Table S1 Coordinates (Å) for $HNPBu^t_3$ from the MP2(fc)/6-311G* geometry calculation.

Atom	*x*	*y*	*z*
H(1)	0.633	-0.003	-2.630
N(2)	-0.220	-0.011	-2.078
P(3)	-0.020	-0.001	-0.503
C(4)	-1.767	-0.244	0.154
C(5)	-2.189	-1.708	-0.064
C(6)	-2.734	0.594	-0.704
C(7)	-1.961	0.101	1.636
C(8)	0.683	1.650	0.139
C(9)	-0.378	2.746	-0.059
C(10)	1.843	2.057	-0.790
C(11)	1.153	1.684	1.598
C(12)	1.107	-1.404	0.129
C(13)	0.838	-2.655	-0.729
C(14)	2.578	-1.039	-0.139
C(15)	0.964	-1.773	1.612
H(16)	-1.685	-2.401	0.609
H(17)	-2.021	-2.013	-1.099
H(18)	-3.263	-1.782	0.142
H(19)	-2.628	1.665	-0.551
H(20)	-2.582	0.380	-1.762
H(21)	-3.757	0.319	-0.421
H(22)	-2.991	-0.150	1.913
H(23)	-1.824	1.163	1.843
H(24)	-1.301	-0.465	2.296
H(25)	-1.204	2.676	0.647
H(26)	0.102	3.718	0.101
H(27)	-0.774	2.732	-1.077
H(28)	1.507	2.092	-1.830
H(29)	2.166	3.066	-0.511
H(30)	2.713	1.408	-0.726

H(31)	2.021	1.048	1.778
H(32)	1.451	2.710	1.844
H(33)	0.368	1.396	2.299
H(34)	-0.130	-3.111	-0.539
H(35)	1.607	-3.401	-0.496
H(36)	0.892	-2.422	-1.795
H(37)	2.744	-0.756	-1.182
H(38)	3.189	-1.927	0.056
H(39)	2.949	-0.245	0.507
H(40)	1.136	-0.927	2.280
H(41)	1.711	-2.539	1.854
H(42)	-0.014	-2.197	1.841

Table S2 Interatomic distances (r_a/pm) and amplitudes of vibration (u/pm) for the DYNAMITE GED structure of $HNPBu^t_3$.[a,b]

No.	Atom pair	r_a / pm	u / pm	Restraint
u_1	H(1)-N(2)	100.6(6)	8.5(Tied to u_2)	-
u_2	C(13)-H(34)	113.9(3)	9.1(4)	7.4(7)
u_3	C(6)-H(19)	114.2(4)	9.2(Tied to u_2)	-
u_4	C(10)-H(30)	114.3(3)	9.2(Tied to u_2)	-
u_5	C(6)-H(20)	114.8(3)	9.2(Tied to u_2)	-
u_6	C(14)-H(39)	114.5(4)	9.2(Tied to u_2)	-
u_7	C(9)-H(25)	114.3(3)	9.2(Tied to u_2)	-
u_8	C(5)-H(16)	114.3(4)	9.2(Tied to u_2)	-
u_9	C(7)-H(23)	114.3(3)	9.2(Tied to u_2)	-
u_{10}	C(13)-H(36)	114.6(4)	9.2(Tied to u_2)	-
u_{11}	C(11)-H(31)	114.6(5)	9.2(Tied to u_2)	-
u_{12}	C(15)-H(42)	114.3(3)	9.2(Tied to u_2)	-
u_{13}	C(5)-H(17)	114.7(3)	9.2(Tied to u_2)	-
u_{14}	C(9)-H(27)	114.8(4)	9.2(Tied to u_2)	-
u_{15}	C(15)-H(40)	114.6(5)	9.2(Tied to u_2)	-
u_{16}	C(7)-H(24)	114.1(6)	9.2(Tied to u_2)	-

