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Supplementary Materials for

The elusive cyclotriphosphazene molecule and its Dewar benzene–type valence isomer (P_3N_3)

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Published 22 July 2020, *Sci. Adv.* **6**, eaba6934 (2020)
DOI: 10.1126/sciadv.aba6934

This PDF file includes:

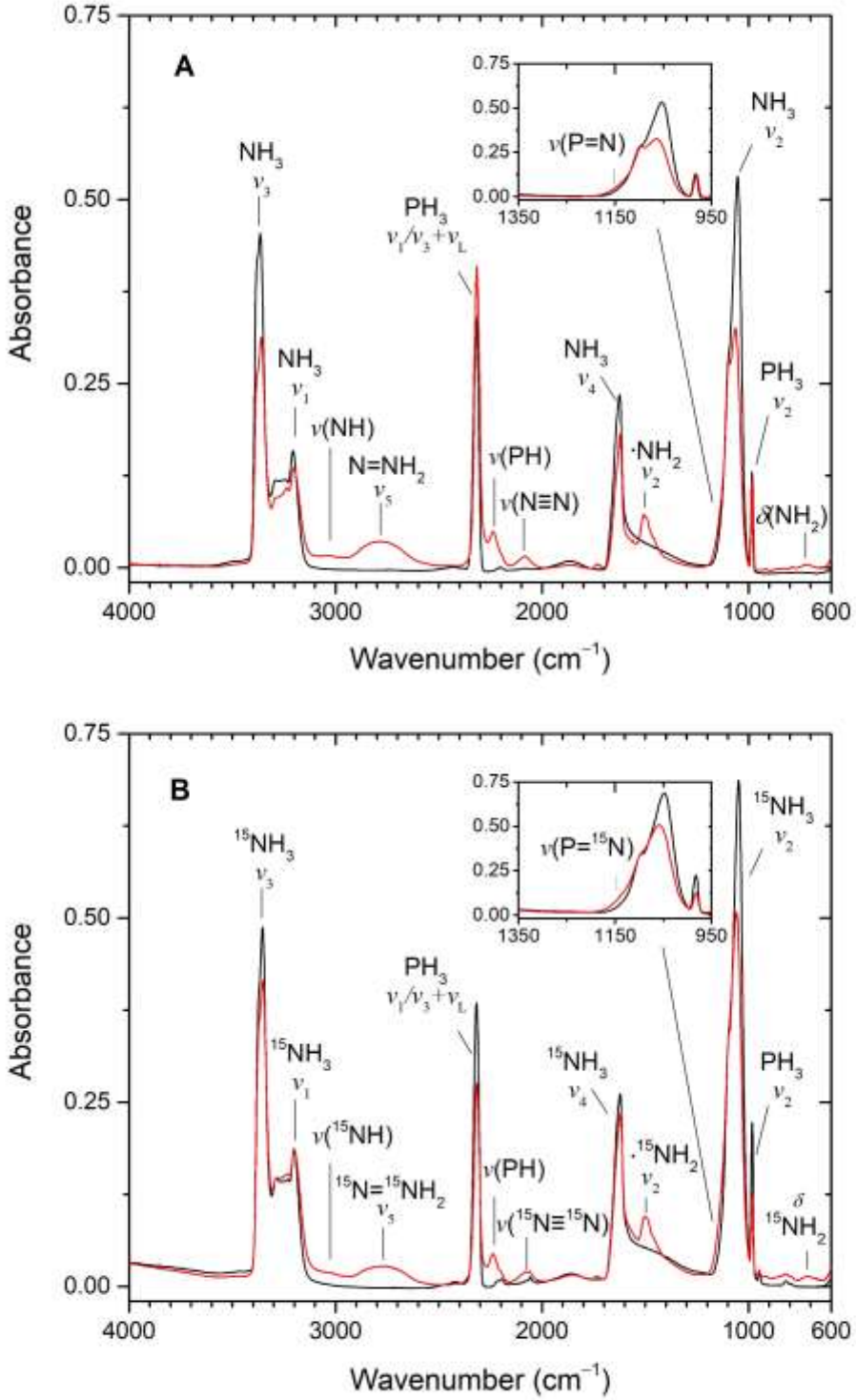


Fig. S1.
FTIR spectra of the phosphine (PH_3) + ammonia (NH_3) (A) and phosphine (PH_3) + ammonia ($^{15}NH_3$) (B) ices before (black) and after (red) processing with energetic electrons.

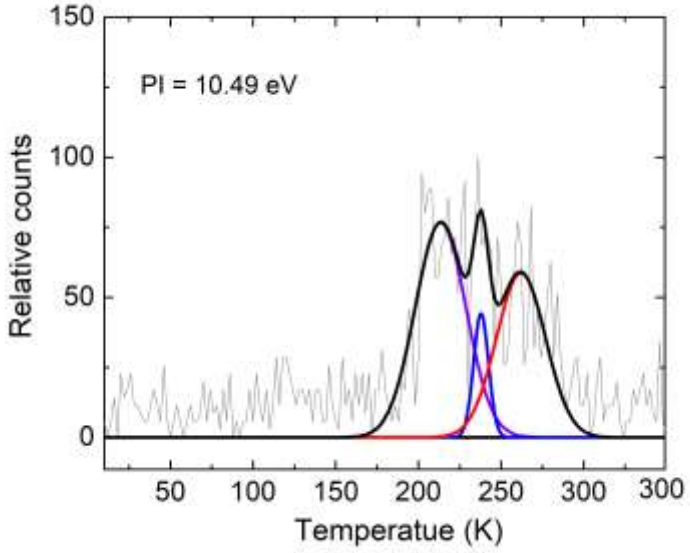


Fig. S2.
PI-ReTOF-MS data at m/z = 138 during the temperature programmed desorption (TPD) phase of the electron processed phosphine (PH_3) + ^{15}N-ammonia ($^{15}NH_3$) ice.

