

Tris(triazolo)benzene and Its Derivatives: High-Density Energetic Materials**

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The synthesis and development of new energetic materials continues to focus on new heterocyclic compounds with high densities, high heats of formation and good detonation properties. Also, in the preparation of energetic compounds, higher performance and lower sensitivity continue to be keen concerns.^[1] The need for high energetic materials continues to expand, of particular interest are nitrogen-rich compounds (e.g., azoles) in combination with energetic substituents such as nitro (NO₂), nitrato (ONO₂), and nitramine (NHNO₂) functionalities, since these compounds have satisfactory oxygen content.^[2] However, the requirements of insensitivity and high energy with concomitant positive oxygen balance are often contradictory to each other, making the development of new high energy density materials an interesting and challenging problem.^[3]

High-energy materials containing large numbers of nitrogen atoms, so called "high-nitrogen" compounds, have been shown to derive energy from the presence of many energetic N–N and C–N bonds.^[4] High energetic compounds which have polynitro groups are one of the important classes of useful energetic materials. Traditional polynitro compounds produce energy primarily from the combustion of the carbon backbone, while consuming the oxygen provided by the nitro groups.^[5] The presence of nitro groups tends to decrease the heat of formation, but contributes markedly to the overall energetic performance. Also, the nitro group enhances the oxygen balance and density, which improves the detonation performances (pressure and velocity).^[6] Ammonium perchlorate (AP) is the main oxidizer used in solid rocket fuels. Oxidizers provide the oxygen needed for oxidation of the fuel to provide the necessary thrust. The search for a smokeless propellant has encouraged scientists to look for chlorine-free oxidizers as a substitute for AP because it contributes to acid rain and ozone layer depletion, in addition to having

deleterious impacts on the human thyroid and being a persistent contaminant in ground water.^[7]

One recent focus in energetic materials research is the synthesis of fused cyclic nitrogen-containing heterocycles. Fused aza-cyclic compounds with ring strain energy could be used as high performance explosives when nitro and other energetic groups are present in the ring. Also, fused cyclic compounds exhibit good thermochemical and physical properties. Nitrogen aromatic heterocycles are insensitive energetic materials. The functionalization of fused heterocycles is more difficult than expected.^[8] High-nitrogen molecules play an important role in the design of new energetic compounds and their use as propellants, explosives and pyrotechnics. Among nitrogen heterocycles, the triazole ring is the one of the promising heterocyclic cores for the preparation of high-energetic materials. Triazole derivatives generally exhibit desired properties such as positive heat of formation, high density, and high nitrogen content together with low sensitivity towards external forces. Various heterocyclic systems have been studied in our group with growing interest.^[9]

Hypergolic fuel-oxidizer systems are important in rocket propellants. Hypergolicity is the spontaneous reaction of one chemical (fuel) when contacted with another (oxidizer).^[10] These self-ignition systems are of special importance in rocket propellants, since such fuel-oxidizer combinations simplify engine design and provide a convenient way of achieving repeated on-and-off capability at no extra cost. The fuel-oxidizers hypergolic systems have been widely used in biquid propellants. In propellant systems, the fuels of choice continue to be hydrazine and its derivatives and common oxidizers include HNO₃, N₂O₄, and H₂O₂. These hypergolic combinations require that a successful fuel has a high energy density per unit mass and a high specific impulse, and that there is a short ignition delay time. Unfortunately these oxidizing agents are extremely corrosive and moisture sensitive and long-time storage is problematic. Recently, there have been considerable developments in preparing hypergolic fuels, but not much change with oxidizers. Therefore, there is an urgent need for an alternative noncorrosive, hydrolytically stable hypergolic oxidizer, with high energy densities and short ignition delays.^[11]

In a continuing effort to seek more powerful, less sensitive, eco-friendly energetic materials, we are interested in fused heterocyclic compounds that contain a high percentage of both nitrogen and oxygen. Tris(triazolo)benzene could be such a type of molecule with three triazole units fused into one benzene ring; a ring system having the advantage of being rich in nitrogen, as well as having high thermal tolerance.^[12] In 1959, Muzik, et al. described the tris(alkyltriazolo)benzene ring system^[13] and in 1993, Samsonov, et al. reported the

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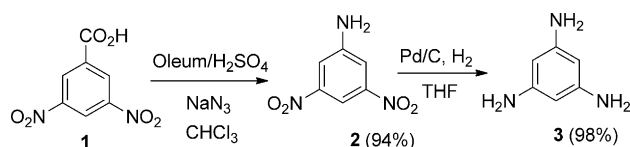
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[**] This work was supported by the Office of Naval Research (N00014-10-1-0097 to V.T. and J.M.S.; N00014-11-AF-0-0002 to D.A.P.).

