



# Novel High Nitrogen Insensitive Energetic Materials

Presented at Workshop on  
“**Synthesis of Advanced Energetic Materials-  
The Path Forward**”

Inn and Conference Center on the  
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By  
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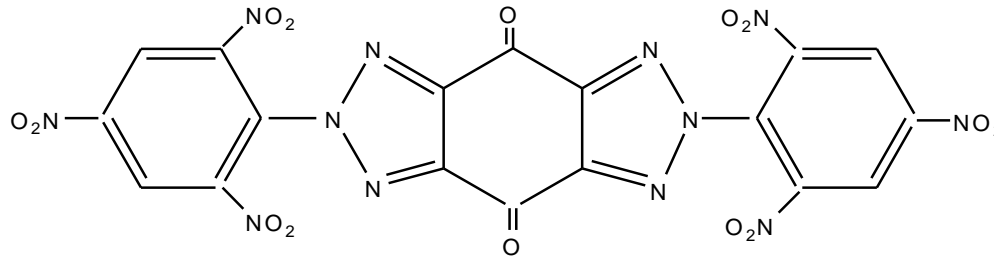


# Objective

The main objective is to develop energetic materials with high thermal stability and insensitivity to impact, friction, and electrostatic discharge.

# Background

Looking into the chemical literature indicates that there is inherent thermal stability in some ring systems such as dibenzotetraazapentalene (TACOT) and dipicrylbenzobistriazoledione.



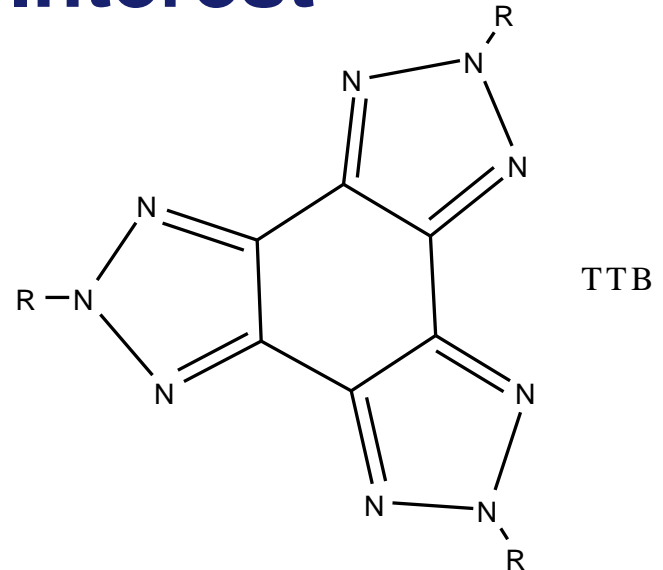
Dipicrylbenzobistriazoledione

mp = 430 °C

d = 1.80g/cc

## Compounds of Interest

Triazole units fused into one ring system. Such a ring system has the advantage of being rich in nitrogen content, as well as having high thermal tolerance.

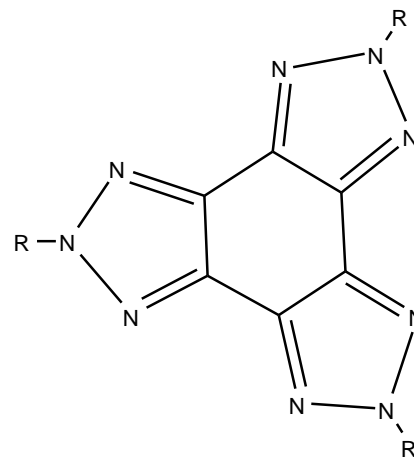


Where R is: Nitroimidazole, H, NO<sub>2</sub>, Nitroalkyl, etc.

# Holden Calculations

Holden calculation for some of the proposed molecules are listed below:

<u>R</u>	<u>Density(g/cc)</u>
NO <sub>2</sub>	2.00
Trinitroimidazole	2.00
Dinitroimidazole	1.98
F	1.98
H	1.76



