High energy density materials from azido cyclophosphazenes†

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Azido substituted cyclophosphazenes were prepared and their standard heats of formation were calculated based on experimentally determined heats of combustion.

Compounds that contain azide are most often highly energetic and some tend to be unstable. However, over the last years, relatively stable azido substituted carbon-nitrogen heterocycles have been reported with densities >1.7 g cm^{-3} and with very high heats of formation,[1] *e.g.*, 4,4′,6,6′-tetra(azido)azo-1,3,5-triazine with $\Delta_f H^\circ$ = +6164 kJ kg^{-1}. The high heats of formation arise from the large number of inherently energetic N–N and C–N bonds. This energy source is in contrast to that for the classic energetic materials such as HMX (1, 3, 5, 7-tetranitro-1, 3, 5, 7-tetra-azacyclooctane) and TNT (trinitrotoluene),[2] where energy is obtained from oxidation of the carbon backbone. In the former cases, because a higher percentage of the decomposition products will be dinitrogen, these nitrogen-rich compounds tend to be promising high energetic materials and may be significantly more environmentally benign.[3]

Despite their high enthalpies of formation and accompanying tendency to be sensitive to friction, impact and heat, the introduction of amino groups into the nitrogen rich organic heterocycles appeared to enhance their thermal stability.[4] However, until now, most research is based on compounds with both carbon-azido and carbon-amino or nitrogen-amino substitutents.[5] Yet the chemistry and properties of energetic materials with *P*-azido and *P*-amino moieties have been discussed only rarely in the scientific literature.[6]

The spirocyclic compounds of cyclophosphazene trimers and tetramers were suggested to have higher energy compared to their ansa isomers.[7] A few reports have suggested use of inorganic heterocycles such as spirocyclic fluorophosphazenes[8] and azido substituted cyclophosphazenes[9] as high energy materials. There is no evidence to support the high energy of these cyclophosphazene compounds in the form of energy calculations based on experimentally obtained thermodynamic data.[10] The focus of the present work is the syntheses of energetic materials based on cyclophosphazenes which may offer alternative energetic compositions.

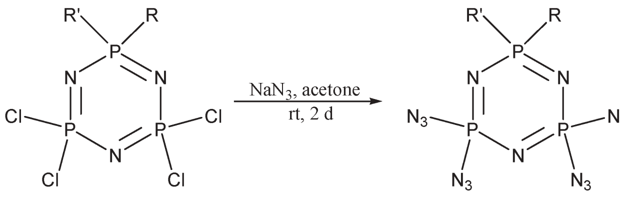
For the first time, we report calculated enthalpies of formation for cyclophosphazene azides based on experimentally determined heats of combustion. While there are a few reports of azido substituted cyclophosphazenes, none of these azido substituted cyclophosphazene tetramers has been structured crystallographically. In this work, the crystal structure of an azidocyclophosphazene, obtained from the reaction of sodium azide with bis[2,4-(dibutylamino)]hexachlorocyclophosphazene tetramer, is given.

Increasing the number of nitrogen atoms in heterocycles results in considerable gain in the standard enthalpy of formation in the resulting compounds.[11] Each phosphorus atom in a cyclophosphazene ring can typically accommodate two azido or amino groups. With the aim of preparing high energy materials based on cyclophosphazene azides, we have reacted $N_3P_3Cl_6$ (**1**), $N_3P_3Cl_5(NMe_2)$ (**2**)[12] and $N_3P_3Cl_2[1,1\text{-}(NH_2)_2]$ (**3**)[13] with sodium azide. Reactions at 25 °C in acetone led to complete replacement of chlorine by azide leading to the formation of $N_3P_3(N_3)_6$ (**4**),[14] $N_3P_3(NMe_2)(N_3)_5$ (**5**)[15] and $N_3P_3(N_3)_4[1,1\text{-}(NH_2)_2]$ (**6**)[16] (Scheme 1).

The reaction mixture was filtered through filter paper and the solvent evaporated to leave the spectroscopically pure product. Compounds **4** and **5** are liquids, while at 25 °C **6** is a solid. Each was characterized by NMR, HRMS, and infrared spectroscopy. Compound **4** was reported to be highly friction sensitive and was known to detonate without warning.[14] This has been our experience. However, the bis(dimethylamino) (**5**) and diamino (**6**) compounds are substantially more stable. Introduction of smaller amounts of hydrogen and carbon enhances the good oxygen balance and reduces sensitivity to detonate due to friction. As a result, **5** and **6** were significantly easier to handle than **4** and, in our hands, there have been no signs of instability. The density of **5** and **6** are 1.67 and 1.79 g cm^{-3}, respectively.