Supporting information for this article is available on the WWW under <http://dx.doi.org/10.1002/ange.201205134>.

synthesis of unsubstituted tris(triazolo)benzene starting from 1,3,5-triaminobenzene trihydrochloride.^[14] However, in the recent literature, to the best of our knowledge there is no report related to the synthesis of tris(triazolo)benzene, none of its N-functionalized derivatives are known, and their utility as possible high-nitrogen energetic materials has not been explored. Herein, we report an improved synthesis of tris(triazolo)benzene and its derivatives from easily available starting materials, and their complete characterization as nitrogen-rich energetic materials.

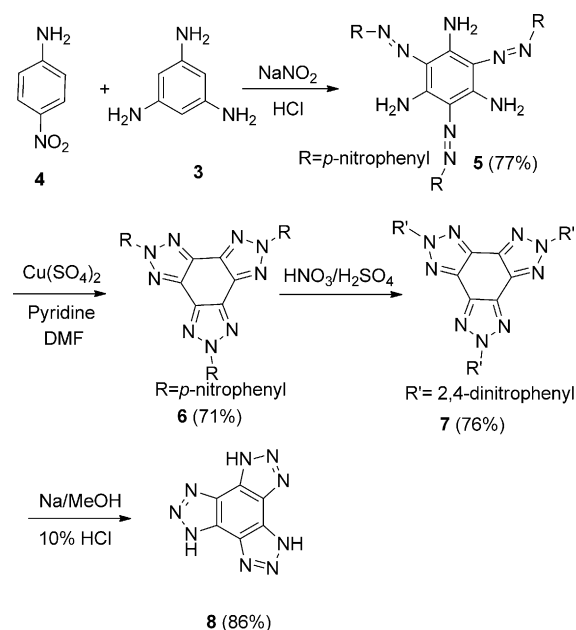
Since 1,3,5-triaminobenzene trihydrochloride is an expensive chemical, a short and high-yielding practical synthesis of triaminobenzene trihydrochloride using various starting materials was tried. The reaction of 3,5-dinitrobenzoic acid (**1**) with sodium azide under strongly acidic conditions produced a high yield (94 %) of 3,5-dinitroaniline (**2**). In this reaction, chloroform was a more useful solvent than dichloromethane. Pure 3,5-dinitroaniline was isolated and was hydrogenated in THF in the presence of 10 % Pd/C under an hydrogen atmosphere (5 atm), to produce 1,3,5-triaminobenzene (**3**) (Scheme 1).^[15]



Scheme 1. Synthesis of 1,3,5-triaminobenzene.

With pure 1,3,5-triaminobenzene in hand rather than making the trihydrochloride salt and subsequently neutralizing using pyridine before adding to diazotized aniline,^[13] we directly added **3** to the diazotized aniline derivatives, resulting in a good yield of diazotized product. Among anilines, *p*-nitroaniline produced the best results in the diazo-coupling reactions. *p*-Nitroaniline (**4**) was diazotized using NaNO₂ in conc. HCl added at ice cold temperature to produce the diazo-coupled product (**5**). Diazo compound **5** was cyclized using copper sulfate and pyridine to produce 2,5,8-tris(4-nitrophenyl)-tris(triazolo)benzene (**6**). Our attempts to deprotect the *p*-nitrophenyl group using sodium alkoxides failed. However, the *N*-2,4-dinitrophenyl group in azoles could be easily deprotected using sodium alkoxides. Therefore, the *p*-nitrophenyl derivative was nitrated to the corresponding dinitrophenyl compound using mixed acids nitration, to produce the best yield (76 %) at 45 °C. Treatment of 2,4-dinitrophenyl derivative **7** with sodium in methanol, followed by acidification produced tris(triazolo)benzene (**8**).^[14] With three equivalents of sodium in methanol, the product was obtained in low yield; while with excess (10 equiv) of sodium, **8** was produced in good yield (86 %) (Scheme 2).