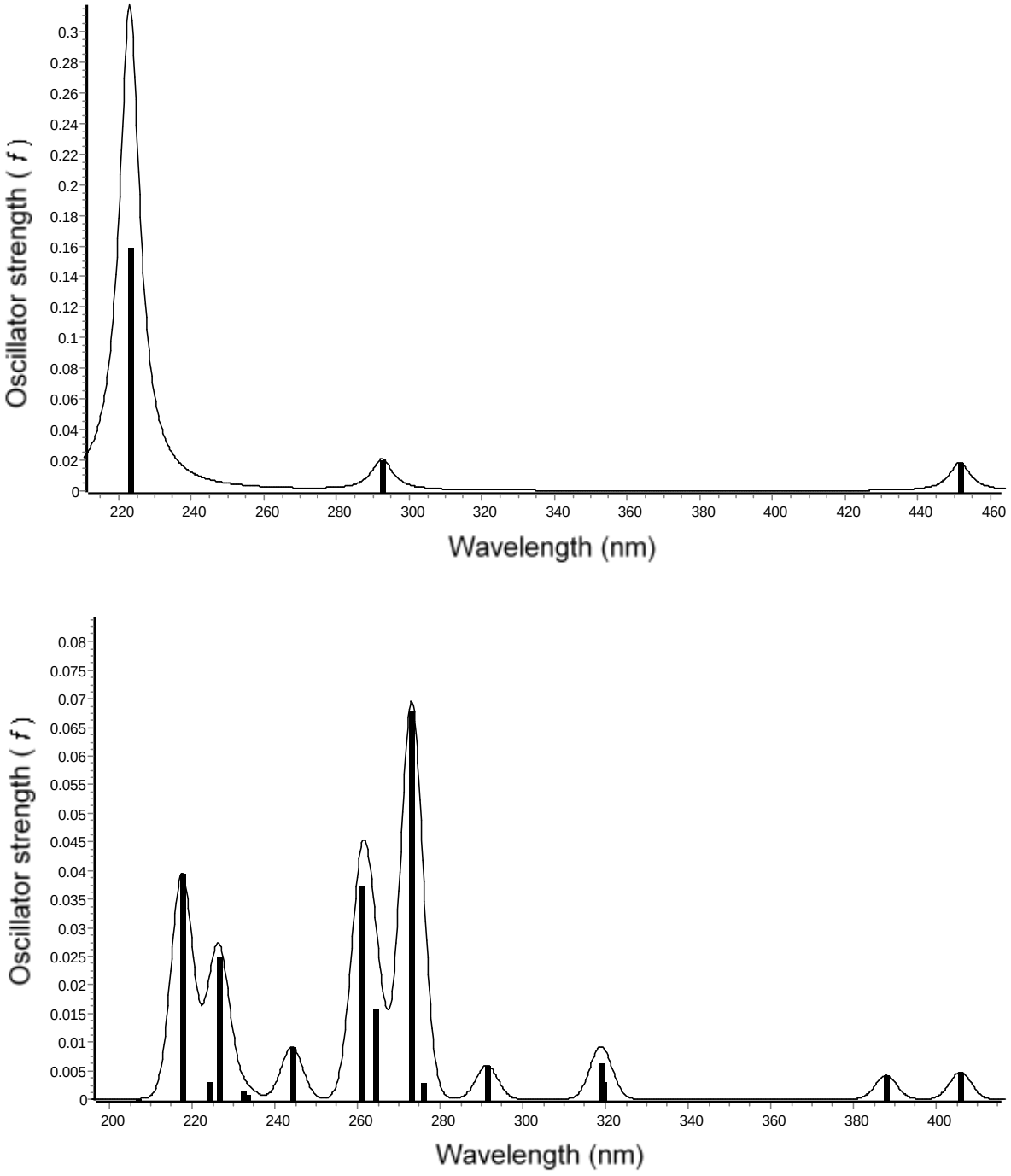


Fig. S3.
Computed ultraviolet–visible (UV-Vis) spectra for cyclotriphosphazene (P_3N_3 isomer 2, top) and 1,3,5-triphosha-2,4,6-triazabicyclo[2.2.0]hexa-2,5-diene (P_3N_3 isomer 5, bottom) at the TD-B3LYP/cc-pVTZ level of theory.

