, a 12 × 12 × 12 Monkhorst Pack *k*-point mesh[8] was employed. The simulations were carried out using the Projector Augmented Wave (PAW)[9] PBE exchange correlational functional. On plotting the P-V curve for the chain like structure, it was found that after 15 GPa, the volumes obtained by using the optPBE-vdW functional were larger than those obtained using standard PBE functional. This is consistent with earlier results where it has been shown that optPBE-vdW overestimates the lattice constants and bond lengths. On the other hand, the volume was considerably smaller for the case of DFT-D2.

Fig. S5. Calculated enthalpies per atom for different forms of crystalline nitrogen using the (left) PBE and (right) DFT-D2 schemes. The enthalpy of the cg structure is used as the

zero-energy reference level.



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