Recent results from our group[17] and others[18] have shown the application of low-melting salts prepared from triazole and tetrazole as high-energy materials. But, attempted quaternization reactions of **5**, **6** and **8** (*vide infra*) with methyl iodide and other electrophiles were unsuccessful. The electron withdrawing nature of cyclophosphazenes may account for this failure.[19]

The standard enthalpy of formation of an energetic compound is a very important characteristic which can be calculated from heats of combustion using Hess thermochemical equations. The standard enthalpies of formation of the chlorophosphazene trimer and tetramer were reported as −811.33 and −1083.03 kJ mol^{-1}, respectively.[20] In a calorimetric experiment in an oxygen



R = R' = Cl (1),
R = Cl, R' = NMe_2 (2)
R = R' = NH_2 (3)

R = R' = N_3 (4)
R = N_3, R' = NMe_2 (5)
R = R' = NH_2 (6)

Scheme 1

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† Electronic supplementary information (ESI) available: Experimental details of **4** and **7**, crystal structure, chair conformation and CIF for **8**. See http://dx.doi.org/10.1039/b510924h

atmosphere, the cyclophosphazenes were reported to burn according to eqn (1).[20] Based on this, **4–6** were assumed to burn in the presence of oxygen according to eqns (2)–(4), respectively. In order to confirm the formation of P_4O_{10}, the solid obtained after burning was dissolved in D_2O and the ^{31}P NMR spectrum was recorded. The spectrum showed only a strong peak at 0 ppm indicating the formation of phosphoric acid.

$$(PNCl_2)_n(s) + 5n/4\ O_2\ (g) \rightarrow n/4\ P_4O_{10}\ (s) + n\ Cl_2\ (g) \qquad (1)$$

$$[P_3N_3(N_3)_6]\ (s) + 14/4\ O_2\ (g) \rightarrow 3/4\ P_4O_{10}\ (s) + 42/4\ N_2\ (g) \qquad (2)$$

$$\begin{gathered}[P_3N_3(N_3)_5(NMe_2)]\ (s) + 29/4\ O_2\ (g) \rightarrow \\ 3/4\ P_4O_{10}(s) + 38/4\ N_2\ (g) + 2\ CO_2 + 12\ H_2O\ (l)\end{gathered} \qquad (3)$$

$$\begin{gathered}[P_3N_3(N_3)_4(NH_2)_2]_2]\ (s) + 17/4\ O_2\ (g) \rightarrow \\ 3/4\ P_4O_{10}\ (s) + 34/4\ N_2\ (g) + 4\ H_2O\ (l)\end{gathered} \qquad (4)$$

The standard molar enthalpy of combustion ($\Delta_c H_m^\circ$) of the samples can be derived from the constant volume combustion energy ($\Delta_c U_m$) by means of the following equation:

$$\Delta_c H_m{}^\circ = \Delta_c U_m + \Delta nRT\Delta n = \textstyle\sum_i n_i(\text{products,g}) - \textstyle\sum_i n_i(\text{reactants,g})$$

Here Σn_i is the total molar amount of the gases in products or reactants. Typical calorimetric experiment[21] results (averaged over three measurements each) of the constant volume combustion energy ($\Delta_c U_m$) of **4**, **5** and **6** are given in Table 1. From these values and eqns (2), (3) and (4), the standard molar enthalpies of combustion ($\Delta_c H_m^\circ$) for **4**, **5** and **6** are −4142.3 −5409.0 and −4393.3 kJ mol^{-1}, respectively The literature values for standard molar enthalpies of formation of CO_2 (g) = −395.51 kJ mol^{-1}, H_2O (l) = −285.83 kJ mol^{-1} and P_4O_{10} (s) = −2984 kJ mol^{-1}. Substituting these values in the designed Hess thermochemical equations for **4**, **5** and **6** (eqns (5)–(7)) the molar enthalpies of formation are calculated and are shown in Table 1.

$$\begin{gathered}\Delta_f H_m{}^\circ\ [P_3N_3(N_3)_6]\ (s) = \Delta_f Hm^\circ\ [P_4O_{10}]\ (s) - \\ \Delta_c H_m{}^\circ\ [P_3N_3(N_3)_6]\ (s)\end{gathered} \qquad (5)$$

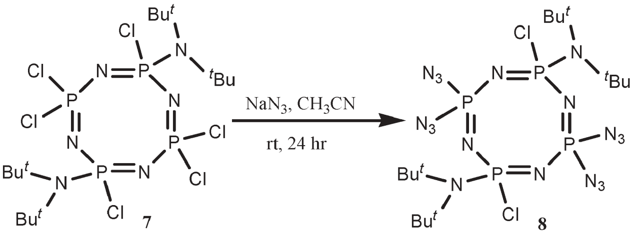
$$\begin{gathered}\Delta_f H_m{}^\circ\ [P_3N_3(N_3)_5(NMe_2)]\ (s) = \{3/4\ \Delta_f H_m{}^\circ\ [P_4O_{10}]\ (s) + \\ 2\ \Delta_f H_m{}^\circ\ [CO_2]\ (g) + 3\ \Delta_f H_m{}^\circ[H2O]\ (1)\} - \\ \Delta_c H_m{}^\circ\ [P_3N_3\ (N_3)_5(NMe_2)]\ (s)\end{gathered} \qquad (6)$$