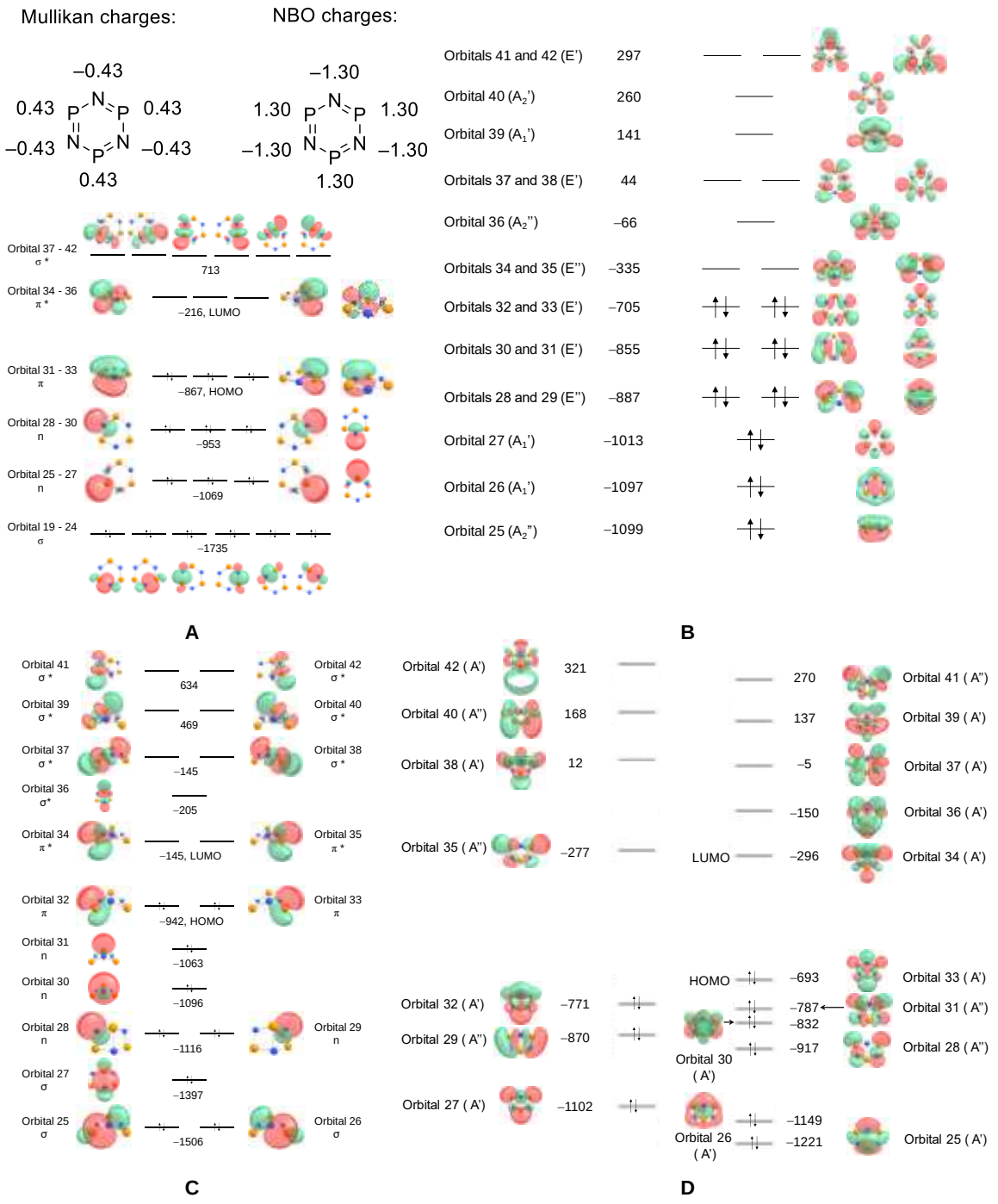


Fig. S4.

Computed Mulliken and natural bond orbital (NBO) charge distributions (e) and Kohn-Sham molecular orbital diagrams. (**A**) Natural bond orbital diagram of cyclotriphosphazene (P_3N_3, **2**, D_{3h}). (**B**) Canonical bond orbital diagram of cyclotriphosphazene (P_3N_3, **2**, D_{3h}). (**C**) Natural bond orbital diagram of 1,3,5-triphosha-2,4,6 triazabicyclo[2.2.0]hexa-2,5-diene (P_3N_3, **5**, C_S). (**D**) Canonical bond orbital diagram of 1,3,5-triphosha-2,4,6 triazabicyclo[2.2.0]hexa-2,5-diene (P_3N_3, **5**, C_S). Molecular orbital energy levels are shown in kJ mol^{-1}.

Table S1.
Experimental parameters

List of experiments				
#	Precursors	Irradiation sources		Photoionization Energy (eV)
		Electron (nA)	Laser (nm)	
1	$PH_3 + NH_3$	0 (blank)	-	10.49
2	$PH_3 + NH_3$	100	-	10.49
3	$PH_3 + NH_3$	100	-	9.10
4	$PH_3 + NH_3$	100	452	10.49
5	$PH_3 + NH_3$	100	388	10.49
6	$PH_3 + {}^{15}NH_3$	100	-	10.49

Data applied to calculate the average irradiation dose per molecule		
Initial kinetic energy of the electrons, E_{init} (keV)		5
Ice		$PH_3 + NH_3$
Irradiation current, I (nA)		100 ± 5
Total number of electrons		$(4.5 \pm 0.5) \times 10^{15}$
Average penetration depth, l_{ave} (nm)[a]		360 ± 40
Maximum penetration depth, l_{max} (nm)[a]		830 ± 90
Average kinetic energy of backscattered electrons, E_{bs} (keV)[a]		3.48 ± 0.35
Fraction of backscattered electrons, f_{bs}[a]		0.41 ± 0.04
Average kinetic energy of transmitted electrons, E_{trans} (keV)[a]		0
Fraction of transmitted electrons, f_{trans}[a]		0
Irradiated area, A (cm^2)		1.0 ± 0.1
Dose (eV/molecule)	PH_3	30.99 ± 5.10
	NH_3	15.49 ± 2.54

Parameters for the vacuum ultraviolet (VUV) light generation[b]			
$2\omega_1 - \omega_2$	Photoionization energy (eV)	10.49 ($3\omega_1$)	9.10
	Flux (10^{11} photons s^{-1})	12 ± 1	10 ± 1
	Wavelength (nm)	118.222	136.246
ω_1	Wavelength (nm)	355	222.566
Nd:YAG (YAG A)	Wavelength (nm)	355	355
Dye laser (DYE A)	Wavelength (nm)	-	445.132
Dye		-	Coumarin 450
ω_2	Wavelength (nm)	-	607
Nd:YAG (YAG B)	Wavelength (nm)	-	532
Dye laser (DYE B)	Wavelength (nm)	-	607
Dye		-	Rhodamine 610 and 640
	Nonlinear medium	Xe	Xe

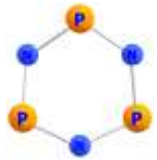
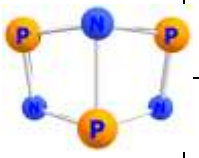
Notes.
[a] Parameters obtained from CASINO software v2.42.
[b] The uncertainty for VUV photon energies is 0.01 eV.

