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Supporting Information

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Polyazido Pyrimidines: High Energy Compounds and Precursors to Carbon Nanotubes

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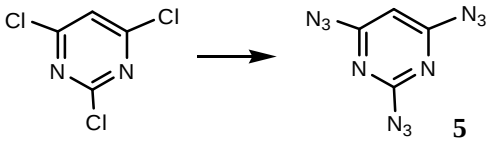
Caution! ***On the basis of the high positive heats of formation, all polyazido products must be handled with extreme care. Plastic spatulas, leather gloves and face shields should be used at all times, especially when handling compound 8 which decomposed violently when it was transferred at the 0.5 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.



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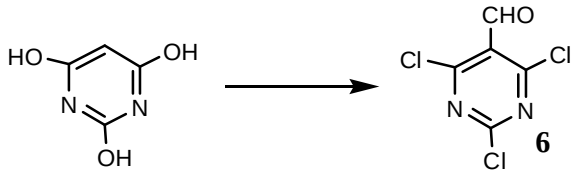
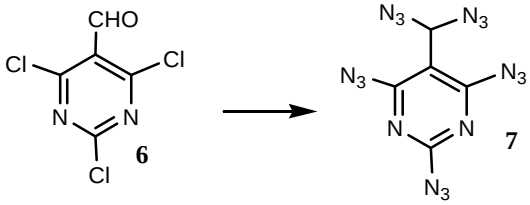
2,4,6-triazidopyrimidine (5*)*. To a solution of trichloropyrimidine (5.0 g, 27 mmol) in 30 mL dry acetone was added NaN_3 (6.0 g, 92.3 mmol), the mixture was stirred at room temperature for 6 hours, 50 mL CH_2Cl_2 was added, the solid was filtered off was washed with CH_2Cl_2 (5 mL), The organic phase was combined and solvent was removed under reduced pressure, recrystallized from methanol or hexane. White solid, (5.0 g, 91%), m.p. 98 ^{o}C. ^{1}H NMRδ5.96 (s, 1H), ^{13}C NMR δ93.9, 161.2, 164.6.

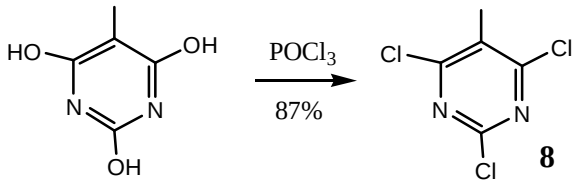


5-Carboxyaldehyde-2,4,6-trichloropyrimidine (6).[1] Barbituric acid (6.0 g) was added to a mixture of $POCl_3$ (15 mL) and N,N-dimethylformamide (3 mL). The solution was refluxed for 8 h, cooled to room temperature, poured into ice-water, and extracted with ethyl acetate three times (50 mL). The organic 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 NMRδ10.39 (s), ^{13}C NMR δ122.9, 161.4, 163.9, 184.5.

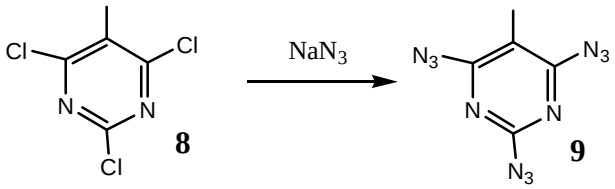


5,5-Diazidomethyl-2,4,6-triazido-pyrimidine (**7**). 0.8 g 5-carboxyaldehyde-2,4,6-trichloropyrimidine (**6**) and NaN_3 (0.9 g) were placed in a 50 mL flask, 25 mL dry THF was added, and the mixture was stirred for 6 h at room temperature. The solid was filtered off and washed with 5 mL CH_2Cl_2. The 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 ^{o}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

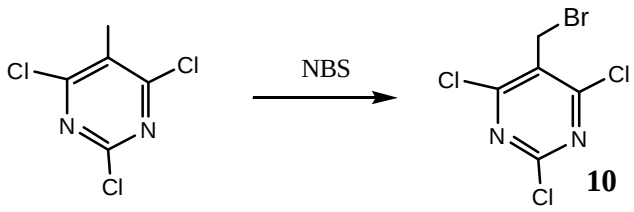
NMRd 6.02(s), ^{13}C NMR d69.3, 102.2, 161.2, 162.6. MS (EI), 257 (M^+-N_3), HRMS-FAB: $C_5H_2N_{17}$ $(M+H)^+$, Calcd 300.0679; Found 300.0665.



