# Polyazidopyrimidines: High-Energy Compounds and Precursors to Carbon Nanotubes**

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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^{-1} of endothermicity to a hydrocarbon compound.[1] In this family of compounds, 3,6-diazido-1,2,4,5-tetrazine (**1**) has the highest reported heat of formation, about 1101 kJ mol^{-1} (6709 kJ kg^{-1}).[2] The compound 4,4′,6,6′-tetraazido-2,2′-azo-1,3,5-triazine (**2**) has a heat of formation of 2171 kJ mol^{-1} (6164 kJ kg^{-1}; Scheme 1).[3] Recently it was demonstrated that **1** and **2** are good precursors to carbon nitride nanomaterials. Thermal decomposition of **1**[4] and **2**[5] yields nitrogen-rich nanolayered,
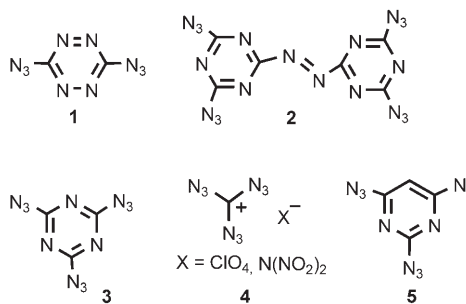
Scheme 1. Examples of reported polyazido compounds.

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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, including tetrazine (as in **1**),[4] triazine (as in **3**),[6] heptazine,[7] triazole,[8] and tetrazole[9], and inorganic anions, including $[P(N_3)_6]^-$,[10] $[B(N_3)_4]^-$,[11] $[Si(N_3)_6]^{2-}$,[12] $[Te(N_3)_5]^-$,[13] $[Ti(N_3)_5]^-$,[14] $[Sb(N_3)_6]^-$,[15] and $[U(N_3)_7]^{3-}$,[16] as well as triazidocarbenium perchlorate and dinitramide (**4**; Scheme 1).[1] Few reports focus on pyrimidine as a basic building block. Although 2,4,6-triazidopyrimidine (**5**) has been known since 1979,[17] it has mainly been used for photochemical reactions. Few physical properties of this compound are known.

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

Currently, except for the triazidocarbon cation in **4**,[1] molecules with three or four azido groups on the same carbon atom have not been available because of their instability, high sensitivity, and difficulty in synthesis. Only a few geminal diazido compounds have been prepared from the $SnCl_2$- or $ZnCl_2$-catalyzed reaction of substituted benzaldehyde or acetophenone with $TMSN_3$.[18] However, heterocycles based on geminal diazido compounds have not been reported. We have prepared pentaazidopyrimidine **7** starting from 5-carboxyaldehyde-2,4,6-triazidopyrimidine (**6**; Scheme 2). The best yield of 35% could be achieved by first substituting the three chlorine atoms on the pyrimidine ring with azido groups and subsequently transforming the aldehyde group into a geminal diazido functionality by using $TMSN_3/SnCl_2$. Remarkably, this pentaazido compound is a liquid at room temperature with a melting point at about −48°C and has good thermal stability up to about 179°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, extreme care is absolutely necessary!

For purposes of comparison, triazido- and tetraazidopyrimidine derivatives **9** and **11** were prepared as outlined in Scheme 2. The solid-state structures of these two compounds were established by single-crystal X-ray analysis (Figure 1).[19]
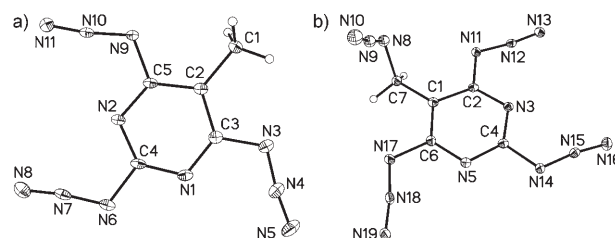

Figure 1. Thermal ellipsoid plot (ellipsoids at 30% probability) of **9** (a) and **11** (b). Hydrogen atoms have been included but not labelled.

