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14. ABSTRACT

Organic polyazido substituted compounds are at the forefront of high energy research. Polyazido organic compounds have high relative heats of formation as one azido group adds about 87 kcal/mol of endothermicity to a hydrocarbon compound.[1] In this family of compounds, 3,6-di(azido)-tetrazine (**1**), has the highest reported heat of formation ~ 1101 kJ mol-1(6709 kJ kg-1).[2] The compound 4,4',6,6'-tetra(azido)azo-1,3,5-triazine (**2**), has a heat of formation of 2171 (6164 kJ kg -1) (Fig. 1).[3] Recently it was demonstrated that **1** and **4** were good precursors to nano carbon nitride materials.[4,5] Thermal decomposition of **1**[4] and **4**[5] yields nitrogen-rich nanolayered, nanoclustered and nanodendritic carbon nitrides depending on the different heating processes.

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Polyazido Pyrimidines: High Energy Compounds and Precursors to Carbon Nanotubes[**](PREPRINT)

Chengfeng Ye,[a] Haoxiang Gao,[a] Jerry A. Boatz,[b] Gregory W. Drake,[c] Brendan Twamley,[a] and Jean'ne M. Shreeve [a]*

Organic polyazido substituted compounds are at the forefront of high energy research. Polyazido organic compounds have high relative heats of formation as one azido group adds about 87 kcal/mol of endothermicity to a hydrocarbon compound.[1] In this family of compounds, 3,6-di(azido)-tetrazine (**1**), has the highest reported heat of formation ~ 1101 kJ mol-1(6709 kJ kg-1).[2] The compound 4,4',6,6'-tetra(azido)azo-1,3,5-triazine (**2**), has a heat of formation of 2171 (6164 kJ kg -1) (Fig. 1).[3] Recently it was demonstrated that **1** and **4** were good precursors to nano carbon nitride materials.[4,5] Thermal decomposition of **1**[4] and **4**[5] yields nitrogen-rich nanolayered, nanoclustered and nanodendritic carbon nitrides depending on the different heating processes.

To date, many of the reported polyazido compounds are based on C-N heteroaromatic cycles, e.g. tetrazine(**1**),[4] triazine (**3**),[6] heptazine,[7] triazole,[8] tetrazole; [9] inorganic anions, e.g. $[P(N_3)_6]^-$,[10] $[B(N_3)_4]^-$,[11] $[Si(N_3)_6]^{2-}$,[12] $[Te(N_3)_5]^-$,[13] $[Ti(N_3)_5]^-$,[14] $[Ti(N_3)_6]^{2-}$,[14] $[Sb(N_3)_6]^-$,[15] etc. as well as triazidocarbenium perchlorate, and dinitramide (**4**) (Fig. 1).[1] Few reports focus on pyrimidine as a basic building block. Although 2, 4, 6-triazopyrimidine (**5**),[16] has been known since 1979, it has mainly

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been used for photochemical reactions. Few physical properties of this compound are known.
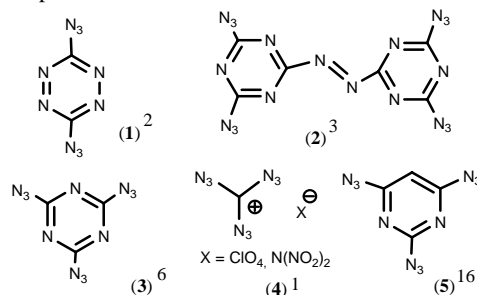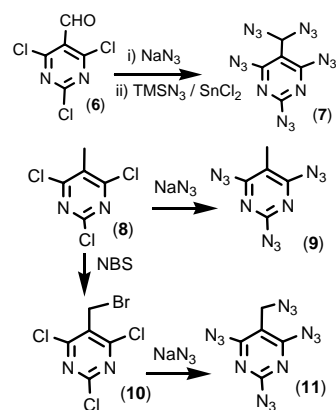

Fig. 1. Examples of reported polyazido compounds.

Preliminary calculations show that 2,4,6-tri(azido)pyrimidine (**5**) has a positive heat of formation comparable to 2,4,6-tri(azido)-1,3,5-triazine (**3**). Now we report the synthesis of a series of polyazidopyrimidine compounds, their calculated heats of formation, and their role as a source of carbon nanotubes via detonation generation.

Scheme 1. Synthesis of polyazidopyrimidines.

