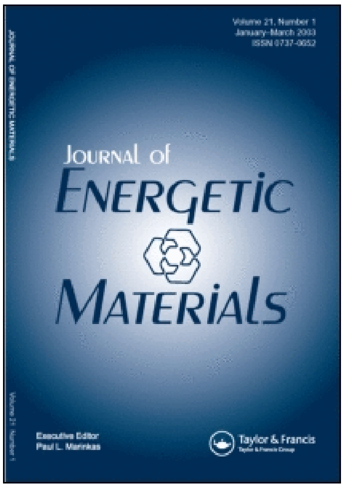

**Journal of Energetic Materials**
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713770432

# Synthesis of 3,6-bis(3-azido-1,2,4-triazol-1-yl)-1,2,4,5-tetrazine

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**To cite this Article** Chavez, David E. and Gilardi, Richard D.(2009) 'Synthesis of 3,6-bis(3-azido-1,2,4-triazol-1-yl)-1,2,4,5-tetrazine', Journal of Energetic Materials, 27: 2, 110 — 117
**To link to this Article: DOI:** 10.1080/07370650802405224
**URL:** http://dx.doi.org/10.1080/07370650802405224

*Journal of Energetic Materials*, 27: 110–117, 2009
ISSN: 0737-0652 print/1545-8822 online
DOI: 10.1080/07370650802405224

# Synthesis of 3,6-bis(3-azido-1,2,4-triazol-1-yl)-1,2,4,5-tetrazine

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*The synthesis of 3,6-bis(3-azido-1,2,4-triazol-1-yl)-1,2,4,5-tetrazine (**3**) (BATTz) is described. The physical and explosive sensitivity properties of this material were determined. The heat of formation was measured to be 1376 kJ/mol by combustion calorimetry. Additionally, X-ray crystallography confirmed the structure of this high-nitrogen primary explosive.*

**Keywords:** azido compounds, explosives, high-nitrogen

## Introduction

The discovery of novel heterocyclic materials with high nitrogen content continues to be a major focus of the energetic materials research performed at the Los Alamos National Laboratory. High-nitrogen materials continue to be an active area of research in the energetic materials arena [1–8]. Recently, we

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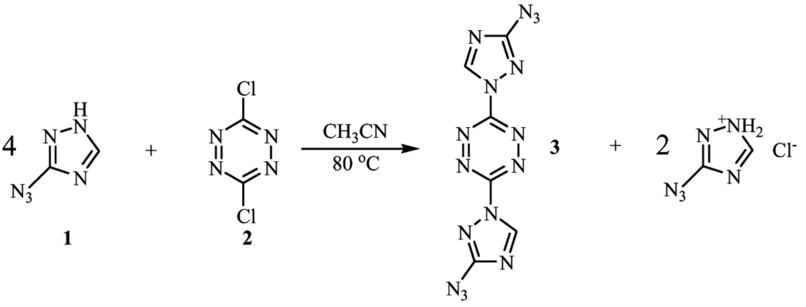
have described our efforts in the area of poly-azido-substituted heterocycles for applications in areas such as primary explosives and as precursors for the preparation of carbon and carbon nitride materials [9–12]. Here the preparation of a new azido-substituted high-nitrogen material is described.

3-azido-1,2,4-triazole (**1**) has been known in the literature since the 1960s. It was prepared by the diazotization of a 3-hydrazino-1,2,4-triazole [13]. Only recently was its preparation by diazotization of 3-amino-1,2,4-triazole reported. The heat of formation of 3-azido-1,2,4-triazole was determined to be 439 kJ/mol through combustion calorimetry [14]. Unfortunately, no description of its explosive sensitivity properties has been provided. 3-azido-1,2,4-triazole has been used as a precursor to several energetic materials, in part due to the dual acid and base nature of this material. For example, 3-azido-1,2,4-triazole is a strong enough base to form perchlorate and nitrate salts [15]. It is also sufficiently nucleophilic to react with alkylating reagents such as methyl iodide, derivatives of 3,5-dinitro-1,2,4-triazole, and other electrophiles [14]. This article describes the reaction of 3-azidotriazole with 3,6-dichloro-1,2,4,5-tetrazine (**2**) [16,17] and the sensitivity and crystal structure of the product 3,6-bis(3-azido-1,2,4-triazol-1-yl)-1,2,4,5-tetrazine (BATTz).