$$\begin{gathered}\Delta_f H_m{}^\circ\ [P_3N_3(N_3)_4(NH_2)_2]\ (s) = (3/4\ \Delta_f H_m{}^\circ\ [P_4O_{10}]\ (s) + \\ \Delta_f H_m{}^\circ[H2O]\ (1)) - \Delta_c H_m{}^\circ\ [P_3N_3\ (N_3)_4(NH_2)_2]\ (s)\end{gathered} \qquad (7)$$

The positive heats of formation are indicative of rather high energies associated with azido derivatives. Not surprisingly, the heats of formation of the azido-substituted cyclophosphazene trimers are positive compared with the negative value reported for $P_3N_3Cl_6$.[20] The energy released on burning of one kg of a compound is an important parameter to be considered for energetic applications. Hence, it is significant to compare the heats of formation in kJ kg^{-1} as is shown in Table 1. These values indicate that the compounds **4–6** would expect to release a considerable amount of energy on burning, thus may potentially have interesting uses.

Table 1 Standard molar enthalpies of formation of the azido derivatives of cyclophosphazene trimers

Compounds	Density/ g cm^{-3}	$\Delta_c U_m$/ kJ mol^{-1}	$\Delta_f H_m^\circ$/ kJ mol^{-1}	$\Delta_f H_m^\circ$/ kJ kg^{-1}
4	—	−4158.9	1904.3	4920.7
5	1.67	−5419.4	1528.6	3929.6
6	1.79	−4403.7	1869.5	5580.7



Scheme 2

Based on the opportunity to introduce additional azide functionalities into a single stable moiety, we have synthesized $N_4P_4Cl_6[2,6\text{-}(t\text{-}BuNH)]_2$ (**7**) according to the literature procedure from the reaction of $N_4P_4Cl_8$ with *n*-dibutylamine.[22] When the latter was further reacted with sodium azide in acetonitrile at 25 °C, $N_4P_4Cl_2(N_3)_4[2,6\text{-}(t\text{-}BuNH)]_2$(**8**), which contains two unsubstituted chlorine atoms, was obtained[23] (Scheme 2).

The presence of chlorine atoms diminished our interest in determining thermodynamic properties and the release of the chlorine gas is harmful from an environmental perspective. However, since **8** is a stable solid which provided an opportunity for structural study. The solid-state structure of **8** was obtained[24] which is the first reported crystal structure of a tetrameric azidocyclophosphazene. The structure (Figure 1) shows that the gem N_3 substitution and the Cl ligands are *trans*-oriented. The orientation of both gem-substituted N_3 groups is *cis* to each other and point towards the *t*-Bu groups. This orientation is preferred to prevent steric crowding as the NH groups form a hydrogen bond

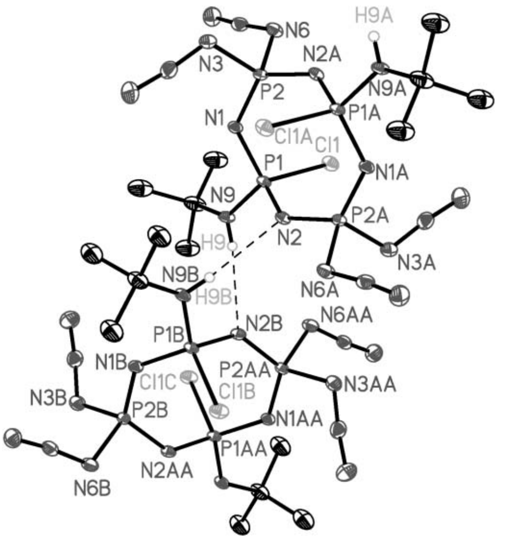


Fig. 1 Thermal ellipsoid plot (30%) showing the hydrogen bonding association *via* N9–H9···N2. Only two molecules and only the N9 hydrogen atoms are shown for clarity. Hydrogen bonding interaction indicated by dashed lines.

with a neighboring ring nitrogen (N9–H9···N2^i = 3.143(3) Å; $i = -x,y,-z + 1/2$; see electronic supplementary information (ESI)†) generating a twisted intermolecular eight membered ring. The phosphazene core in **8** is in the typical chair conformation and has similar but slightly elongated P–N bonds (0.01 Å–0.02 Å) and more acute P–N–P (5°–6°) angles than the parent halogenated cyclotetraphosphazene, $N_4P_4Cl_8$.[25] The azido P–N bond and angle are similar to the only other azido phosphazene,1,3,5-N_3-1,3,5-R_3-cyclotriphosphazene (R = 2,6(bis(4-*tert*-butylphenyl)phenyl).[26]

In conclusion, we have synthesized azido substituted cyclophosphazenes and for the first time calculated the standard heats of formation based on experimentally determined heats of combustion. The magnitude of these positive heats of formation suggests that these materials may have energetic applications. While the azido phosphazene trimers are liquids, we are able to report the first crystal structure of an azido substituted cyclophosphazene tetramer.