Currently, except for the triazidocarbon cation,[1] molecules with three or four azido groups on the same carbon atom have not been available due to their instability, high sensitivity and difficulty in synthesis. Only several geminal diazido compounds have been prepared from the reaction of substituted benzaldehyde or acetophenone with $TMSN_3$, catalyzed by $SnCl_2$ or $ZnCl_2$.[17] However, heterocycles based on geminal diazido compounds have not been reported. We have prepared penta(azido)pyrimidine (**7**) starting from 5-carboxyaldehyde-2,4,6-triazidopyrimidine, (**6**) (Scheme 1). The best yield can be achieved by first substituting the three chlorine atoms on the pyrimidine ring with azide ion; then transforming the aldehyde into geminal diazido using $TMSN_3/SnCl_2$. Remarkably, this pentazido- compound is a liquid at room temperature with a melting point at ~ -48 $^{\circ}$C and has good thermal stability up to ~179 $^{\circ}$C. It is noteworthy that **7** can be purified by column chromatography and routine handling while avoiding external heating. This suggests that **7** is not as detonation sensitive as **1**. *However*, e*xtreme care is absolutely necessary!*

For comparison purposes, triazido-, and tetrazido-pyrimidine derivatives (**9** and **11,** respectively) were prepared as outlined in Scheme 1**.** The solid state structures of these two compounds were established by single crystal X-ray analysis (Fig.

2). Compound **9** is also planar and packs in layers,[18] in a fashion similar to **3**.[6a] However, in **9**, the molecules have significant ov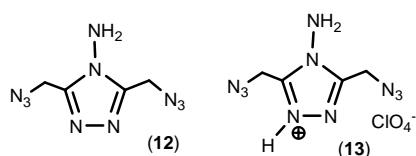erlap with the adjacent layer. The layers are also further apart (3.19 Å), as the steric bulk of the methyl group prevents closer association. There are no significant intermolecular interactions in either **3** or **9**. The structure of **11** is quite different.[19] The packing no longer displays flat planar sheets, but stacks along the *a* axis. These stacks are composed of two alternating molecules. The gap between the molecules in these stacks is ~3.26 Å at the widest with 10 ° angles between the heterocycles. There are also weak non-classical hydrogen bonds between the methylene group and terminal azido nitrogen atoms, both within the stack (C7 – N13, ~ 3.31Å) and between the stacks (C7 – N19, ~ 3.41Å). This compound was difficult to crystallize and has disorder of the alkyl azido group as well as rotational twinning (See CCSD-612107, 612108).[19]

Fig. 2. Thermal ellipsoid plot (30%) of **9** (left) and **11** (right). Hydrogen atoms have been included but not labeled.

The melting point of the triazido-analogue (**9**) is 103 °C, while the addition of one extra alkyl azido group (**11**) reduces the melting point drastically by ~ 80 °C to 22.5 °C (Table 1). The introduction of a fourth azido group does not result in any obvious decrease in thermal stability. The presence of a fifth azido group (vide supra) led to a decrease in the melting point by an additional 70 °C, with just a slight decrease in thermal stability (Table 1).

A possible rationale for the lower melting point observed for the azidoalkyl substituted pyrimidine is the inefficient packing caused by the azido alkyl group. The azido group in **11** is disordered (vide supra) and has free rotation around the methylene carbon C7. This phenomenon has also been confirmed with other examples, e.g., 3, 5-diazidomethyl-4-amino-triazole (**12**, m.p. 92 °C) and its perchlorate salt (**13**, m.p. 75 °C) have much lower melting points than 3,5-dimethyl-4-amino-triazole [20] (m.p. 196 °C) and its perchlorate salt (m.p. 94 °C) (Fig. 2). Thus, introducing azido-alkyl groups could be an efficient way to reduce the melting point and increase the heat of formation which is essential for the preparation of energetic ionic liquids.[21, 22]

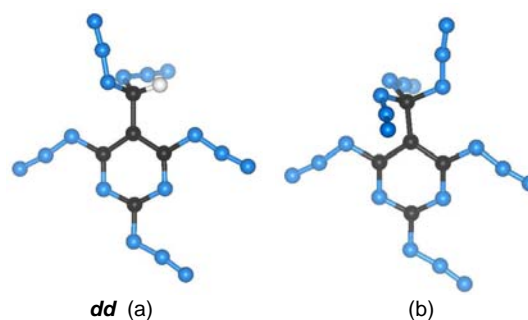***Fig. 3.*** 3,5-diazidomethyl-1,2,4-triazole and its perchlorate