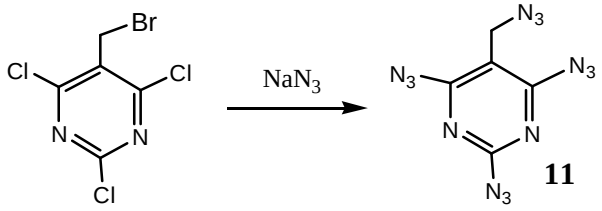
2,4,6-Trichloro-5-methyl-pyrimidine (8):[2] To a solution containing 4.4 g 5-methyl-barbituric acid in 15 mL $POCl_3$, was added 2.0 mL N,N-dimethylaniline . The mixture was refluxed overnight, cooled to room temperature, poured into ice, and then extracted with CH_2Cl_2. After removal of the solvent, the residue was purified by sublimation under vacuum (white solid, 5.3 g, 87%, M.P. 68-69 ^{o}C).



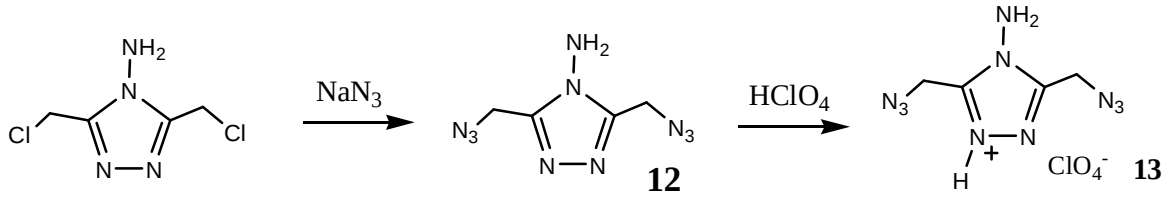
5-Methyl-2,4,6-triazido-pyrimidine (**9**): 2,4,6-Trichloro-5-methyl-pyrimidine (**8**) (0.4 g) and 0.6 g NaN_3 were placed in a 50 mL flask, and 25 mL THF was added followed by addition of 0.1 g TBAB. The mixture was stirred overnight at room temperature. The solid was filtered and washed with 5 mL 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 d1.92 (s); ^{13}C NMR d 9.1, 104.5, 158.1, 162.2. HRMS Calcd for $C_5H_3N_{11}^+$ 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 ^{o}C (M.P.132 ^{o}C; lit 133-134 ^{o}C;[3] 1.58 g, 90%). ^{1}H NMR d 4.61 (s); ^{13}C NMR d 23.6, 127.7, 158.4, 162.6.

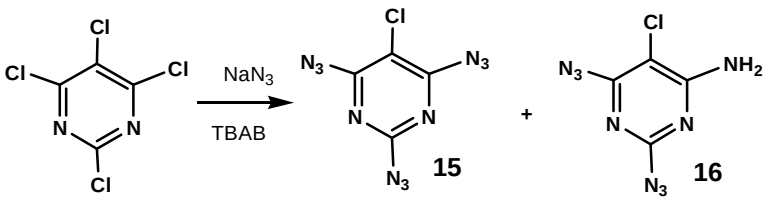


5-Azidomethyl-2-4-6-triazido-pyrimidine (**11):** A mixture of 5-bromomethyl-2,4,6-trichloropyrimidine (**10)** (0.2 g) and NaN_3 (0.4 g) in 15 mL THF was stirred at room temperature overnight. The solid was filtered and washed with 5 mL THF, the organic phase was combined and the solvent removed to leave a colorless oil (0.18 g, 99%). It solidified on standing in the refrigerator to give (**11**) (M.P. 22.5 ^{o}C). ^{1}H NMR d 4.18 (s), ^{13}C NMR d43.0, 102.4, 160.6, 163.5. HRMS $C_5H_2N_{14}^{+}$, 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 ^{o}C, 0.19g, 89%.) ^{1}H NMR (CD_3CN) d 4.55 (s, 4H), 5.34 (s, 2H), ^{13}C NMR (CD_3CN) d 44.2, 152.8. MS (EI), 194 (M^+, 100), (152, M^+-N_3). Calcd for $C_4H_6N_{10}$ C, 24.74; H, 3.11; N, 72.14; Found: C, 24.94; H, 3.01; N, 71.84.