u_{17}	C(10)-H(28)	114.8(3)	9.2(Tied to u_2)	-
u_{18}	C(11)-H(33)	114.5(5)	9.2(Tied to u_2)	-
u_{19}	C(14)-H(37)	114.7(3)	9.2(Tied to u_2)	-
u_{20}	C(14)-H(38)	114.8(3)	9.3(Tied to u_2)	-
u_{21}	C(5)-H(18)	114.8(3)	9.3(Tied to u_2)	-
u_{22}	C(7)-H(22)	114.8(4)	9.3(Tied to u_2)	-
u_{23}	C(9)-H(26)	114.8(3)	9.3(Tied to u_2)	-
u_{24}	C(10)-H(29)	114.8(3)	9.3(Tied to u_2)	-
u_{25}	C(11)-H(32)	114.8(3)	9.3(Tied to u_2)	-
u_{26}	C(13)-H(35)	114.8(5)	9.3(Tied to u_2)	-
u_{27}	C(15)-H(41)	114.8(3)	9.3(Tied to u_2)	-
u_{28}	C(6)-H(21)	114.8(3)	9.3(Tied to u_2)	-
u_{29}	C(8)-C(11)	153.0(2)	7.9(4)	-
u_{30}	C(4)-C(7)	153.0(2)	7.9(Tied to u_{29})	-
u_{31}	C(12)-C(15)	153.0(2)	7.9(Tied to u_{29})	-
u_{32}	C(4)-C(5)	153.0(2)	8.0(Tied to u_{29})	-
u_{33}	C(8)-C(9)	153.0(2)	8.0(Tied to u_{29})	-
u_{34}	C(12)-C(14)	153.0(2)	8.0(Tied to u_{29})	-
u_{35}	C(4)-C(6)	153.0(2)	8.0(Tied to u_{29})	-
u_{36}	C(12)-C(13)	153.0(2)	8.0(Tied to u_{29})	-
u_{37}	C(8)-C(10)	153.0(2)	8.0(Tied to u_{29})	-
u_{38}	N(2)-P(3)	158.6(4)	6.4(Tied to u_{29})	-
u_{39}	P(3)-C(4)	189.3(5)	8.6(3)	-
u_{40}	P(3)-C(8)	191.8(6)	8.8(Tied to u_{39})	-
u_{41}	P(3)-C(12)	191.9(6)	8.9(Tied to u_{39})	-
u_{42}	C(9)...C(10)	242.7(18)	6.2(6)	7.2(7)
u_{43}	C(13)...C(14)	245.1(16)	6.3(Tied to u_{42})	-
u_{44}	C(5)...C(6)	240.5(19)	6.3(Tied to u_{42})	-
u_{45}	C(14)...C(15)	263.9(29)	6.5(Tied to u_{42})	-
u_{46}	C(9)...C(11)	248.5(17)	6.6(Tied to u_{42})	-
u_{47}	C(5)...C(7)	251.3(20)	6.5(Tied to u_{42})	-
u_{48}	C(13)...C(15)	251.2(17)	6.6(Tied to u_{42})	-

u_{49}	C(6)...C(7)	250.0(44)	6.6(Tied to u_{42})	-
u_{50}	C(10)...C(11)	247.1(55)	6.6(Tied to u_{42})	-
u_{51}	N(2)...C(4)	265.7(19)	7.8(9)	7.7(8)
u_{52}	P(3)...C(6)	288.4(18)	10.7(6)	-
u_{53}	P(3)...C(10)	280.4(24)	11.3(Tied to u_{52})	-
u_{54}	P(3)...C(13)	271.4(18)	11.0(Tied to u_{52})	-
u_{55}	P(3)...C(5)	279.9(17)	11.6(Tied to u_{52})	-
u_{56}	P(3)...C(9)	282.1(19)	11.9(Tied to u_{52})	-
u_{57}	P(3)...C(14)	273.9(21)	12.2(Tied to u_{52})	-
u_{58}	N(2)...C(8)	290.2(21)	11.4(Tied to u_{52})	-
u_{59}	N(2)...C(12)	289.3(15)	11.3(Tied to u_{52})	-
u_{60}	P(3)...C(7)	280.7(20)	11.2(Tied to u_{52})	-
u_{61}	P(3)...C(15)	286.6(20)	11.6(Tied to u_{52})	-
u_{62}	P(3)...C(11)	295.3(19)	11.5(Tied to u_{52})	-
u_{63}	N(2)...C(6)	298.4(40)	17.1(Tied to u_{52})	-
u_{64}	C(8)...C(12)	321.7(17)	9.4(8)	8.4(8)
u_{65}	C(4)...C(8)	313.3(19)	9.4(Tied to u_{64})	-
u_{66}	C(4)...C(12)	312.1(17)	9.4(Tied to u_{64})	-
u_{67}	N(2)...C(13)	300.2(31)	18.2(Tied to u_{52})	-
u_{68}	N(2)...C(10)	320.2(51)	15.0(Tied to u_{64})	-
u_{69}	C(5)...C(13)	299.3(51)	15.6(Tied to u_{64})	-
u_{70}	C(10)...C(14)	337.8(56)	12.7(11)	13.4(14)
u_{71}	C(6)...C(9)	330.7(61)	13.0(Tied to u_{70})	-
u_{72}	N(2)...C(5)	318.6(36)	15.5(Tied to u_{64})	-
u_{73}	C(8)...C(14)	343.9(35)	10.8(Tied to u_{70})	-
u_{74}	C(4)...C(9)	332.1(40)	10.8(Tied to u_{70})	-
u_{75}	C(5)...C(12)	330.6(38)	10.9(Tied to u_{70})	-
u_{76}	N(2)...C(9)	340.4(34)	13.4(Tied to u_{70})	-
u_{77}	C(7)...C(8)	338.3(40)	12.0(Tied to u_{70})	-
u_{78}	C(11)...C(12)	360.6(29)	10.7(13)	12.7(13)
u_{79}	C(4)...C(15)	342.3(39)	12.3(Tied to u_{70})	-
u_{80}	C(11)...C(15)	363.2(58)	13.9(Tied to u_{78})	-