The heats of formation of **7**, **9**, **11**, and 5-triazidomethyl-2,4,6-triazidopyrimidine (**14**) were predicted using quantum chemical calculations (see supporting information for computation details). The optimized geometries of pentazido-

and hexazido-pyrimidine (**14**) are shown in Fig. 4 which are proven to be at local minima in the potential energy surface. The incremental contribution of each additional azide ligand to the heat of formation in the sequence **9→11, 11→7, and 7→14** is +365, +354, and +385 kJ/mol, respectively (Scheme 3). Similar behavior is observed in the corresponding sequence of isodesmic reference compounds $CH_3CH_{3-n}(N_3)_n$; n = 0-3, in which the incremental changes in heats of formation as a function of the number "n" of azide ligands are +351, +337 and +323 kJ/mol, respectively. For **7**, using 20 kcal as its heat of sublimation, the heat of formation for the solid state was estimated to be 1723.2 kJ mol^{-1} or 5764 kJ kg^{-1}, which would be the third highest heat of formation reported for energetic materials, just lower than that of **2** (6164 kJ kg^{-1}) and **1** (6709 kJ kg^{-1}).

Table 1. Physical properties of polyazido compounds

Compd.	Density (g cm^{-3})	m.p. (°C)	T_d (°C) (DSC)	$\Delta H^o_{f\ 298}$ (kJ mol^{-1})
1	1.72	130	130	1101[a]
3	1.72	94	180	1050[b]
7	1.71	-48	179	1807.1[c]
9	1.55	103	195	1087.4[c]
11	1.65	22.5	193	1452.7[c]
14	-	-	-	2192.0[c]

[a] experimental value, ref 2; [b] experimental value, ref 6b; [c] calculated value in gas phase.
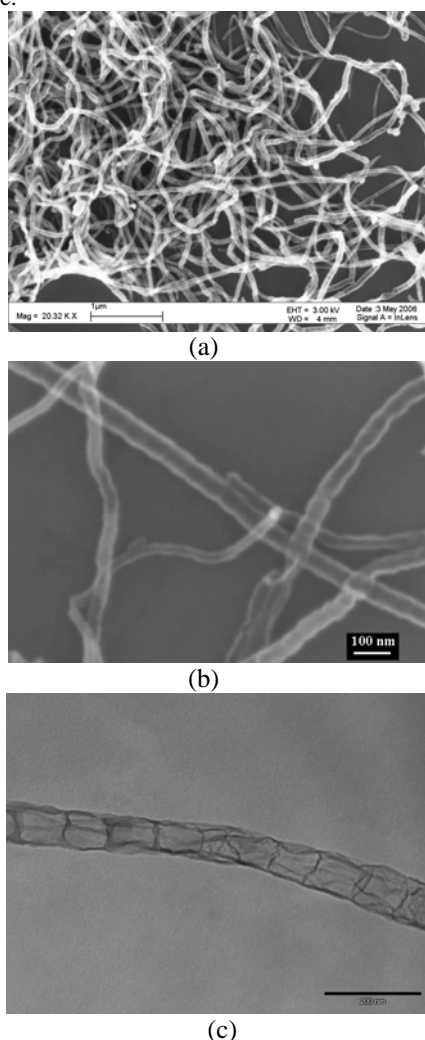

dd (a)   (b)

Fig. 4. B3LYP/6-311G(d,p) optimized geometries of (**7**) pentazido-(a) and (**14**) hexazido-pyrimidine (b**).**

Carbon nanotubes (CNTs) formed by catalytic detonation of polyazidopyrimidine.

Since their discovery in 1990, carbon nanotubes (CNT) have been shown to be extremely promising for applications in materials science and medicinal chemistry due to interesting electronic, mechanical, and structural properties. Synthesis of nanomaterials in large scale by detonation of explosive precursors is a new promising method owing to low cost. Polyazido compounds with little or no hydrogen content are regarded as such ideal precursors for nanomaterials. Kroke first reported the preparation of CNTs using 2,4,6-triazido-1,3,5-triazine (**3**) by this detonation method in 1999,[23] but the yield was only ~ 2%. Optimization of the detonation conditions in the presence of transition metals, e.g. Fe, Ni, Cu, Ti, improved the yields to > 60%.[24]