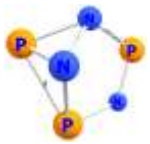
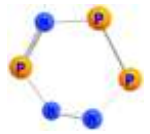
Table S2.
Infrared absorption peaks before and after irradiation for phosphine (PH_3) + ammonia (NH_3)/ ^{15}N-ammonia ($^{15}NH_3$) ices[a]

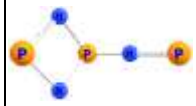
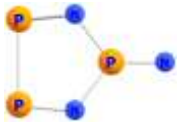
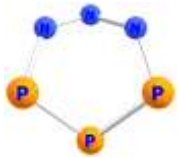
Pristine ice, before irradiation (5 K)		
Assignment	Position with ^{14}N (cm^{-1})	Position with ^{15}N (cm^{-1})
PH_3 (ν_2)	983	983
NH_3 (ν_2)	1053	1047
PH_3 (ν_4)	1099	1099
NH_3 (ν_4)	1625	1620
PH_3 ($2\nu_4$)	2198	2198
PH_3 (ν_1/ν_3)	2319	2318
PH_3 ($\nu_1/\nu_3 + \nu_L$)	2432	2430
NH_3 (ν_1)	3207	3200
NH_3 (ν_3)	3366, 3383	3353, 3373
New peaks after irradiation (5 K)		
$-NH_2$ wagging	720	710
$\nu_{(P=N)}$	1153	1139
$\bullet NH_2$ (ν_2)	1506	1500
$\nu_{N\equiv N}$	2085	2076
ν_{P-H}	2235	2235
$N=NH_2$ (ν_5)	2782	2770
ν_{N-H}	3039	3028

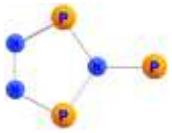
Note.
[a] References. Shimanouchi (1977), Teles et al. (1989), Socrates (2004), Zheng et al. (2008), Turner et al. (2015), Bouilloud et al. (2015).

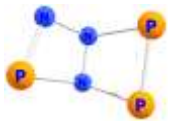
Table S3.
Computed geometries, infrared (IR) spectra, and energetics.

Computed Cartesian coordinates (Å), vibrational frequencies (cm^{-1}), IR intensities (km mol^{-1}), and energies (hartree) for various P_3N_3 isomers.										
#	Structure	Cartesian coordinate				Vibrational frequency		IR intensity		Energy
		Atom	X	Y	Z	Harmonic	An-harmonic	Harmonic	An-harmonic	B3LYP/cc-pVTZ *CCSD(T)/CBS*
2		N	–1.557083	0.000000	0.000000	1150.0 1150.0 797.9 713.7 713.7 686.1 592.9 381.0 381.0 397.5 61.3 61.3	1231.9 1094.6 835.8 527.7 552.5 840.8 538.2 325.4 113.6 294.4 -1307.6[a] -1307.6[a]	1350.6 1350.6 0.0 167.7 167.7 0.0 0.0 237.2 237.2 102.0 0.0 0.0	1553.5 1386.8 224.2 316.8 24.3 7.3 4.9 261.1 408.0 148.9 0.0 0.0	–1188.4754050 *–1186.8903061*
		N	0.778541	1.348473	0.000000					
		N	0.778541	–1.348473	0.000000					
		P	–0.851007	–1.473987	0.000000					
		P	–0.851007	1.473987	0.000000					
		P	1.702013	0.000000	0.000000					
5		N	–0.775929	–0.593423	1.397798	1016.6 771.4 643.2 571.7 422.7 354.7 254.7 1006.8	1001.3 761.0 630.3 564.0 395.9 349.6 252.0 989.9	156.8 152.4 330.4 82.5 263.5 67.2 26.2 10.5	147.2 121.5 307.1 71.3 280.8 69.6 26.2 5.9	–1188.4281965 *–1186.8506355*
		N	–0.775929	–0.593423	–1.397798					
		N	0.703584	0.801994	0.000000					
		P	–1.114481	0.355451	0.000000					

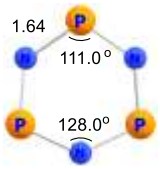
		P	0.736051	–0.068865	1.520360	791.2 696.6 471.1 263.0	772.3 679.1 463.8 258.8	1389.9 5.0 123.7 17.8	1308.0 2.3 121.5 17.7	
		P	0.736051	–0.068865	– 1.520360					
7		N	– 5.906222	6.760355	3.607326	1089.0 865.9 726.6 697.2 670.5 548.2 534.1 482.6 430.3 360.7 285.0 251.0	1066.1 862.1 712.3 684.3 657.6 531.7 524.8 467.9 422.7 353.6 281.2 247.9	170.3 81.9 346.6 96.0 187.9 108.0 60.3 101.2 10.2 95.6 74.1 25.0	96.1 34.9 256.8 68.5 163.1 89.0 70.8 82.8 11.1 96.7 72.0 24.2	–1188.3843848 *–1186.8033357*
		N	– 6.576872	8.069936	4.052492					
		N	– 5.416041	6.827761	6.136810					
		P	– 7.639859	6.649462	3.960619					
		P	– 4.772333	6.217097	4.833394					
		P	– 6.857922	7.717179	5.819989					
8		N	– 5.650809	6.602225	3.304007	1340.2 938.8 727.0 718.1 589.4 571.6 496.9 391.4 374.5 309.0 258.2 180.2	1319.5 916.3 710.9 691.9 576.0 560.1 487.4 380.7 367.9 305.2 245.1 172.7	431.4 208.8 232.9 14.8 154.5 183.8 101.7 32.6 23.4 120.7 66.2 82.2	273.3 163.8 223.6 55.2 282.8 55.1 87.0 34.2 30.2 116.2 68.5 83.1	–1188.3973839 *–1186.8028525*
		N	– 6.014921	5.481092	2.891643					
		N	– 8.411927	5.505697	3.920616					
		P	– 8.504451	7.139640	3.819807					
		P	– 6.675101	7.999877	3.163639					
		P	– 7.447931	4.627928	2.918878					
		N	– 1.278557	–0.047391	0.000000	1342.7 925.2	1324.1 909.0	293.3 13.6	276.0 15.4	–1188.3782223 *–1186.7910712*