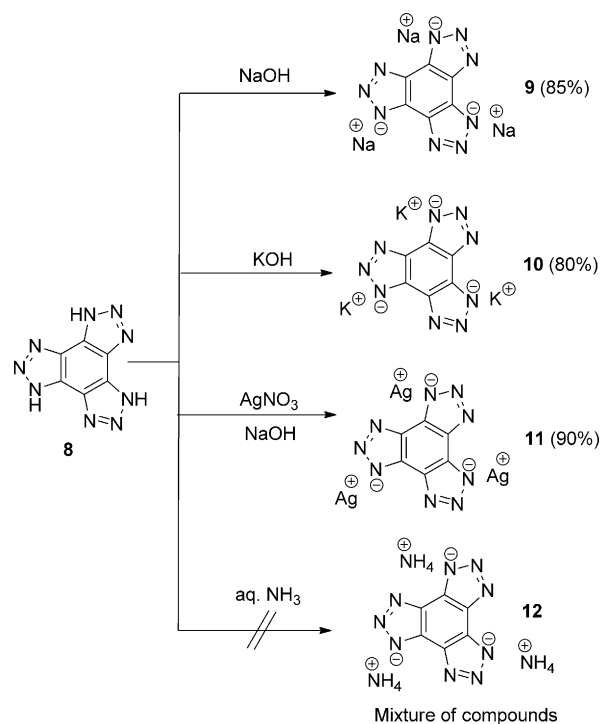
Trianionic metal salts of tris(triazolo)benzene have not been reported in the literature. When tris(triazolo)benzene was reacted with sodium hydroxide, trisodium salt **9** resulted. Similarly, the potassium salt **10** was obtained when **8** was reacted with potassium hydroxide. Silver salt (**11**) of tris-



Scheme 2. Synthesis of tris(triazolo)benzene from **3**.

(triazolo)benzene was prepared by treating the sodium (**9**) or potassium (**10**) salt with silver nitrate. Treatment of tris(triazolo)benzene with aqueous ammonia produced a mixture of compounds which were difficult to separate (Scheme 3).

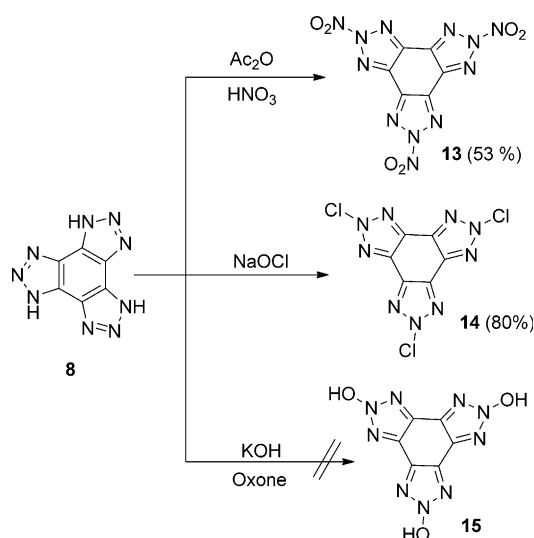
Trisubstituted derivatives of tris(triazolo)benzene such as trinitrotris(triazolo)benzene (**13**) could be interesting energetic materials. Nitration of **8** using 100 % HNO₃ did not produce the product with the starting material being recov-



Scheme 3. Metal salts of tris(triazolo)benzene.

ered. Nitration in mixed acids (HNO_3 and H_2SO_4) produced an unknown mixture of compounds. Finally, the nitration of tris(triazolo)benzene was successful in acetic anhydride and conc. HNO_3 to produce the pure trinitro derivative, **13**. Compound **13** is stable when stored in a refrigerator, but when stored at room temperature, after few days, the product decomposes producing an acidic smell. Since chlorobenzotriazole has many interesting properties, the trichloro derivative of **8** could be a very interesting molecule, and could have oxidation properties superior to *N*-chlorobenzotriazole.

Tris(triazolo)benzene was treated with sodium hypochlorite solution in acetic acid to give the pure trichloro derivative (**14**) (80%). When the potassium salt of tris(triazolo)benzene was treated with oxone, the trihydroxy derivative (**15**) was not produced (Scheme 4).



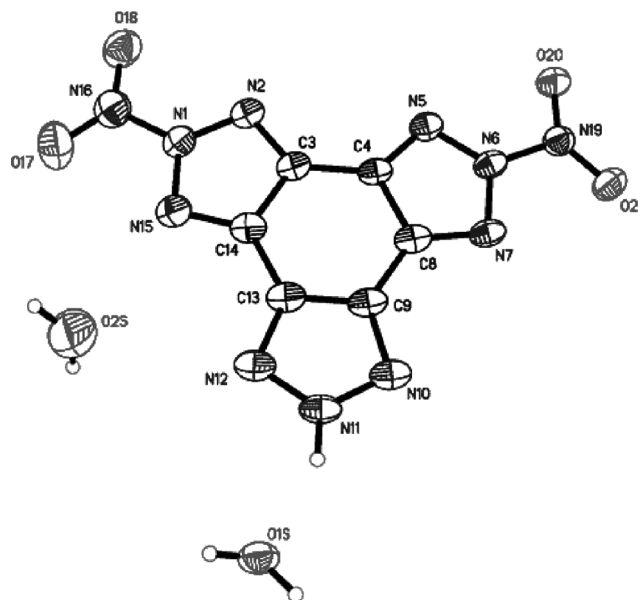
Scheme 4. N-Functionalization of tris(triazolo)benzene.