Compound **3** is very detonation sensitive, and its explosive nature increases with higher purity and crystal size.[6a] We find 2,4,6-triazopyrimidine (**5**) to be much less sensitive to detonation than **3**. Therefore, **5** was examined as the carbon source and self-

heating producer for CNTs. Among the catalysts explored e.g., Cu powder, Cu(OAc)$_2$,[25] AgNO$_3$, Ni(ClO$_4$)$_2$, etc., we found that Ni(ClO$_4$)$_2$ was the best catalyst for the production of CNTs. The synthetic method is straightforward; **5**, (0.3 g 1.47 mmol) and Ni(ClO$_4$)$_2$ (0.02 g, 0.07 mmol) were placed in a 75 mL stainless steel vessel, which was then closed with a valve and heated to 250 °C over ~ 20 min. The vessel was then allowed to cool to room temperature. The product was observed as a fleecy, puffy, fiber-like black residue which was easily removed from the vessel with forceps. On touching glass (e.g., a glass vial), the black residue agglomerated. This material floats and disperses well in ethanol. SEM and TEM pictures of as-prepared samples clearly show the presence of characteristic hollow channel CNT structures (lengths ~3 - 20 microns, and diameters of ~ 60-80 nm up to 100 nm, see Fig. 5). The yield of CNTs is estimated to be > 90%. They have a bamboo-like morphology (see Fig 5d), and these "compartmentalized nanotubes"[26] are segmented with a relatively uniform segment length of about 90 nm. EDX (energy dispersion X-ray) shows that the walls of these CNTs are nitrogen free.

(a)

(b)

(c)

Fig 5. SEM (a, b) and TEM (c) images of CNTs generated by the detonation of **5** using Ni(ClO$_4$)$_2$ as a catalyst.

In conclusion, we have successfully synthesized a series of polyazidopyrimidine compounds, in which the azidomethyl group dramatically decreases the melting points. Theoretical calculations show that these compounds exhibit highly promising energetic properties. 2,4,6-Triazido-pyrimidine was found to be a novel and less sensitive precursor to carbon nanotubes in high yields.

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[18] Crystal data for **9**:.C$_5$H$_3$N$_{11}$, MW = 217.18., T= 89(2) K, $P2_1$/c, a = 9.838(3) Å, b = 15.295(4) Å, c = 6.3070(16) Å, β = 100.683(4)°, V = 932.5(4) Å^3, Z= 4, ρ_{calc} = 1.547 Mg/m^3, μ = 0.118 mm^{-1}, reflections collected / unique 13723 /1690, R_1 = 0.0337, wR_2 = 0.0932 (*I*>2σ*I*), GOF = 1.032, CCDC-612107 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif

[19] Crystal data for **11**: C$_5$H$_2$N$_{14}$, MW = 258.21, T=89(2) K, $P2_1$/a, a = 6.5156(14) Å, b = 22.149(5) Å, c = 7.2649(16) Å, β = 97.540(4)°, V = 1039.3(4) Å^3, Z= 4, ρ_{calc} = 1.650 Mg/m^3, μ = 0.128 mm^{-1}, reflections collected / unique 27871 /2123, R_1 = 0.0370, wR_2 = 0.0936 (*I*>2σ*I*), GOF = 1.055, Sample was rotationally twinned (179.8° about reciprocal (0, 0, 1) with a refined BASF = 0.252(3)) and the alkyl azide disordered

50%. CCDC-612108 contains the supplementary
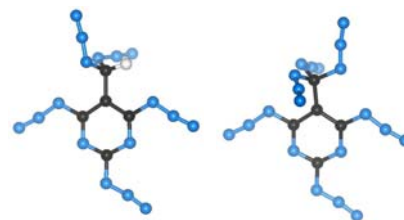crystallographic data for this paper.

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Polyazido Pyrimidines: High Energy Compounds and Precursors to Carbon Nanotubes

The azidomethyl group dramatically decreases the melting points of corresponding azido-pyrimidines. Theoretical calculations show that these polyazide compounds exhibit highly promising energetic properties. 2,4,6-Triazido-pyrimidine was found to be a novel precursor to carbon nanotubes in the presence of $Ni(ClO_4)_2$.

Supporting Information

Polyazido Pyrimidines: High Energy Compounds and Precursors to Carbon Nanotubes

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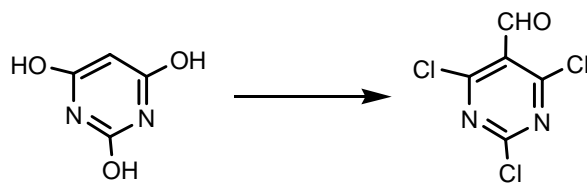
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*Caution! On the basis of the high positive heats of formation, all polyazido products must be handled with extreme care. Plastic spatulas, leather gloves and face shields should be used at all times, especially when handling compound 8 which decomposed violently when it was transferred at the 0.5 g scale. Scaling up (>2 mmol) the synthesis of **8** and **12** should not be attempted.*