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15 Compound 2 (1.16 g, 3.25 mmol) was dissolved in dry acetone and sodium azide was added (2.11 g, 32.45 mmol). The mixture was stirred at 25 °C for two days. It was filtered to remove NaCl, and the solvent was removed to give mono(dimethyl-amino)pentaazido cyclotriphosphazene (**5**). Yield: 1.1 g, 87.3%. IR: 2152 cm^{-1} (vs) N_3; NMR: ^1H, δ 2.75 [d, 6H, NMe_2 ($^3J_{PH}$ = 13.24 Hz)]; ^{13}C, δ 36.89 [d, NMe_2, ($^2J_{PC}$ = 3 Hz)]; $^{31}P\{^1H\}$, δ 18.65 [t, $P(NMe_2)$, (*J* = 49 Hz)], 12.09 {d, [$P(N_3)_2$], (*J* = 49 Hz)}; HRMS: Calcd for $C_2H_7P_3N_{19}$: 390.0345, Found: 390.0293.

16 Compound **6** was synthesized according to ref. 6. MP 81 °C; Yield 24%.; Spectral data for **6**: IR: 2183 cm^{-1} (s, N_3); NMR ^1H, δ 4.66 (d, 4H, P–NH_2); ^{31}P $\{^1H\}$ δ 14.66 (t, P–NH_2, *J* = 49.3 Hz), 12.42 (d, P–N_3, *J* = 49.9 Hz); HRMS: Calcd for $P_3N_{17}H_5$: 336.0126, Found: 336.0136.

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21 The heat of combustion was determined using a Parr (series 1425) semimicro oxygen bomb calorimeter. The substances were burned in an oxygen atmosphere at a pressure of 3.04 MPa. The energy equivalent of the calorimeter was determined with a standard reference sample of benzoic acid (SRM 39i, NIST). Since a Parr 45C10 alloy fuse wire was used, a correction of 2.3 (IT) cal cm^{-1} of wire burned has been applied in all standardization and calorific value determinations. Acid correction has been omitted for all semimicro samples. The bomb was examined for evidence of unburned compound after each run, and, if more than a slight trace was present, the run was discarded.

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23 The reaction of $N_4P_4Cl_6[2,6\text{-}(t\text{-}BuNH)]_2$ (**7**) (4.30 g, 8.0 mmol) and excess sodium azide (6.50 g, 100.0 mmol) in 50 mL acetonitrile was carried out at 25 °C for 24 h. Separation of pure $N_4P_4(N_3)_4Cl_2[2,6\text{-}(t\text{-}BuNH)]_2$ (**8**) was achieved when crystals of this product grew slowly as the chloroform solution was evaporated. The isolated yield was 90%. White solid, MP 129 °C IR: 2155 (vs) ν_{N_3}, 2976 (m) ν_a (Me), and 3265 (m, br) cm^{-1} ν_a (N–H). NMR: 1H, δ 1.41 [s, 9H (*t*-Bu)], 3.16 [d (*J* = 3 Hz) N–H]; 13C, δ 31.1 (d, *J* = 6 Hz); 31P{1H}, δ −2.3 (t, *J* = 43 Hz), −6.8 (*t*, J = 43).

24 Crystal data for **8** at 84 K with Mo Kα (λ = 0.71073 Å) radiation: $C_8H_{20}Cl_2N_{18}P_4$, *M* = 563.20, Monoclinic, space group *C*2/*c* (no. 15), *a* = 18.452(4), *b* = 9.5500(19), *c* = 14.060(3) Å, β = 103.67(3)°, *V* = 2407.4(9) Å^3, *Z* = 4, ρ = 1.554 mg m^{-3}, μ = 0.574 mm^{-1}, ω scans, θ range = 2.27 to 27.50°, 15727 reflections measured, GoF on F^2 = 1.061 for 2774 unique observed data, (R_{int} = 0.0233), 6 restraints and 159 parameters, R_1 = 0.0444, wR_2 = 0.1134 for [$I > 2\sigma(I)$]. CCDC 278747. See http://dx.doi.org/10.1039/b510924h for crystallographic data in CIF or other electronic format. The *t*-Bu group was disordered and modeled in two positions with occupancies of 0.74 and 0.16. Loose restraints were applied to keep C–C distances reasonable.

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