The structures of the tris(triazolo)benzene and its derivatives are supported by IR, ^1H , ^{13}C NMR and, in some cases, ^{15}N NMR spectroscopic data as well as elemental analysis (or high-resolution mass spectrometry, HRMS). The ^{13}C NMR spectra of **8** showed only a single peak at 132 ppm in $[\text{D}_6]\text{DMSO}$ (dimethylsulfoxide), which suggests that the hydrogen is shifting from the N1 to the N3 nitrogen atom of the triazole rings of tris(triazolo)benzene. All the salts of **8** showed two ^{13}C peaks which shows that the negative charge is on the N1 nitrogen. In the substituted triazoles **13** and **14** all the carbon atoms are equivalent; in the ^{13}C NMR spectrum only one carbon peak was observed, which indicates that substitution occurred on the middle nitrogen atom. The resonance bands appeared at 136 and 134 ppm, respectively. In case of metal salts **9** and **10** two ^{13}C peaks were observed, which confirms that the negative charge is on the nitrogen (N1) adjacent to the carbon (Scheme 3).

^{15}N NMR spectra of **7**, **8**, **10** and **13** are discussed here. In tris(triazolo)benzene (**8**) the N1/N3 signal appeared as a single peak at 81 ppm whereas N2 appeared at 30 ppm. For the 2,4-dinitrophenyl derivative (**7**), N2 appeared upfield to N1/N3 nitrogen. In case of the trinitro derivative **13**, the

N1/N3 and N2 peaks appeared at a close range around 70 ppm. Surprisingly in the case of metal salts **9** and **10**, the N1 and N3 nitrogen peaks appeared as a single peak upfield from N2 nitrogen.

To obtain a better understanding of N-substitution on the tris(triazolo)benzene, attempts to crystallize trinitro compound **13** in acetone/water at room temperature led to single crystals of bis(2-*N*-nitrotriazolo)triazolobenzene (**16**) suitable for X-ray structuring resulting from the decomposition of **13** (Figure 1). Compound **16** crystallizes in the monoclinic space



agent. Chloramines are used as disinfectants and antiseptics;^[17c] chlorotris(triazolo)benzene with three N–Cl bonds may be a very strong disinfectant and useful in water purification.

While trichlorotris(triazolo)benzene (**14**) has poor solubility in common organic solvents, it is more soluble in *N,N*-dimethylformamide. Surprisingly trichlorotris(triazolo)benzene (**14**) was found to be hypergolic when a drop of dimethylsulfoxide was added to the solid. Trichlorotris(triazolo)benzene (**14**) was also hypergolic with aniline, diethylenetriamine, and hydroxyethylethylenediamine, as well as with the commonly used fuels, hydrazine hydrate and monomethylhydrazine. To observe and measure actual ignition delay, a droplets test was selected because it is flexible, accurate, simply carried out, and very useful for screening materials and assessing their potential for hypergolic activity. A small amount of a fuel (hydrazine hydrate or monomethylhydrazine) sample (10–50 μL) was dropped into a glass vial containing an excess of **14**. A high-speed camera recording 500 frames per second was used to record the time duration from the moment the fuel contacted the surface of the oxidizer until the first sign of a visible flame—the ignition delay time. Chemical delay measurements show that **14** is a good hypergolic oxidizer with shorter ignition delay times with hydrazine hydrate (8 ms) and methylhydrazine (1 ms) compared to white fuming nitric acid (WFNA) (19 ms with hydrazine hydrate and 20 ms with methylhydrazine).^[18] Compound **14** is hydrolytically stable and might be considered as an alternative to traditional oxidizer WFNA in rocket propellant systems.