General Methods. ^{1}H and ^{13}C NMR spectra were recorded on a 300 MHz nuclear magnetic resonance spectrometer operating at 300.13, and 75.48 MHz, respectively, using $CDCl_3$ as solvent unless otherwise indicated. Chemical shifts were reported relative to TMS. High resolution mass spectroscopy was carried out on a JEOL JMS - AX505HA mass spectrometer.
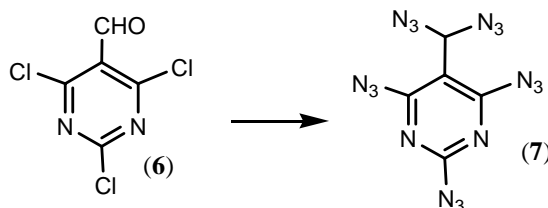

2,4,6-triazidopyrimidine (5*)*. To a solution of trichloropyrimidine (5.0 g, 27 mmol) in 30 mL dry acetone was added NaN_3 (6.0 g, 92.3 mmol), the mixture was stirred at room temperature for 6 hours, 50 mL CH_2Cl_2 was added, the solid was filtered off, and was washed with CH_2Cl_2 (5 mL), The organic phase was combined and solvent was removed under reduced pressure, recrystallized from methanol or hexane. White solid, (5.0 g, 91%), m.p. 98 $^{\circ}$C. ^{1}H NMR δ 5.96 (s, 1H), ^{13}C NMR δ 93.9, 161.2, 164.6.
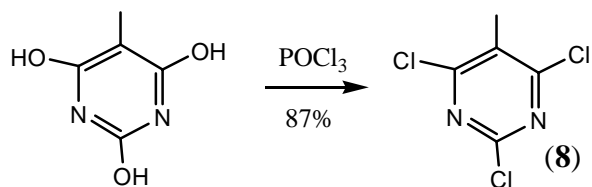
5-Carboxyaldehyde-2,4,6-trichloropyrimidine (7).[1] Barbituric acid (6.0 g) was added

to a mixture of $POCl_3$ (15 mL) and N,N-dimethylaniline (3 mL). The solution was

refluxed for 8 h, cooled to room temperature, poured into ice-water, and extracted with

ethyl acetate three times (50 mL). The organic phase was combined and dried over

Na_2SO_4. After evaporation of solvent, the residue was recrystallized from hexane (5.8 g,

59%) and stored in the refrigerator. ^{1}H NMR δ 10.39 (s), ^{13}C NMR δ 122.9, 161.4,
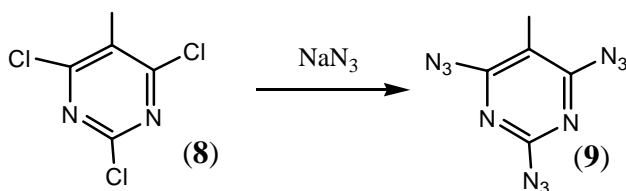
163.9, 184.5.

5,5-Diazidomethyl-2,4,6-triazido-pyrimidine (**7**). 0.8 g 5-carboxyaldehyde-2,4,6-

trichloropyrimidine (**6**) and NaN_3 (0.9 g) were placed in a 50 mL flask, 25 mL dry THF

was added, and the mixture was stirred for 6 h at room temperature. The solid was

filtered off and washed with 5 mL CH_2Cl_2. The filtrate was evaporated under vacuum,

and then dissolved in 15 mL dry CH_2Cl_2. The insoluble material was filtered off.

$SnCl_2.2H_2O$ (0.2 g), and $TMSN_3$ (1.35 g) was added dropwise to the filtrate at 0 °C, and

the mixture was stirred for 30 min until the aldehyde was consumed. The solid formed

was removed by filtration and washed with CH_2Cl_2 (5mL). After removal of the solvent,

the residue was purified by column chromatograph, colorless liquid (0.39 g, 35%). [1]H
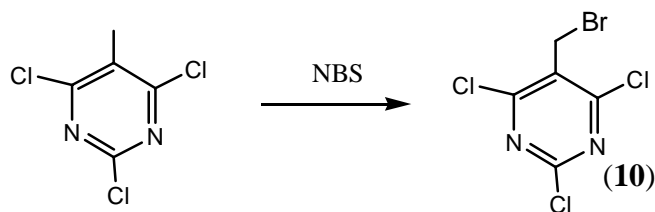
NMR δ 6.02(s), ^{13}C NMR δ 69.3, 102.2, 161.2, 162.6. MS (EI), 257 (M$^+$-N$_3$), HRMS-FAB: C$_5$H$_2$N$_{17}$ (M+H)$^+$, Calcd 300.0679; Found 300.0665.
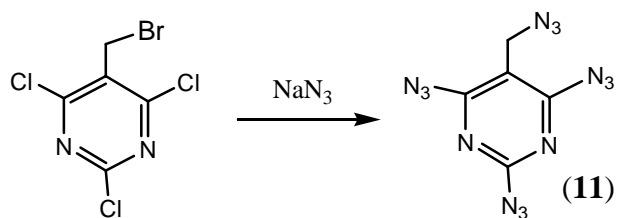