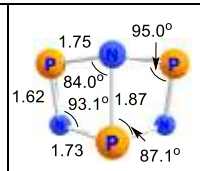
9		N	1.099910	0.172373	–1.238257	753.3 578.6 443.9 392.5 291.2 82.0 862.4 653.1 312.7 109.4	738.3 563.6 437.1 383.6 285.8 84.4 845.8 638.3 308.1 112.1	76.1 4.5 36.5 11.9 2.7 1.7 86.8 0.8 2.9 2.5	69.4 4.3 28.5 10.2 2.4 1.7 65.4 0.7 2.8 2.6	
		N	1.099910	0.172373	1.238257					
		P	–2.650635	–0.662387	0.000000					
		P	0.159154	0.882904	0.000000					
		P	2.074982	–0.354949	0.000000					
10		N	0.000000	0.000000	–2.767520	1234.0 1074.7 618.7 436.2 309.5 261.2 341.0 127.8 1088.9 688.3 405.5 286.1	1215.4 1049.8 601.7 429.4 302.9 257.4 333.1 114.5 1067.0 670.3 399.2 275.1	29.5 1.0 0.4 0.9 10.1 0.0 21.2 3.4 17.6 97.7 6.7 3.7	31.1 0.1 1.2 0.9 9.6 0.0 18.9 2.9 18.4 84.0 6.0 2.9	–1188.3688094 *–1186.7843256*
		N	0.000000	–1.355983	–0.222598					
		N	0.000000	1.355983	–0.222598					
		P	0.000000	0.000000	–1.249722					
		P	0.000000	1.203285	1.351087					
		P	0.000000	–1.203285	1.351087					
11		N	1.289534	0.107182	–1.112066	1226.0 786.8 710.9 549.2 498.7 271.1 186.0 1115.5	1239.7 769.4 692.9 541.5 494.5 270.1 185.1 1039.8	113.9 83.4 32.6 218.0 10.7 121.0 12.9 49.1	84.2 48.6 29.7 158.0 8.2 115.5 10.7 42.0	–1188.3758355 *–1186.7789150*
		N	1.731017	0.571358	0.000000					
		N	1.289534	0.107182	1.112066					
		P	–0.260564	–0.318680	–1.543002					

		P	–1.593716	0.322952	0.000000	697.3 441.0 367.6 115.0	678.5 433.2 363.9 135.9	23.5 477.6 112.5 101.4	19.5 481.2 87.9 72.6	
		P	–0.260564	–0.318680	1.543002					
12		N	0.000000	0.000000	–0.568685	1059.2 942.4 821.8 537.9 386.1 237.4 414.4 108.9 932.8 711.5 627.7 174.0	966.7 909.7 797.0 531.4 367.6 177.7 404.2 103.4 903.0 693.9 631.6 157.1	203.9 314.8 485.2 296.7 19.5 0.0 93.2 296.4 50.6 144.4 15.1 33.4	134.3 35.3 290.0 158.0 37.0 0.0 89.3 270.2 41.2 89.9 9.4 32.1	–1188.3639095 *–1186.7729981*
		N	0.000000	0.682211	1.850868					
		N	0.000000	–0.682211	1.850868					
		P	0.000000	0.000000	–2.265016					
		P	0.000000	–1.443845	0.424290					
		P	0.000000	1.443845	0.424290					
13		N	–0.416363	0.150436	6.728593	1306.4 920.2 825.4 700.7 575.5 529.4 484.0 372.6 264.7 230.1 125.7 94.2	1287.5 896.2 814.5 685.8 548.6 520.7 462.8 354.5 253.1 218.9 110.0 81.1	24.9 88.0 216.0 265.2 142.6 316.1 194.7 40.0 75.0 61.9 47.8 361.9	19.3 72.6 182.3 234.0 89.8 289.6 181.6 31.5 71.7 57.6 61.8 385.0	–1188.3373918 *–1186.7567192*
		N	0.870772	0.885579	8.659447					
		N	1.244265	–0.805506	4.378863					
		P	0.001269	1.647022	7.492296					
		P	0.525225	–0.664060	8.162766					
		P	0.858841	–0.679510	5.828435					
		N	–6.102938	3.452653	0.711106	1074.2 1044.5	1033.7 1016.8	2.6 232.7	11.7 65.2	–1188.3473377 *–1186.7566780*

14		N	–6.019605	2.057324	0.883093	1005.0 826.8 723.6 635.2 567.2 525.5 423.5 352.7 232.6 193.8	979.6 810.4 709.2 627.6 560.7 518.9 416.2 348.2 230.7 193.9	63.2 497.2 214.7 89.1 62.3 96.9 35.2 96.2 45.7 39.7	70.6 332.4 199.5 78.1 58.0 93.6 23.7 95.9 45.3 40.1	
		N	–4.943280	3.727799	0.018710					
		P	–7.755292	3.663961	0.046793					
		P	–7.632476	1.597728	0.316480					
		P	–4.468699	2.148785	–0.000541					

Computed Cartesian coordinates (Å), vibrational frequencies (cm^{-1}), IR intensities (km mol^{-1}), and energies (hartree) for 2 and 5 at the CCSD(T)/cc-pVTZ level of theory.