u_{81}	C(7)...C(15)	335.5(71)	15.6(Tied to u_{70})	-
u_{82}	C(7)...C(11)	353.2(59)	14.3(Tied to u_{78})	-
u_{83}	N(2)...C(14)	335.5(39)	13.4(Tied to u_{70})	-
u_{84}	C(7)...C(9)	351.8(70)	14.6(Tied to u_{70})	-
u_{85}	C(11)...C(14)	380.1(54)	13.2(Tied to u_{78})	-
u_{86}	C(5)...C(15)	355.0(66)	13.9(Tied to u_{78})	-
u_{87}	C(10)...C(12)	378.8(37)	9.2(Tied to u_{78})	-
u_{88}	C(4)...C(13)	346.6(38)	9.3(Tied to u_{78})	-
u_{89}	C(6)...C(8)	374.4(36)	9.2(Tied to u_{78})	-
u_{90}	C(7)...C(12)	368.0(44)	10.1(Tied to u_{78})	-
u_{91}	C(8)...C(15)	381.0(39)	12.3(13)	12.0(12)
u_{92}	C(4)...C(11)	388.2(43)	12.4(Tied to u_{91})	-

[a] Estimated standard deviations, obtained in the least squares refinement, are given in parentheses.

[b] Other amplitudes were included but not refined, being fixed at the values obtained using the HF/6-31G* force field.

Table S3 Least squares correlation matrix (× 100) for the DYNAMITE GED refinement of $HNPBu^t_3$.[a]

	p_3	p_{12}	p_{33}	u_2	u_{29}	k_1	k_2
p_2	78						
p_4			73				
p_7		-65					
p_{32}				58	58	68	
p_{33}							-65
u_2					74	82	
u_{29}						91	
u_{52}						50	

[a] Only elements with absolute values ≥ 50% are shown; k_1 and k_2 are scale factors.

Table S4 Experimental gas-phase coordinates (Å) from the DYNAMITE refinement of $HNPBu^t_3$.

Atom	*x*	*y*	*z*
H(1)	-0.441	0.909	0.000
N(2)	0.000	0.000	0.000
P(3)	1.587	0.000	0.000
C(4)	1.889	-1.857	-0.229
C(5)	1.533	-2.256	-1.665
C(6)	0.987	-2.755	0.625
C(7)	3.357	-2.183	0.065
C(8)	2.291	0.593	1.684
C(9)	1.942	-0.430	2.771
C(10)	1.550	1.870	2.095
C(11)	3.794	0.887	1.758
C(12)	2.274	0.963	-1.513
C(13)	1.322	0.564	-2.646
C(14)	1.981	2.435	-1.204
C(15)	3.708	0.546	-1.856
H(16)	2.338	-1.899	-2.398
H(17)	0.482	-1.886	-1.952
H(18)	1.525	-3.405	-1.741
H(19)	1.263	-2.688	1.736
H(20)	-0.116	-2.456	0.494
H(21)	1.112	-3.853	0.302
H(22)	3.537	-3.301	-0.140
H(23)	3.609	-1.988	1.167
H(24)	4.073	-1.583	-0.597
H(25)	2.315	-0.084	3.798
H(26)	0.798	-0.537	2.840
H(27)	2.380	-1.461	2.508
H(28)	0.551	1.612	2.604
H(29)	2.192	2.467	2.842
H(30)	1.350	2.544	1.189

H(31)	4.361	0.222	1.010
H(32)	3.990	1.989	1.491
H(33)	4.190	0.688	2.818
H(34)	1.724	0.839	-3.680
H(35)	0.358	1.182	-2.523
H(36)	1.013	-0.542	-2.604
H(37)	2.492	2.777	-0.232
H(38)	0.843	2.570	-1.085
H(39)	2.308	3.090	-2.089
H(40)	4.406	0.745	-0.966
H(41)	4.066	1.191	-2.741
H(42)	3.767	-0.553	-2.178

Figure S1 Experimental and final weighted difference (experimental - theoretical) molecular-scattering intensities from the DYNAMITE refinement of $HNPBu^t_3$.