2,4,6-Trichloro-5-methyl-pyrimidine (9):[2] To a solution containing 4.4 g 5-methyl-barbituric acid in 15 mL POCl$_3$, was added 2.0 mL N,N-dimethylaniline . The mixture was refluxed overnight, cooled to room temperature, poured into ice, and then extracted with CH$_2$Cl$_2$. After removal of the solvent, the residue was purified by sublimation under vacuum (white solid, 5.3 g, 87%, M.P. 68-69 ^{o}C).
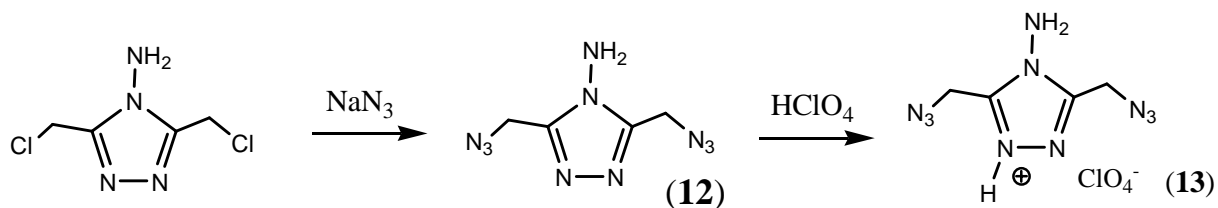

5-Methyl-2,4,6-triazido-pyrimidine (**9**): 2,4,6-Trichloro-5-methyl-pyrimidine (**8**) (0.4 g) and 0.6 g NaN$_3$ were placed in a 50 mL flask, and 25 mL THF was added followed by addition of 0.1 g TBAB. The mixture was stirred overnight at room temperature. The solid was filtered and washed with 5 mL THF. The organic phases were combined and the solvent removed. The residue was crystallized from methanol to give **9** (white solid, 0.35 g, 80%, M. P. 103 ^{o}C). ^{1}H NMR δ1.92 (s); ^{13}C NMR δ 9.1, 104.5, 158.1, 162.2. HRMS Calcd for C$_5$H$_3$N$_{11}$$^+$ 217.0573; Found 217.0565.

5-Bromomethyl-2,4,6-trichloropyrimidine (10):[3] 1.26 g of 5-methyl-2,4,6-trichloropyrimidine (**8**) was dissolved in 10 mL of dry carbon tetrachloride and 1.3 g. of N-bromosuccinimide was added. Then 120 mg of AIBN was introduced. The solution was refluxed with stirring, and monitored by GC-MS. Nearly 36 hrs are necessary to complete the reaction. The solid was filtered and after evaporation of the carbon tetrachloride, the crude product (**10**) was purified by vacuum sublimation at 110 $^{\circ}$C (M.P.132 $^{\circ}$C; lit 133-134 $^{\circ}$C;[3] 1.58 g, 90%). ^{1}H NMR δ 4.61 (s); ^{13}C NMR δ 23.6, 127.7, 158.4, 162.6.
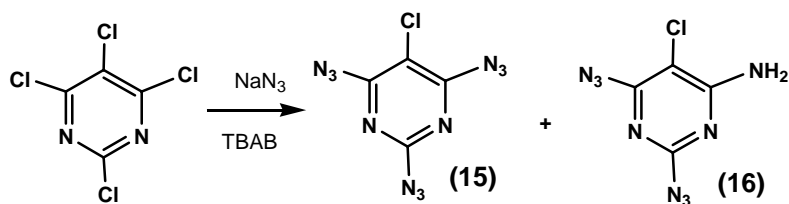

5-Azidomethyl-2-4-6-triazido-pyrimidine (11): A mixture of 5-bromomethyl-2,4,6-trichloropyrimidine (**10**) (0.2 g) and NaN$_3$ (0.4 g) in 15 mL THF was stirred at room temperature overnight. The solid was filtered and washed with 5 mL THF, the organic phase was combined and the solvent removed to leave a colorless oil (0.18 g, 99%). It solidified on standing in the refrigerator to give (**11**) (M.P. 22.5 $^{\circ}$C). ^{1}H NMR δ 4.18 (s), ^{13}C NMR δ43.0, 102.4, 160.6, 163.5. HRMS C$_5$H$_2$N$_{14}{}^{+}$, Calcd 258.0587; Found 258.0583.