## Results and Discussion

The reaction of 3-azido-1,2,4-triazole with 3,6-dichloro-1,2,4,5-tetrazine has not been reported. In fact, there exist no examples of azido-substituted triazolyl-tetrazines in the literature. Due to the ability of 3-azido-1,2,4-triazole to act as a base and a nucleophile, it was perfectly suited as a reaction partner with 3,6-dichloro-1,2,4,5-tetrazine. As shown in Scheme 1, 4 equivalents of (**1**) was reacted with 1 equivalent of (**2**) in refluxing acetonitrile. After several hours, an orange product began to precipitate. Isolation and analysis of the precipitate showed that (**3**) was prepared in 67% yield. The material was subjected to a flame test and displayed a fast burn rate. Due to the high amount of nitrogen atoms in the molecule, (**3**) is likely an efficient gas generator.



**Scheme 1.** Synthesis of compound 3,6-bis(3-azido-1,2,4-triazol-1-yl)-1,2,4,5-tetrazine.

This material was then subjected to thermal and explosive sensitivity analyses. Differential scanning calorimetry showed that (**3**) begins to decompose at 172°C with a peak exotherm at 213°C and an energy release of 2000 J/g. A heat of formation for (**3**) was measured to be 329 kcal/mol or 4.62 kJ/g, which is an extremely large heat of formation. This value was determined experimentally using combustion calorimetry. Compound (**3**) was found to have an impact sensitivity value of 12.6 cm (LANL type 12, 2.5 kg weight, PETN = 12.4 cm). The friction sensitivity of (**3**) was measured to be 4.2 kg (BAM, PETN = 6.2 kg). The sensitivity of (**3**) toward electrostatic discharge was 10 positives results out of 13 at 0.25 J (PETN = 5 positives out of 13). Taken together, the small-scale sensitivity of (**3**) indicates that it behaves similarly to PETN.

The small sensitivity of (**1**) was also obtained for comparison. The data are provided in Table 1. 3-azido-1,2,4-triazole (**1**) is much more similar to RDX with respect to impact, spark, and friction. Thus, it appears that substituting (**1**) with the tetrazine ring leads to an overall increase in the sensitivity.

The CHEETAH 4.0 code was used to predict the explosive performance and specific impulse of (**1**). Using the experimentally determined values for the density and the heat of formation, a detonation velocity of 8.0 km/s and a detonation pressure of 24 GPa were predicted. The calculated specific impulse ($I_{SP}$) for the (**1**) was 222 s.

**Table 1**
Small-scale sensitivity for **1** and **3**

| | Impact (cm) | Friction (kg) | Spark (0.25 J) | DSC (°C) |
|---|---|---|---|---|
| **1** | 22.1 | 16 | 13 no go | 120 (mp) |
| **3** | 12.6 | 4.2 | 10/13 go | 172 (dec) |
| PETN | 12.4 | 6.4 | 5/12 go | 161 (dec) |

### *X-ray Crystallographic Analysis*

An X-ray crystal structure of (**3**) was obtained by growing crystals from acetonitrile or nitromethane (Figs. 1 and 2). X-ray crystallographic analysis proved the triazole ring system to be

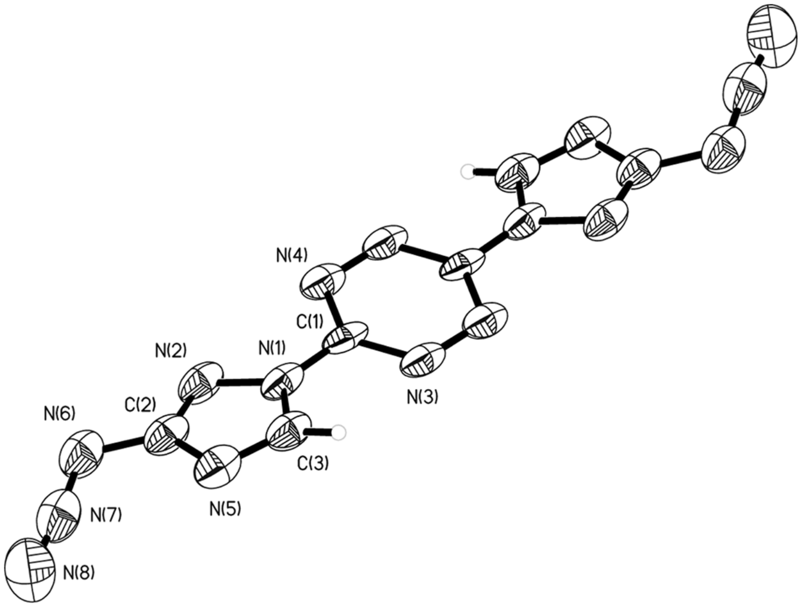


**Figure 1.** ORTEP of 3,6-bis(3-azido-triazol-1-l)-1,2,4,5-tetrazine (**3**). Results of X-ray analysis of LANL diazido sample. Since the molecule sits on a crystallographic center of symmetry, only half of the atoms, those labeled, were independently determined for this crystal form.

attached to the tetrazine at the 1 position of the 1,2,4-triazole ring. The density of (**3**) was measured to be 1.76 g/cm$^3$ and crystallized in the Pbca space group, with $a = 6.390(4)$, $b = 5.522(3)$, and $c = 31.930(18)$ Å, $V = 1126.6(11)$. One thousand one hundred forty-six independent data were collected and routinely solved and refined to $R = 0.056$.