#	Structure	Cartesian coordinate				Vibrational frequency	IR intensity	Energy
		Atom	X	Y	Z			
2		N	0.000000000	–1.357811384	–0.783932765	1156.6 1156.6 796 718.4 718.4 681.2 582.6 389.4 374.7 374.7 47.7 47.7	362.7 362.7 0 25.7 25.7 0 0 9.1 22.5 22.5 0 0	–1186.7489860
		N	0.000000000	0.000000000	1.567865531			
		N	0.000000000	1.357811384	–0.783932765			
		P	0.000000000	–1.472599899	0.850205945			
		P	0.000000000	0.000000000	–1.700411895			
		P	0.000000000	1.472599899	0.850205945			
		N	–0.767797490	–0.755338509	0.000000000	995.5 989.4	29.6 5.7	–1186.7112500

5		N	0.819297506	0.556420670	1.391229202	810.5 775.1 705.9 651. 7 576.6 471.7 439.1 352 258.3 250.9	285.3 33.9 0.8 46.9 13.7 12.8 28 6.4 1.2 1.4	
		N	0.819297506	0.556420670	–1.391229202			
		P	1.078591792	–0.437181377	0.000000000			
		P	–0.736137376	0.137778118	1.507865530			
		P	–0.736137376	0.137778118	–1.507865530			

Computed energies (hartree) , Cartesian coordinates (Å), vibrational frequencies (cm^{-1}), and IR intensities (km mol^{-1}) for molecules in homodesmic equations in Fig.4.

#, Point group, ground state, energy	Structure	Cartesian coordinate				Vibrational frequency	IR intensities
		Atom	X	Y	Z		
4, D_{6h}, $^1A_{1g}$, –232.333370142		C	–1.204427	–0.695376	0.000000	414.495 414.495 624.2568 624.2568 691.3666 726.8656 867.7764 867.7764 988.6997 988.6997 1015.2756 1021.9988 1030.5874	0.0 0.0 0.0 0.0 103.6 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0
		C	0.000000	–1.390752	0.000000		
		C	1.204427	–0.695376	0.000000		
		C	–1.204427	0.695376	0.000000		
		C	0.000000	1.390752	0.000000		

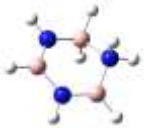
		C	1.204427	0.695376	0.000000	1062.2357 1062.2357 1176.5196 1200.4044 1200.4044 1335.1282 1389.8784 1518.8531 1518.8531 1637.4657 1637.4657 3156.7562 3166.547 3166.547 3182.2539 3182.2539 3192.3369	4.7 4.7 0.0 0.0 0.0 0.0 0.0 7.9 7.9 0.0 0.0 0.0 0.0 0.0 39.4 39.4 0.0
		H	2.141516	1.236405	0.000000		
		H	2.141516	–1.236405	0.000000		
		H	–2.141516	–1.236405	0.000000		
		H	0.000000	–2.472810	0.000000		
		H	0.000000	2.472810	0.000000		
		H	–2.141516	1.236405	0.000000		
15, D_{3h}, $^1A_1'$, –242.769939040		B	–1.449877	0.000000	0.000000	289.2197 289.22 409.6742 526.4896 526.4935 717.2149 717.2164 727.6788 862.0875 922.6932 922.6949 934.2511 940.6205	0.0 0.0 20.9949 0.4746 0.4751 0.0 0.0 57.4975 0.0 0.0 0.0 188.6854 0.0138
		N	–0.703669	1.218790	0.000000		
		B	0.724938	1.255630	0.000000		
		N	1.407338	0.000000	0.000000		
		B	0.724938	–1.255630	0.000000		

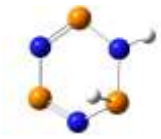
		N	–0.703669	–1.218790	0.000000	940.6213 946.72 1048.3404 1082.0921 1082.0935 1233.2693 1319.2114 1396.2688 1396.2712 1478.6673 1478.6678 2617.2868 2617.2872 2626.8028 3624.3344 3626.2234 3626.2234	0.0138 0.0 0.0 0.0466 0.0466 0.0 0.0 26.1501 26.1588 483.3297 483.3262 285.3187 285.3457 0.0 0.0 46.2867 46.2906
		H	–2.641308	0.000000	0.000000		
		H	–1.206870	2.090360	0.000000		
		H	1.320654	2.287440	0.000000		
		H	2.413739	0.000000	0.000000		
		H	1.320654	–2.287440	0.000000		
		H	–1.206870	–2.090360	0.000000		
16, C_2, ^{1}A, –234.734136539		C	–0.689398	0.331883	1.213481	165.4996 275.0875 402.1241 457.6293 503.0213 656.6271 732.2743 821.8747 828.9879 880.6672 909.8246 936.6682 1007.1044	0.2832 0.0411 0.0112 1.1267 0.0178 23.8902 9.2735 0.3109 0.5352 5.8859 1.0707 5.0244 0.0009
		C	–1.495398	–0.074927	–0.024940		
		C	–0.663768	–0.041214	–1.278677		
		C	0.689398	–0.331883	1.213481		
		C	1.495398	0.074927	–0.024940		

		C	0.663768	0.041214	–1.278677	1020.0909 1047.8068 1071.5118 1100.9864 1162.1087 1164.0556 1250.6673 1271.0372 1295.1227 1360.3773 1370.9862 1371.6786 1387.1131 1426.7488 1477.0361 1483.1197 1495.0695 1503.397 1715.3846 2986.5329 2986.5974 3007.2044 3013.7142 3029.9838 3030.6166 3055.7256 3058.133 3127.1484 3150.7054	1.5173 4.1991 0.1284 0.0035 0.0788 5.2583 0.0307 0.5879 2.0985 1.7572 1.3313 0.2802 0.021 0.0607 0.0257 7.8425 4.7963 2.1996 3.5512 56.7039 0.0828 13.004 17.038 0.4461 96.6135 57.7624 57.7604 10.1184 40.9682
		H	1.194279	0.084466	–2.223768		
		H	–1.194279	–0.084466	–2.223768		
		H	–1.238999	0.076995	2.121662		
		H	–0.562521	1.418654	1.217723		
		H	–2.362268	0.581402	–0.142891		
		H	–1.909311	–1.081714	0.109460		
		H	2.362268	–0.581402	–0.142891		
		H	1.909311	1.081714	0.109460		
		H	0.562521	–1.418654	1.217723		
		H	1.238999	–0.076995	2.121662		
		C	0.744423	–0.185114	–1.206934	192.9391 302.4636	0.5227 0.9879