4-Amino-3,5-diazidomethyl-1,2,4-triazole (12): 4-Amino-3,5-bis(chloromethyl)-4H-

1,2,4-triazole (0.2 g),[4] NaN$_3$(0.25 g), and 50 mg TBAB were placed in a 50 mL flask, and

10 mL THF was added. The mixture was stirred overnight. The solid which formed was

removed by filtration and washed with THF (5mL). After removal of the solvent, the

residue was crystallized from chloroform, **12,** (white solid, M.P. 103 °C, 0.19g, 89%.) ^{1}H

NMR (CD$_3$CN) δ 4.55 (s, 4H), 5.34 (s, 2H), ^{13}C NMR (CD$_3$CN) δ 44.2, 152.8. MS (EI),

194 (M$^+$, 100), (152, M$^+$-N$_3$). Calcd for C$_4$H$_6$N$_{10}$ C, 24.74; H, 3.11; N, 72.14; Found: C,
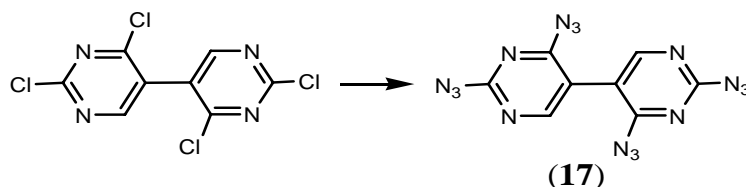
24.94; H, 3.01; N, 71.84.

4-Amino-3,5-diazidomethyl-1-H-1,2,4-triazolium perchlorate (13): 4-Amino-3,5-

bis(azido)-4H-1,2,4-triazole (**12**) (0.15 g) and perchloric acid (0.13 g, 60%) were

dissolved in methanol, and stirred for 4 h. After removing the solvent, the residue was

dried under vacuum overnight to leave a solid (**13**) (M.P. 74 °C). ^{1}H NMR (DMSO-d$_6$) δ

5.60 (s, 4H), ^{13}C NMR (DMSO-d$_6$) δ 43.0, 152.8. Calcd for C$_4$H$_7$ClN$_{10}$O$_4$ •H$_2$O, C,

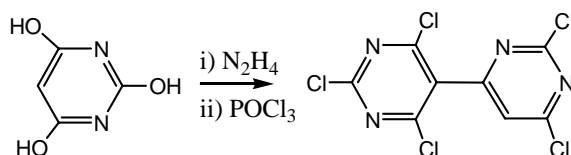15.37; H, 2.90; N, 44.80; Found C, 15.31; H, 2.40; N, 44.84.

To a solution of 0.2 g (0.92 mmol) of 2,4,5,6-tetrachloropyrimidine in 10 mL dry acetone was added 0.3 g (4.6 mmol) NaN_3 and tetrabutylammonium bromide (15 mg), and the mixture was stirred 2 days. The solid was filtered and washed with 5 mL CH_2Cl_2. The combined filtrate was subjected to evaporation and the residue was purified by chromatography (hexane:CH_2Cl_2 = 8:2).
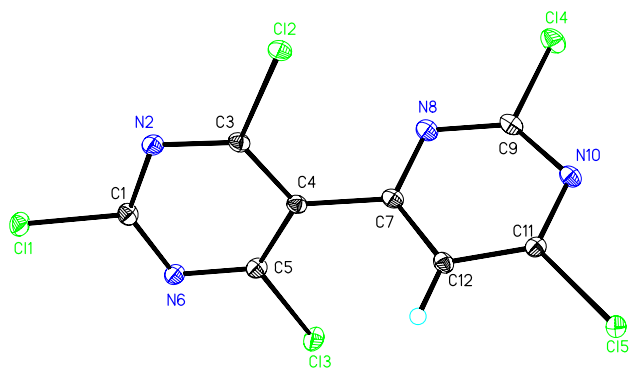
5-Chloro-2,4,6-triazido-pyrimidine (15): white solid (M.P. 90 ^{o}C, 55%). ^{13}C NMR δ 101.5, 158.1, 160.8. HRMS Calcd for $C_4H_{11}Cl$ 237.0027; Found 237.0018.

6-Amino-5-chloro-2,4-diazido-pyrimidine (16), white solid (M.P.124 ^{o}C, 21%). ^{1}H NMR (DMSO-d_6) δ 3.54 (s, 2H); ^{13}C NMR (DMSO-d_6) δ94.0, 156.7, 157.9, 161.8. Calcd for $C_4H_2ClN_9$ C 22.71, H 0.95, N 59.58; Found C 22.52, H 0.80, N 59.17.