## Experimental

### Synthesis

*3,6-bis(3-azido-triazol-1-yl)-1,2,4,5-tetrazine* (**3**). To a solution of (**1**) (1.10 g, 10 mmol) in acetonitrile (20 mL) was added (**2**) (0.38 g, 2.5 mmol). The reaction was then heated to reflux and stirred for 6 h with precipitation of an orange solid. The reaction mixture was then cooled to 23°C and allowed to stand for 2 h. The mixture was then filtered and washed with cold acetonitrile to give 2.0 g (67%). mp: 172°C (dec). IR (KBr) 3115, 2176, 2148, 1510, 1485, 1446, 1315, 1271, 1179 cm$^{-1}$. $^1$H NMR (deuteriomethylsulfoxide) $\delta$ 9.9 (s, 2H) ppm. $^{13}$C NMR (deuteriomethylsulfoxide) $\delta$ 147.15, 157.38, 160.93 ppm. Elemental analysis calculated for $C_6H_2N_{16}$: C, 24.17; H, 0.68; N, 75.16. Found: C, 24.14; H, 0.67; N, 75.18.

### Crystallography

$C_6H_2N_{16}$, FW = 298.24, Orthorhombic, Pbca, $a = 6.390(4)$ Å, $b = 5.522(3)$ Å, $c = 31.930(18)$ Å, $\alpha = 90°$, $\beta = 90°$, $\gamma = 90°$, $V = 1126.6(11)$ Å$^3$, Z = 4, $\rho_{calc} = 1.758$ Mg/m$^3$, $\mu = 0.136$ mm$^{-1}$, $F(000) = 600$, $R_1 = 0.0762$ for 935 observed ($I > 2\sigma I$) reflections and 0.0909 for all 1146 reflections, goodness-of-fit = 1.280, 105 parameters.

A thin orange plate of dimensions 0.80 × 0.70 × 0.01 mm$^2$ was mounted on glass fiber using a small amount of epoxy. Data were collected on a Bruker three-circle platform diffractometer equipped with a SMART 1000 CCD detector. The crystals were irradiated using graphite monochromated MoK$_\alpha$ radiation ($\lambda = 0.71073$). The crystal was collected at room temperature.

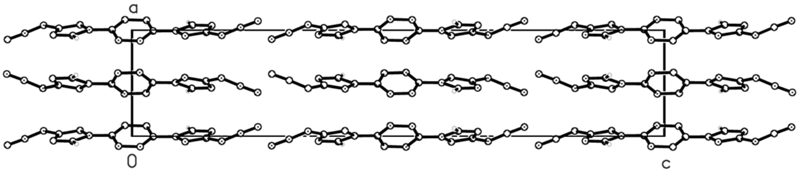


**Figure 2.** A view of the packing in the crystal. The molecules are not exactly planar but display twists of 10–15 degrees about the bonds connecting the triazole entities with the azido groups and the tetrazine ring.

Data collection was performed and the unit cell was initially refined using *SMART* [18]. Data reduction was performed using *SAINT* [19] and *XPREP* [20]. Corrections were applied for Lorentz, polarization, and absorption effects using *SADABS* [21]. The structure was solved and refined with the aid of the programs in the *SHELXTL-plus* system of programs [22]. The full-matrix least-squares refinement on $F^2$ included atomic coordinates and anisotropic thermal parameters for all non-H atoms. The H atoms were included using a riding model.

CCDC 689887 contains the supplementary crystallographic data for this article. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre [23].

## Conclusions

A new azido-substituted high-nitrogen material, 3,6-bis(3-azido-1,2,4-triazol-1-yl)-1,2,4,5-tetrazine (BATTz) has been synthesized from 3-azido-1,2,4-triazole and 3,6-dichloro-1,2,4,5-tetrazine. This material was found to have sensitivity very similar to PETN. The material has a very fast burn rate and may find uses as a sensitive gas generator.

## Acknowledgment

This work was supported by the DoD/DOE Joint Munitions Technology Development Program. The author also thanks Dennis Montoya for the sensitivity analysis, Lloyd Davis for the thermal analysis, and Stephanie Hagelberg for the elemental analyses. The Los Alamos National Laboratory is operated by Los Alamos National Security, LLC, for the DOE/NNSA.