Compound **9** is planar and packs in layers, in a fashion similar to the packing of **3**.[6a] However, in **9** the molecules have significant overlap with the adjacent layer. The layers are also farther 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. 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 about 3.26 Å at the maximum separation with 10° angles between the heterocycles. There are also weak nonclassical hydrogen bonds between the methylene group and terminal azido nitrogen atoms, both within the stacks (C7–N13, ca. 3.31 Å) and between the stacks (C7–N19, ca. 3.41 Å). This compound was difficult to crystallize and exhibits disorder in the azidomethyl group as well as rotational twinning.[19]

The melting point of the triazido analogue **9** is 103°C, while the addition of one extra azido group reduces the melting point drastically by about 80°C to 22.5°C in **11** (Table 1). The introduction of this fourth azido group does not result in any obvious decrease in thermal stability. The presence of a fifth azido group in **7** 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 (azidomethyl)pyrimidine compound is the inefficient packing caused by the azidomethyl group. The azido group in **11** is disordered (see above) and exhibits free rotation around
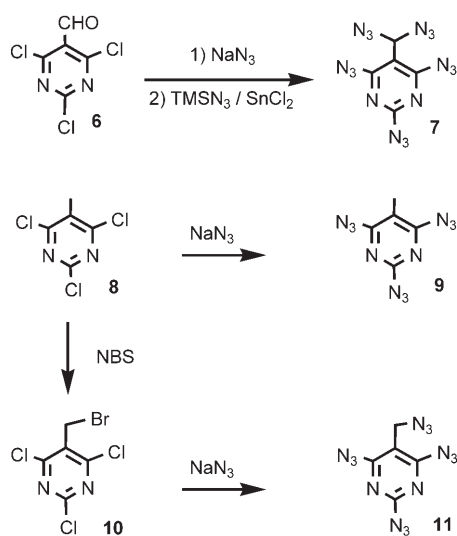
Scheme 2. Synthesis of polyazidopyrimidines; TMS = SiMe₃.

Table 1: Physical properties of polyazido compounds.

Compd.	Density [g cm⁻³]	M.p. [°C]	T_d (DSC) [°C]	$\Delta_f H°_{298}$[a] [kJ mol⁻¹]
1	1.72	130	130	1121.7[b]
3	1.72	94	180	1136.0[c]
7	1.71	−48	179	1807.1
9	1.55	103	195	1087.4
11	1.65	22.5	193	1452.7
12				2192.0

[a] Calculated value in the gas phase. [b] $\Delta_f H°_{298}$ (solid) = 1101 kJ mol⁻¹, reference [2]. [c] $\Delta_f H°_{298}$ (solid) = 1050 kJ mol⁻¹, reference [6b].

the methylene carbon atom C7. This phenomenon has also been confirmed with other examples; for example, 3,5-diazidomethyl-4-amino-triazole (m.p. 92°C) and its perchlorate salt (m.p. 75°C) have much lower melting points than 3,5-dimethyl-4-amino-triazole (m.p. 196°C)[20] and its perchlorate salt (m.p. 94°C; see the Supporting Information). Thus, introducing azidoalkyl groups could be an efficient way to reduce the melting point and increase the heat of formation, both of which are essential for the preparation of energetic ionic liquids.[21]

The heats of formation of **7**, **9**, **11**, and 5-triazidomethyl-2,4,6-triazidopyrimidine (**12**) were predicted using quantum chemical calculations (see the Supporting Information for computation details). The optimized geometries of pentaazidopyrimidine **7** and hexaazidopyrimidine **12** are shown in Figure 2; both geometries are proven to be at local minima in
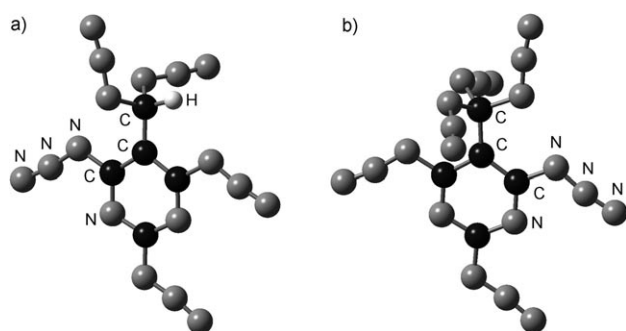

Figure 2. Optimized geometries at the B3LYP/6-311G(d,p) level of **7** (a) and **12** (b).

the potential-energy surface. The incremental contribution of each additional azido ligand to the heat of formation in the sequence **9→11**, **11→7**, and **7→12** is $+365$, $+354$, and $+385$ kJ mol^{-1}, respectively (Table 1). 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 n are $+351$, $+337$, and $+323$ kJ mol^{-1}, 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} (5764 kJ kg^{-1}), which would be the third-highest heat of formation reported for energetic materials, just lower than those of **2** (6164 kJ kg^{-1}) and **1** (6709 kJ kg^{-1}).