As shown in Table 1, the tris(triazolo)benzene and its derivatives exhibit energetic properties. Tris(triazolo)benzene derivatives **7**, **8**, **13**, and **14** exhibit positive heats of formation that are superior to those of trinitrotoluol (TNT) and pentaerythritol tetranitrate (PETN). The densities of these compounds are in the range of 1.69–1.94 g cm^{-3} which equals or exceeds that of common explosives. For sodium, potassium, and silver salts **9**, **10** and **11**, densities are in the range of 2.1–2.8 g cm^{-3} . Impact sensitivity measurements were made using

standard BAM Fallhammer techniques.^[19] For all of the compounds, the impact sensitivities range from those of the relatively less sensitive **7** (19.0 J) and **8** (18.0 J) to the very sensitive compound **13** (3.0 J). Thermal stabilities of the energetic compounds were determined with differential scanning calorimetry (DSC) at a scan rate of 5°C min^{-1} . Compound **7** decomposed at 400°C , whereas tris(triazolo)benzene (**8**) decomposed at 352°C . Sequential decomposition was observed for the trinitro derivative **13**; decomposition was initiated at 38°C , with the second decomposition at 161°C and finally the tris(triazolo)benzene core decomposed at 356°C . The trichloro derivative **14** decomposed at 207°C . Metal salts **9**, **10**, and **11** decomposed at 162, 283, and 391°C , respectively.

By using the calculated values of the heats of formation and the experimental values for the densities (gas pycnometer, 25°C) of the new tris(triazolo)benzene derivatives, the detonation pressures (P) and detonation velocities (D) were calculated based on traditional Chapman–Jouget thermodynamic detonation theory using Explo 5.05 (Table 1).^[20] The detonation pressures of tris(triazolo)benzene and its derivatives lie in the range $P = 19.41$ to 31.2 GPa (compared with TNT 19.53 GPa and PETN 31.39 GPa). Detonation velocities lie between $D = 6234$ and 8376 ms^{-1} (compared with TNT 6881 ms^{-1} and PETN 8564 ms^{-1}). The calculated properties coupled with the rather high thermal and hydrolytic stabilities suggest that these high-nitrogen materials may be attractive candidates for energetic applications.

In summary, tris(triazolo)benzene (**8**) was synthesized by using straightforward methods. Metal salts (**9**, **10** and **11**) and *N*-substituted nitro (**13**) and chloro (**14**) derivatives of **8** were synthesized in high yields. Their physical and detonation properties were determined. These tris(triazolo)benzene compounds were fully characterized by using IR and multinuclear ^1H , and ^{13}C NMR (some cases ^{15}N NMR) spectroscopy, and elemental analysis (or HRMS). A single-crystal X-ray structure of dinitrotris(triazolo)benzene (**16**) was obtained. Trichloro derivative **14** oxidized alcohols to aldehydes thus demonstrating some interesting properties. Also, **14** was found to be a powerful hypergolic oxidizer with various commonly used fuels resulting in better ignition delay times than those compared to WFNA. These tris(triazolo)benzene compounds exhibit good physical and detonation properties, such as high thermal stabilities, high densities, high heats of formation, and moderate to good high detonation pressures and velocities. Calculated detonation values for these compounds are comparable to those of explosives such as TNT and PETN, which suggests that they might be of interest for future applications as environmentally friendly and high-performing nitrogen materials.

Received: June 30, 2012

Revised: August 1, 2012

Published online: September 3, 2012

Table 1: Physical properties of tris(triazolo)benzene derivatives compared with TNT and PETN.

Compd.	$T_{\text{dec.}}^{[a]}$ [$^\circ\text{C}$]	$d^{[b]}$ [g cm^{-3}]	$\Delta H_f^{[c]}$ [kJ g^{-1}]	$P^{[d]}$ [GPa]	$D^{[e]}$ [m s^{-1}]	$IS^{[f]}$ [J]	$OB^{[g]}$ [%]
7	400	1.69	695 (0.9)	19.85	7032	19.0	–92
8	356	1.77	463 (2.3)	19.41	7160	18.0	–107
9	162	2.10	–	–	–	7.5	–89
10	283	2.41	–	–	–	5.0	–76
11	391	2.80	–	–	–	3.5	–46
13	38	1.82	710 (2.1)	31.20	8376	3.0	–28
14	207	1.80	711 (2.3)	13.67	6234	5.0	–63
16	129	1.79	618 (2.1)	26.9	7946	5.5	–46
TNT	295	1.65	–67 (0.3)	19.53	6881	15.0	–74
PETN	150	1.77	–407(0.4)	31.39	8564	4.0	5

[a] Thermal decomposition temperature under nitrogen gas (DSC, 5°C min^{-1}). [b] From gas pycnometer (25°C). [c] Heat of formation (calculated with Gaussian 03). [d] Calculated detonation pressure (Explo 5.05). [e] Calculated detonation velocity (Explo 5.05). [f] Impact sensitivity (BAM Drophammer). [g] Oxygen balance.

Keywords: detonation properties · energetic materials · nitrogen-rich compounds · triazoles

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