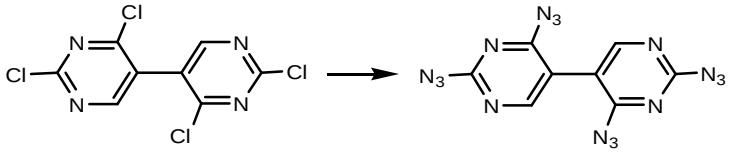
4-Amino-3,5-diazidomethyl-1-H-1,2,4-triazolium perchlorate (13): 4-Amino-3,5-bis(azido)-4H-1,2,4-triazole (**12**) (0.15 g) and perchloric acid (0.13 g, 60%) were dissolved in methanol, and stirred for 4 h. After removing the solvent, the residue was dried under vacuum overnight to leave a solid (**13**) (M.P. 74 ^{o}C). ^{1}H NMR (DMSO-d_6) d 5.60 (s, 4H), ^{13}C NMR (DMSO-d_6) d 43.0, 152.8. Calcd for $C_4H_7ClN_{10}O_4 \cdot H_2O$, 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 ^oC, 55%). ^{13}C NMR d 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 ^oC, 21%). ^1H NMR (DMSO-d_6) d 3.54 (s, 2H); ^{13}C NMR (DMSO-d_6) d94.0, 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.



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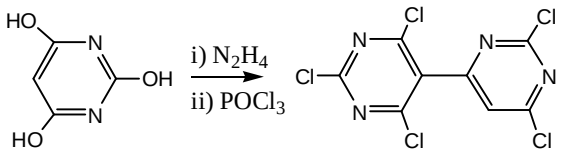
2,2',4,4'-Tetrazido-5,5'-bispyrimidine (17): A solution of 2,2',4,4'-tetrachloro-5,5'-bipyrimidine (0. 2 g)[5] and NaN_3 (0.25 g) in 20 mL THF was stirred at room temperature overnight. The solid was filtered and washed with 5 mL CH_2Cl_2. The combined filtrate was subjected to evaporation and the residue was recrystallized from methanol/chloroform to give needle crystals (0.19 g., 88%; M.P. 160 ^oC). ^1H-NMR: d 8.36 (s); ^{13}C NMR d 111.6, 160.2, 161.7, 161.8. HRMS Calcd for $C_8H_2N_{16}$ 322.0648; Found 322.0646.



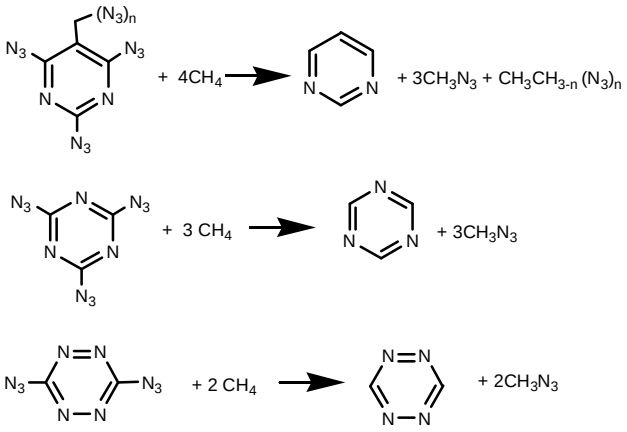
18

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•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: d7.45 (s) ^{13}C NMR d 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.

CCDC-612109 contains the supplementary crystallographic data. [6]

Computation details:

The isodesmic (i.e., bond-conserving) reactions[7] shown below (Scheme 1), 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 (Table 1).[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 1. Isodesmic reactions used for calculation of polyazides.

Table 1. 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]
pyrimidine	195.8 [e]
s-triazine	226.0 [f]
1,2,4,5-tetrazine	489.9 [g]

[a] Ref. 16; [b] This work, obtained using G2 method; [c] Ref. 17; [d] This work, obtained using G2(MP2) method; [e] Ref 18; [f] ref19; [g] ref 20.

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