The formation of carbon nanotubes (CNTs) was investigated by catalytic detonation of the polyazidopyrimidines above. Since their discovery in 1990, CNTs have been shown to be extremely promising for applications in materials science and medicinal chemistry owing to interesting electronic, mechanical, and structural properties. Synthesis of nanomaterials on a large scale by detonation of explosive precursors is a new promising method owing to its 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 **3** by this detonation method in 1999,[22] but the yield was only about 2%. Optimization of the detonation conditions in the presence of transition metals, for example, Fe, Ni, Cu, and Ti, improved the yields to greater than 60%.[23]

Compound **3** is very detonation-sensitive, and its explosive nature increases with higher purity and crystal size.[6a] We found **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, for example, Cu powder, Cu(OAc)$_2$,[24] AgNO$_3$, and Ni(ClO$_4$)$_2$, we found that Ni(ClO$_4$)$_2$ was the best catalyst for the production of CNTs. The synthetic method is straightforward. Compound **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 the course of about 20 minutes. The vessel was then allowed to cool to room temperature. The product was observed as a fleecy, puffy, fiber-like black residue, which could easily be removed from the vessel with forceps. On touching with 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 ca. 3–20 μm, diameters ca. 60–80 nm and up to 100 nm; Figure 3). The yield of CNTs is estimated to be greater than 90%. They have a bamboo-like morphology (Figure 3c), and these "compartmentalized nanotubes" are segmented with a relatively uniform segment length of about 90 nm.
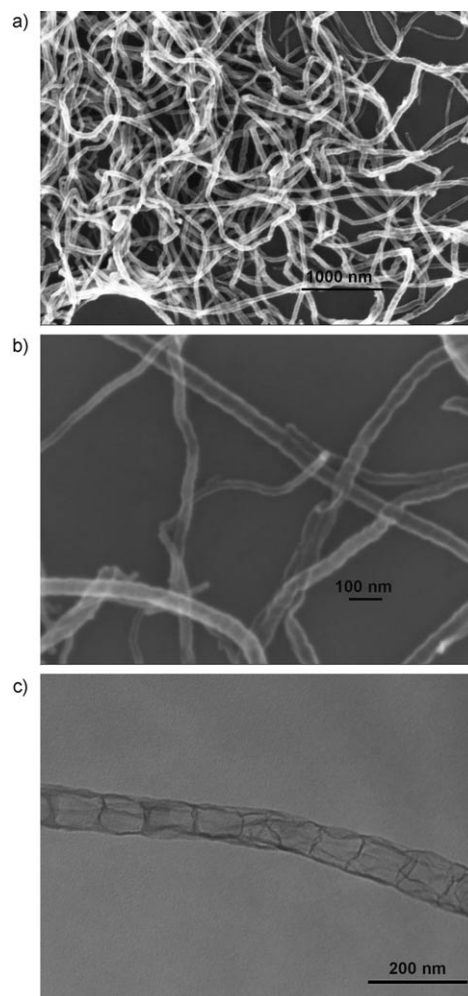

Figure 3. SEM (a, b) and TEM (c) images of CNTs generated by catalytic detonation of **5**.

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-Triazidopyrimidine was found to be a novel and less sensitive precursor for the formation of carbon nanotubes in high yields.

Caution! All polyazides must be handled with extreme care and with appropriate safety precautions.

[1] M. A. Petrie, J. A. Sheehy, J. A. Boatz, G. Rasul, G. K. S. Prakash, G. A. Olah, K. O. Christe, *J. Am. Chem. Soc.* **1997**, *119*, 8802–8808.

[2] M. H. V. Huynh, M. A. Hiskey, D. E. Chavez, D. L. Naud, R. D. Gilardi, *J. Am. Chem. Soc.* **2005**, *127*, 12537–12543.

[3] M. H. V. Huynh, M. A. Hiskey, E. L. Hartline, D. P. Montoya, R. Gilardi, *Angew. Chem.* **2004**, *116*, 5032–5036; *Angew. Chem. Int. Ed.* **2004**, *43*, 4924–4928.

[4] M. H. V. Huynh, M. A. Hiskey, J. G. Archuleta, E. L. Roemer, R. Gilardi, *Angew. Chem.* **2004**, *116*, 5776–5779; *Angew. Chem. Int. Ed.* **2004**, *43*, 5658–5661.

[5] M. H. V. Huynh, M. A. Hiskey, J. G. Archuleta, E. L. Roemer, *Angew. Chem.* **2005**, *117*, 747–749; *Angew. Chem. Int. Ed.* **2005**, *44*, 737–739.

[6] a) E. Kebenich, T. M. Klapötke, J. Knizek, H. Noth, A. Schulz, *Eur. J. Inorg. Chem.* **1998**, 2013–2016; b) E. G. Gillan, *Chem. Mater.* **2000**, *12*, 3906–3912.

[7] D. R. Miller, D. C. Swenson, E. G. Gillan, *J. Am. Chem. Soc.* **2004**, *126*, 5372–5373.