17, C_2, ^{1}A, –233.505099764		C	–0.744423	0.185114	–1.206934	481.8532 523.9391 574.1656 674.6703 764.5417 781.4027 853.4061 930.5509 963.2795 981.538 996.1132 1015.2768 1046.6757 1069.2666 1175.3345 1191.4256 1205.1412 1269.5693 1359.7365 1363.317 1406.0412 1443.7304 1471.8029 1482.1846 1637.3059 1703.3881 2957.343 2970.8836 3057.1751 3058.1185 3148.6368	5.9654 0.1501 0.1454 64.0232 10.7262 1.0432 0.8815 7.9173 1.2101 2.1722 0.0012 2.3723 1.3516 2.5936 0.0704 5.0889 1.1515 5.285 1.456 1.0928 2.5141 0.7539 4.1559 4.7107 1.6342 0.1983 14.2484 58.2359 19.7819 39.1902 0.3736
		C	–1.410551	–0.171054	0.097036		
		C	1.410551	0.171054	0.097036		
		C	0.713405	0.160928	1.237464		
		C	–0.713405	–0.160928	1.237464		
		H	–1.198608	–0.370016	2.182536		
		H	–2.474266	–0.373752	0.100548		
		H	1.198608	0.370016	2.182536		
		H	2.474266	0.373752	0.100548		
		H	1.250243	0.296747	–2.045052		
		H	0.855266	–1.266555	–1.367727		
		H	–1.250243	–0.296747	–2.045052		

		H	–0.855266	1.266555	–1.367727	3155.4623 3170.2163 3179.3992	5.5656 44.31 18.3952
18, D_{3d}, $^1A_{1g}$, –235.965463122		C	1.267416	–0.731743	–0.227386	231.255 231.2589 375.499 434.6226 434.623 523.3675 796.8905 796.8913 800.4636 864.5787 864.5811 920.9245 920.9257 1035.7022 1035.7022 1045.6406 1077.8806 1095.3885 1131.0103 1185.3928 1289.5503 1289.5512 1293.636 1293.6381 1357.1253 1371.8791 1378.0704 1378.0706 1389.8706	0.0025 0.0024 0.0 0.0 0.0 0.7194 0.0 0.0 0.0 1.8948 1.8959 1.7787 1.7772 0.0 0.0 2.1996 0.0 0.0 0.0 0.0 1.8329 1.8319 0.0 0.0 0.0 0.0 0.0 0.0 0.3082
		C	1.267416	0.731743	0.227386		
		C	0.000000	1.463486	–0.227386		
		C	0.000000	–1.463486	0.227386		
		C	–1.267416	–0.731743	–0.227386		
		C	–1.267416	0.731743	0.227386		
		H	2.155339	–1.244386	0.149833		
		H	1.329654	–0.767676	–1.320452		
		H	2.155339	1.244386	–0.149833		
		H	1.329654	0.767676	1.320452		
		H	–2.155339	–1.244386	0.149833		

		H	–1.329654	–0.767676	–1.320452	1389.8723 1488.3222 1488.3276 1492.8503 1492.8537 1497.857 1511.9937 2994.9036 2994.9087 2995.3033 3003.1788 3003.1836 3006.4349 3044.2586 3044.2596 3045.9296 3045.9322 3048.2948 3053.5853	0.3088 0.0 0.0 4.9583 4.9586 13.2967 0.0 24.5639 24.5736 0.0 0.0 0.0 74.0487 123.4467 123.4286 0.0 0.0 0.0 148.3876
		H	0.000000	–1.535352	1.320452		
		H	0.000000	–2.488771	–0.149833		
		H	–1.329654	0.767676	1.320452		
		H	–2.155339	1.244386	–0.149833		
		H	0.000000	1.535352	–1.320452		
		H	0.000000	2.488771	0.149833		
19, *C*₁, ^{1}A, –243.908416333		B	–1.464871	0.141600	0.159105	169.3766 217.8222 330.9252 387.35 462.3488 601.5665 622.0879 646.7141 698.8268 821.9993 829.2309 861.581 888.8971	12.9333 1.0651 5.449 7.6754 1.7942 10.8308 1.3206 50.3739 11.104 3.9084 9.1514 4.0319 3.1851
		N	–0.779642	1.429082	–0.275820		
		B	0.760172	1.507934	0.327624		
		N	1.409699	0.202959	–0.143648		
		B	0.754938	–1.015910	–0.203303		

		N	–0.695007	–1.008757	0.099752	906.2208 932.8266 966.3439 995.6139 1047.7331 1080.1886 1107.7349 1138.1651 1213.9729 1233.9393 1305.2501 1349.8518 1421.3731 1501.8317 1612.5016 2413.3394 2471.8435 2606.8089 2640.6082 3447.4616 3547.4905 3613.6361 3624.6313	58.7929 9.8319 33.6553 29.6391 3.7305 15.0779 40.5545 65.2781 21.6233 74.1546 70.0826 81.5496 276.7218 286.8767 51.7315 211.7991 254.2002 207.191 135.3397 17.2093 25.431 31.87 26.6642
		H	–2.605963	0.172492	0.491907		
		H	–1.303682	2.255097	–0.009672		
		H	1.269165	2.495719	–0.144077		
		H	2.392869	0.230396	–0.356233		
		H	1.280897	–2.050715	–0.478571		
		H	–1.140676	–1.891090	0.294555		
		H	0.613764	1.585385	1.530457		
		H	–0.690524	1.453659	–1.29095		
20, *C*₁, ^{1}A, –1189.68653724		P	–4.405824	2.889366	–0.314709	86.088 126.2082 289.5724 338.2455 390.2859 530.0768 555.4939	4.824 0.6798 5.2584 11.8834 17.5408 39.1986 17.7582
		P	–1.455124	2.667811	–0.327224		
		P	–2.943613	0.217844	0.320181		

		N	–4.236327	1.105503	–0.249618	611.2853 643.5174 688.8991 826.0243 902.9644 953.0729 1090.9587 1167.6392 1251.6423 2255.9743 3560.6371	4.7445 18.9643 86.4639 46.8807 11.8538 76.6745 180.8172 251.4477 133.8962 138.1889 52.2951
		H	–5.036664	0.584889	–0.583857		
		N	–1.693509	1.184906	0.439181		
		N	–2.815366	3.409885	–0.633340		
		H	–4.386892	3.103736	1.103756		

Note.