2,2',4,4'-Tetrazido-5,5'-bispyrimidine (17): A solution of 2,2',4,4'-tetrachloro-5,5'-bipyrimidine (0. 2 g)[5] and NaN_3 (0.25 g) in 20 mL THF was stirred at room temperature overnight. The solid was filtered and washed with 5 mL CH_2Cl_2. The combined filtrate was subjected to evaporation and the residue was recrystallized from methanol/chloroform to give needle crystals (0.19 g., 88%; M.P. 160 ^{o}C). ^{1}H-NMR: δ 8.36 (s); ^{13}C NMR δ 111.6, 160.2, 161.7, 161.8. HRMS Calcd for $C_8H_2N_{16}$ 322.0648; Found 322.0646.
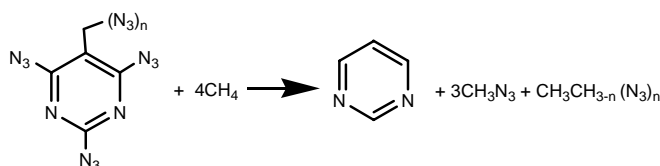
2,2',4,4'6-Pentachloro-5,6'-bispyrimidine (18):   To a refluxing solution of barbituric acid (2.56 g) in water (80 mL), was added hydrazine hydrate ($N_2H_4 \cdot H_2O$) (0.5 g) in 10 mL water. After 5 min, a white precipitate formed, and the suspension was stirred for 40 min. The solid was collected by filtration, washed with water (20 mL) and dried in vacuum (0.5 g) which was subjected to chlorination according to the procedure for compound **8**. The crude product was recrystallized from hexane (0.41 g, M.P. 137 ^{o}C).

^{1}H-NMR: δ 7.45 (s) ^{13}C NMR δ 121.1, 127.2, 160.4, 161.45, 161.51, 162.2, 163.8.

Calcd for $C_8HCl_5N_4$ C, 29.08; H, 0.31; N, 16.96; Found: C 29.18, H 0.26, N 16.91.

Crystal data see ref 6.

Computation details:

The isodesmic (i.e., bond-conserving) reactions[7] shown below, where n = 0,1,2,3, were used to compute the heats of formation. The density functional theory methods in the GAMESS [8] quantum chemistry code were used to calculate the isodesmic reaction enthalpies, using the form of the hybrid B3LYP functional [9] containing the VWN5 correlation functional [10], and the 6-311G(d,p) basis set.[11] The reaction enthalpies thus obtained were combined with experimental heats of formation of the smaller "reference" molecules in the reaction to obtain theoretical heats of formation for **7**, **9**, **11**, and **14,** following procedures described in more detail elsewhere.[12] In those instances in which experimental heats of formation for the reference compounds are lacking, these values were computed using the Gaussian-2[G2] method[13] or its G2(MP2) variant[14] in the Gaussian03 program suite.[15]

Scheme 2. isodesmic reactions used for calculation of polyazides.

Table 2. Heats of formation of isodesmic reference compounds.

Compd	$\Delta_f H^0_{298}$ (kJ mol^{-1})
CH_4	-74.87[a]
CH_3N_3	296.5 [b]
CH_3CH_3	-83.8 [c]
$CH_3CH_2N_3$	266.9 [d]
$CH_3CH(N_3)_2$	603.8 [d]
$CH_3C(N_3)_3$	927.2 [d]
$C_4N_2H_4$	195.8 [e]

[a] Ref. 16, [b] This work, obtained using G2 method. [c] Ref. 17; [d] This work, obtained using G2(MP2) method. [e] Ref 18.

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6. Crystal data for pentachlorodipyrimidine: $C_8HCl_5N_4$, M_r = 330.38, T = 89(2) K, Cc, a = 8.5556(15), b = 21.272(5), c = 7.3967(13) Å, β = 119.441(2)°, V = 1172.3(4) Å^3, Z = 4, ρ_{calcd} = 1.872 Mg/m^3, μ = 1.215 mm^{-1}, reflections collected / unique 8499 / 2117, R_{int} = 0.0194, Flack = -0.02(5), R_1 = 0.0224, wR_2 = 0.0587 ($I > 2\sigma(I)$), GOF = 1.081, Crystal Size = 0.28 x 0.17 x 0.08 mm^3, $2\theta_{max}$ = 50.5°. Data were collected on a Bruker SMART APEX (Mo Kα, λ = 0.71073Å) with a Cryocool NeverIce Low Temperature device, using omega scans of 0.3° per frame for 20 seconds. 2400 frames were collected. CCDC-612109 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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