

High energy density materials from azido cyclophosphazenes

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Supplementary Information:

Materials and general procedure: The solvents were dried according to standard procedures. Hexachlorocyclotriphosphazene (**1**) and sodium azide were used as received from Otsuka Chemical Co. and Acros, respectively. (Dimethylamino)-pentachlorocyclophosphazene²¹ (**2**) and hexaazidocyclophosphazene¹⁵ (**3**) were prepared according to literature procedures. ³¹P, ¹H and ¹³C NMR spectra were recorded using a 300 MHz NMR spectrometer operating at 121.48, 300.13, and 75.48 MHz, respectively, with CDCl₃ as solvent. Chemical shifts were reported relative to H₃PO₄ and Me₄Si. IR spectra were recorded using NaCl plates for neat liquids and KBr pellets for solids. HRMS was recorded on a high resolution mass spectrometer.

Synthesis of hexaazidocyclotriphosphazene (4): Hexachlorocyclotriphosphazene (0.35 g, 1.0 mmol) was dissolved in dry acetone, and sodium azide (0.58 g, 8.9 mmol) was added. The procedure was repeated as in ref 15 to yield **4** as liquid product (0.35 g, 90% yield).

Synthesis of 2, 6-dibutylaminohexachlorocyclotetraphosphazene (7): The reaction was carried out according to the procedures described in earlier literature,¹⁹ using *tert*-butyl amine (1.46 g, 20 mmol) and octachlorotetracyclophosphazene (4.64 g, 10 mmol) in 40 mL chloroform. On warming the reaction mixture to room temperature, the mixture was appropriately fitted and set to reflux under N₂-atmosphere for 4 h. On cooling, the solvent was evaporated to about 10 mL, poured into a beaker, and left to slowly

evaporate, yielding colorless oil. An evaluation of the NMR (^1H , ^{13}C and ^{31}P) spectra of the crude oily product was a mixture of compounds. By the next morning, the formation of crystal products was noticed on the walls of the beaker (kept in a hood, but set to slowly evaporate using perforated paper cover). After 4 days, the crystals were carefully selected using a spatula, and washed with ice-cold pentane ($0\text{ }^\circ\text{C}$). Further evaluation of the NMR spectra of both solid and oil indicated that one of the possible substitution isomers in the oil was now neatly separated as the crystal. The yield of the colorless crystal was 58.7 % of the crude oily product, and identified by ^1H , ^{13}C and ^{31}P NMR data to be $\text{N}_4\text{P}_4\text{Cl}_6[2,6-(t\text{-BuNH})]_2$. Mp: $140\text{ }^\circ\text{C}$. *cf.* {Lit. $\text{N}_4\text{P}_4\text{Cl}_6[2,4-(t\text{-BuNH})]_2 = 127\text{ }^\circ\text{C}$ }. IR: $2976\text{ (m)}\ \nu_a(\text{Me})$ and $3269\text{ (m, br)}\ \text{cm}^{-1}\ \nu_a(\text{N-H})$. NMR: ^1H , δ 1.41 (s, 9H, t-Bu), 3.16 [d, ($J=3\text{ Hz}$) N-H]; ^{13}C , δ 31.1 [d ($J=6\text{ Hz}$)], ^{31}P { ^1H }, δ -5.6[t ($J=38\text{ Hz}$)], -10.5 [t ($J=38\text{ Hz}$)].

Crystal structure of 8

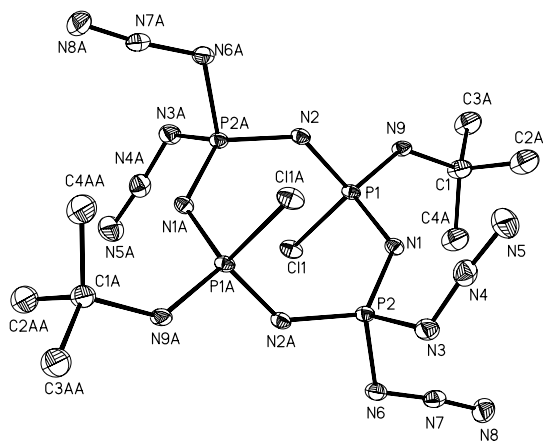


Figure 1S. Thermal ellipsoid (30%) plot of **8**. H atoms not shown. Selected bond lengths (\AA) and angles ($^\circ$): N1-P1, 1.582(2), N1-P2, 1.5777(19), N2-P1, 1.583(2), P2-N2a, 1.568(2), P1-Cl1, 2.0687(9), P2-N3, 1.703(2), P2-N6, 1.698(2), P1-N9, 1.606(2); P2-N1-P1, 128.53(13), P1-N2-P2a, 131.52(13); N1-P1-N2, 118.23(11), N1-P2-N2a, 122.11(10).

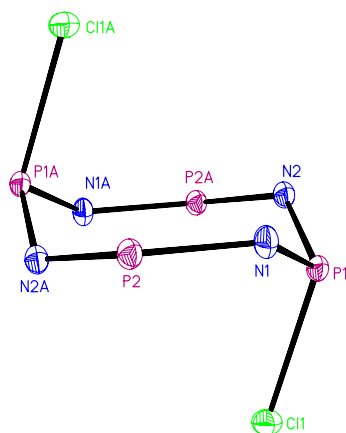


Figure 2S. Thermal ellipsoid plot (30%) of the chair conformation core of **6**. Only the unreacted *trans* Cl atoms are shown for clarity.S