[a] Symmetry changes in “finite displacements ”often results in imaginary numerical frequencies.

Table S4.
Computed ultraviolet–visible (UV-Vis) absorptions and assignments for cyclotriphosphazene (P_3N_3 isomer **2**) and 1,3,5-triphosha-2,4,6-triazabicyclo[2.2.0]hexa-2,5-diene (*P_3N_3* isomer **5**).

Isomer	Wavelength (nm)	Oscillator strength (*f*)	Transition assignment	Orbital transitions
2	451.60	0.0185	HOMO → LUMO	32 → 34 (0.49700) 33 → 35 (0.49700)
	292.56	0.0203	HOMO–1 → LUMO	30 → 35 (0.49591) 31 → 34 (0.49591)
	223.08	0.1589	HOMO–2 → LUMO	28 → 35 (0.48021) 29 → 34 (–0.48020) 28 → 34 (0.48020) 29 → 35 (0.48020)
5	405.71	0.0047	HOMO–1 → LUMO HOMO → LUMO	32 → 34 (0.12088) 33 → 34 (0.68854)
	387.78	0.0041	HOMO–1 → LUMO+1 HOMO → LUMO+1	32 → 35 (0.13323) 33 → 35 (0.68981)
	319.44	0.0030	HOMO–2 → LUMO HOMO–1 → LUMO+1	31 → 34 (0.57831) 32 → 35 (0.38477)
	318.66	0.0063	HOMO–2 → LUMO+1 HOMO–1 → LUMO+1 HOMO → LUMO	31 → 35 (0.26424) 32 → 34 (0.63495) 33 → 34 (–0.12347)
	291.33	0.0059	HOMO–3 → LUMO HOMO–2 → LUMO+1 HOMO–1 → LUMO	30 → 34 (–0.20605) 31 → 35 (0.61684) 32 → 34 (–0.25440)
	275.97	0.0028	HOMO → LUMO+2	33 → 36 (0.68783)
	273.10	0.0680	HOMO–4 → LUMO HOMO–3 → LUMO+1 HOMO–2 → LUMO HOMO–1 → LUMO+1	29 → 34 (0.13219) 30 → 35 (–0.27759) 31 → 34 (–0.37087) 32 → 35 (0.48534)
	264.34	0.0158	HOMO–4 → LUMO+1 HOMO–3 → LUMO	29 → 35 (–0.27652) 30 → 34 (0.60848)

			HOMO–2 → LUMO+1 HOMO → LUMO+2	31 → 35 (0.16853) 33 → 36 (0.10012)
	260.99	0.0374	HOMO–4 → LUMO HOMO–3 → LUMO+1 HOMO–2 → LUMO HOMO–1 → LUMO+1	29 → 34 (–0.17743) 30 → 35 (0.60196) 31 → 34 (–0.10239) 32 → 35 (0.27081)
	244.24	0.0091	HOMO–4 → LUMO HOMO–3 → LUMO+1	29 → 34 (0.66238) 30 → 35 (0.20261)
	233.25	0.0007	HOMO–5 → LUMO+1 HOMO–1 → LUMO+2	28 → 35 (–0.13672) 32 → 36 (0.67684)
	232.41	0.0015	HOMO–5 → LUMO HOMO–2 → LUMO+2	28 → 34 (0.66663) 31 → 36 (–0.19117)
	226.58	0.0249	HOMO–5 → LUMO HOMO–2 → LUMO+2	28 → 34 (0.18031) 31 → 36 (0.66346)
	224.32	0.0031	HOMO–5 → LUMO+1 HOMO–4 → LUMO+1 HOMO–3 → LUMO+2 HOMO–1 → LUMO+2	28 → 35 (0.64809) 29 → 35 (–0.18804) 30 → 36 (–0.11816) 32 → 36 (0.12227)
	217.67	0.0394	HOMO–5 → LUMO+1 HOMO–4 → LUMO+1 HOMO–3 → LUMO HOMO–3 → LUMO+2	28 → 35 (0.22431) 29 → 35 (0.48555) 30 → 34 (0.13975) 30 → 36 (0.40612)
	206.86	0.0001	HOMO → LUMO+3	33 → 37 (0.69676)

Table S5.
Nucleus-independent chemical shift (NICS, in ppm) for C_6H_6, $B_3N_3H_6$, and P_3N_3 at the B3LYP/cc-pVTZ level of theory.

h / Å	C_6H_6	$B_3N_3H_6$	P_3N_3
0.0	–8.2	–1.7	2.8
0.1	–8.3	–1.7	2.6
0.2	–8.6	–1.9	2.2
0.3	–9.0	–2.1	1.5
0.4	–9.5	–2.3	0.6
0.5	–10.0	–2.6	–0.3
0.6	–10.4	–2.8	–1.2
0.7	–10.6	–2.9	–2.0
0.8	–10.7	–3.0	–2.7
0.9	–10.6	–3.0	–3.2
1.0	–10.4	–3.0	–3.5
1.1	–10.0	–2.9	–3.8
1.2	–9.6	–2.7	–3.8
1.3	–9.0	–2.6	–3.8
1.4	–8.4	–2.4	–3.7
1.5	–7.8	–2.2	–3.6
1.6	–7.3	–2.1	–3.4
1.7	–6.7	–1.9	–3.2
1.8	–6.1	–1.7	–3.0
1.9	–5.6	–1.6	–2.8
2.0	–5.1	–1.5	–2.5