[8] H. Xue, Y. Gao, B. Twamley, J. M. Shreeve, *Chem. Mater.* **2005**, *17*, 191–198.

[9] A. Hammerl, T. M. Klapötke, *Inorg. Chem.* **2002**, *41*, 906–912.

[10] R. Haiges, S. Schneider, T. Schroer, K. O. Christe, *Angew. Chem.* **2004**, *116*, 5027–5032; *Angew. Chem. Int. Ed.* **2004**, *43*, 4919–4924.

[11] W. Frank, T. Habereder, A. Hammerl, T. M. Klapötke, B. Krumm, P. Mayer, H. Noth, M. Warchhold, *Inorg. Chem.* **2001**, *40*, 1334–1340.

[12] A. C. Filippou, P. Portius, G. Schnakenburg, *J. Am. Chem. Soc.* **2002**, *124*, 12396–12397.

[13] T. M. Klapötke, B. Krumm, P. Mayer, I. Schwab, *Angew. Chem.* **2003**, *115*, 6024–6026; *Angew. Chem. Int. Ed.* **2003**, *42*, 5843–5846.

[14] R. Haiges, J. A. Boatz, S. Schneider, T. Schroer, M. Yousufuddin, K. O. Christe, *Angew. Chem.* **2004**, *116*, 3210–3214; *Angew. Chem. Int. Ed.* **2004**, *43*, 3148–3152.

[15] R. Haiges, J. A. Boatz, A. Vij, V. Vij, M. Gerken, S. Schneider, T. Schroer, M. Yousufuddin, K. O. Christe, *Angew. Chem.* **2004**, *116*, 6844–6848; *Angew. Chem. Int. Ed.* **2004**, *43*, 6676–6680.

[16] M.-J. Crawford, A. Ellern, P. Mayer, *Angew. Chem.* **2005**, *117*, 8086–8090; *Angew. Chem. Int. Ed.* **2005**, *44*, 7874–7878.

[17] V. Y. Pochinok, L. F. Avramenko, A. V. Pochinok, P. A. Kondratenko, V. I. Nagornyi, T. P. Naidenova, N. P. Chibisova, *Ukr. Khim. Zh.* **1979**, *45*, 1074–1077.

[18] a) K. Nishiyama, T. Yamaguchi, *Synthesis* **1988**, 106–108; b) K. Nishiyama, M. Oba, A. Watanabe, *Tetrahedron* **1987**, *43*, 693–700.

[19] Crystal data for **9**: $C_5H_3N_{11}$, $M_r = 217.18$., $T = 89(2)$ K, monoclinic, space group $P21/c$, $a = 9.838(3)$, $b = 15.295(4)$, $c = 6.3070(16)$ Å, $\beta = 100.683(4)°$, $V = 932.5(4)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.547$ g cm^{-3}, $\mu = 0.118$ mm^{-1}, reflections collected/unique 13723/1690, $R1 = 0.0337$, $wR2 = 0.0932$ ($I > 2\sigma I$), GOF = 1.032. Crystal data for **11**: $C_5H_2N_{14}$, $M_r = 258.21$, $T = 89(2)$ K, monoclinic, space group $P21/a$, $a = 6.5156(14)$, $b = 22.149(5)$, $c = 7.2649(16)$ Å, $\beta = 97.540(4)°$, $V = 1039.3(4)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.650$ g cm^{-3}, $\mu = 0.128$ mm^{-1}, reflections collected/unique 27871/2123, $R1 = 0.0370$, $wR2 = 0.0936$ ($I > 2\sigma I$), GOF = 1.055, sample was rotationally twinned (179.8° about reciprocal (0,0,1) with a refined BASF of 0.252(3)), and the azidomethyl group was disordered 50%. CCDC-612107 and CCDC-612108 contain 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.

[20] P. C. Wade, B. R. Vogt, T. P. Kissick, L. M. Simpkins, D. M. Palmer, R. C. Millonig, *J. Med. Chem.* **1982**, *25*, 331–333.

[21] R. P. Singh, R. D. Verma, D. T. Meshri, J. M. Shreeve, *Angew. Chem.* **2006**, *118*, 3664–3682; *Angew. Chem. Int. Ed.* **2006**, *45*, 3584–3601.

[22] E. Kroke, M. Schwarz, *Adv. Mater.* **1999**, *11*, 158–161.

[23] T. Utschig, M. Schwarz, G. Miehe, E. Kroke, *Carbon* **2004**, *42*, 823–828.

[24] a) Y. Lu, Z. P. Zhu, W. Wu, Z. Y. Liu, *Chem. Commun.* **2002**, 2740–2741; b) Y. Lu, Z. P. Zhu, Z. Y. Liu, *Carbon* **2004**, *42*, 361–370.