## References

[1] Christe, K. O. 2007. Recent advances in the chemistry of N5$^+$, N5$^-$ and high oxygen compounds. *Propellants, Explosives, Pyrotechnics*, 32: 194.

[2] Schroer, T., R. Haiges, S. Schneider, and K. O. Christe. 2005. The race for the first generation of the pentazolate anion in solution is far from over. *Chemical Communications*, 12: 1607.

[3] Klapoetke, T. M. and C. M. Sabate. 2008. Bistetrazoles: Nitrogen-rich, high-performing, insensitive energetic compounds. *Chemistry of Materials*, 20: 3629.

[4] Darwich, C. T., M. Klapoetke, J. M. Welch, and M. Suceska. 2007. Synthesis and characterization of 3,4,5-triamino-1,2,4-triazolium 5-nitrotetrazolate. *Propellants, Explosives, Pyrotechnics*, 32: 235.

[5] Guo, Y., H. Gao, B. Twamley, and J. M. Shreeve. 2007. Energetic, nitrogen rich salts of N,N-bis[1(2)H-tetrazol-5-yl] amine. *Advanced Materials*, 19: 2884.

[6] Ye, C., H. Gao, J. A. Boatz, G. W. Drake, B. Twamley, and J. M. Shreeve. 2006. Polyazidopyrimidines: High energy compounds and precursors to carbon nantubes. *Angewandte Chemie International Edition*, 45: 7262.

[7] Wang, R., H. Gao, C. Ye, and J. M. Shreeve. 2007. Strategies toward triazolyl or triazolium-functionalized unsymmetrical energetic salts. *Chemistry of Materials*, 19: 144–152.

[8] Tyurin, A., A. M. Churakov, Y. A. Strelenko, M. O. Ratnikov, and V. A. Tartakovsky. 2006. Synthesis of first non-annulated 1,2,3,4-tetrazine 1,3-dioxides. *Russian Chemical Bulletin*, 55: 1648.

[9] Huynh, M. H. V., M. A. Hiskey, E. L. Hartline, D. P. Montoya, and R. D. Gilardi. 2004. Polyazido high nitrogen compounds: Hydrazo and azo-1,3,5-triazines. *Angewandte Chemie International Edition*, 43: 4924.

[10] Huynh, M. H. V., M. A. Hiskey, D. E. Chavez, D. L. Naud, and R. D. Gilardi. 2005. Synthesis, characterization and energetic properties of diazido heteroaromatic C−N compound. *Journal of the American Chemical Society*, 127: 12537.

[11] Huynh, M. H. V., M. A. Hiskey, J. G. Archuleta, and E. D. Roemer. 2005. Preparation of nitrogen-rich nanolayered, nanoclustered and nanodendritic carbon nitrides. *Angewandte Chemie International Edition*, 44: 737.

[12] Huynh, M. H. V., M. A. Hiskey, J. G. Archuleta, E. L. Roemer, and R. D. Gilardi. 2004. 3,6-Di(azido)-1,2,4,5-tetrazine: A precursor for the preparation of carbon nanospheres and nitrogen rich carbon nitride. *Angewandte Chemie International Edition*, 43: 5658.

[13] Denault, G. C., P. C. Marx, and H. H. Takimoto. 1968. Energy of combustion and differential thermograms of organic azides. *Journal of Chemical & Engineering Data*, 13: 514.

[14] Kofman, T. P. and K. N. Krasnov. 2004. Reactions o 3-azido-1,2,4-triazole with electrophiles. *Russian Journal of Organic Chemistry*, 40: 1651.

[15] Xue, H., Y. Gao, B. Twamley, and J. M. Shreeve. 2005. New energetic salts based on nitrogen containing heterocycles. *Chemistry of Materials*, 17: 191.

[16] Chavez, D. E. and M. A. Hiskey. 1999. 1,2,4,5-Tetrazine-based energetic materials. *Journal of Energetic Materials*, 17: 357.

[17] Helm, M. D., A. Plant, and J. P. A. Harrity. 2006. A novel approach to functionalized pyridazinone arrays. *Organic and Biomolecular Chemistry*, 4: 4278.

[18] Bruker. 2001. *SMART v5.625.* Madison, WI: Bruker AXS Inc.

[19] Bruker. 2002. *SAINT v6.45A.* Madison, WI: Bruker AXS Inc.

[20] Bruker. 2001. *XPREP v6.14.* Madison, WI: Bruker AXS Inc.

[21] Bruker. 2000. *SADABS v2.10*, Madison, WI: Bruker AXS Inc.

[22] Bruker. 2000. *SHELXTL v6.12.* Madison, WI: Bruker AXS Inc.

[23] Cambridge Crystallographic Data Centre. http://www.ccdc.cam.ac.uk/data_request/cif