# Literature Search

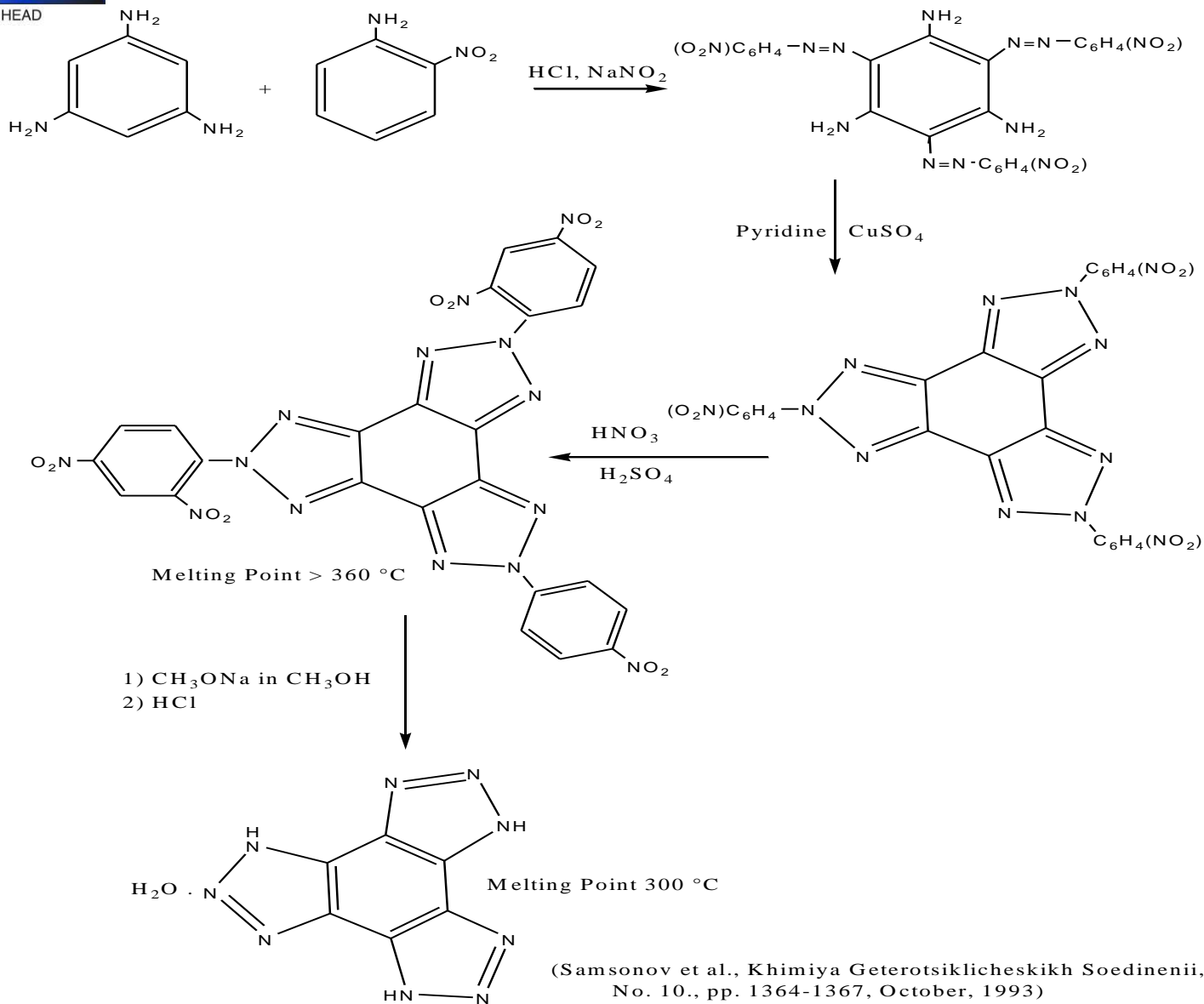
A 1952 article in a Czech. publication describes synthesis of tris(alkyltriazolo)benzene ring system.

*(Muzik, F., et al., Org. Res Inst., Czech, 1952, 46, 774).*

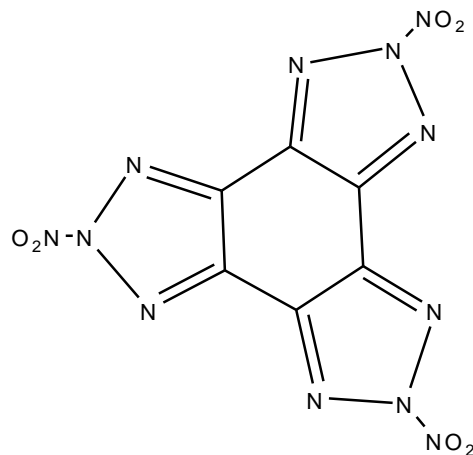
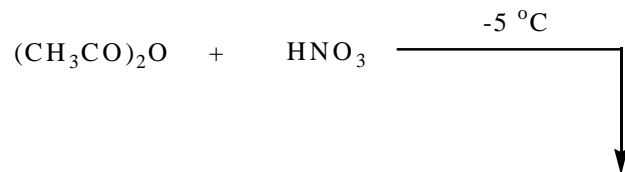
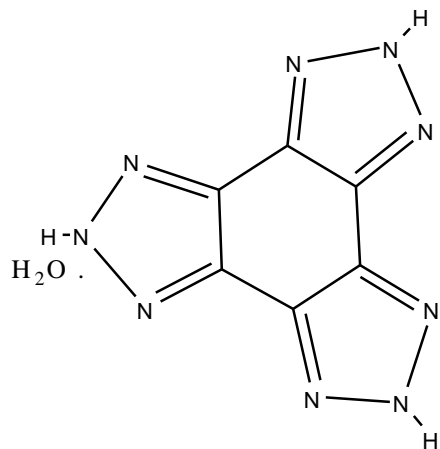
A 1993 Russian publication, by Samsonov et al., reports the synthesis of unsubstituted tris(triazolo)benzene.

*(Khimiya Geterotsiklicheskikh Soedinenii, No. 10., pp. 1364-1367, October, 1993).*

# Synthesis of Tris(triazolo)benzene



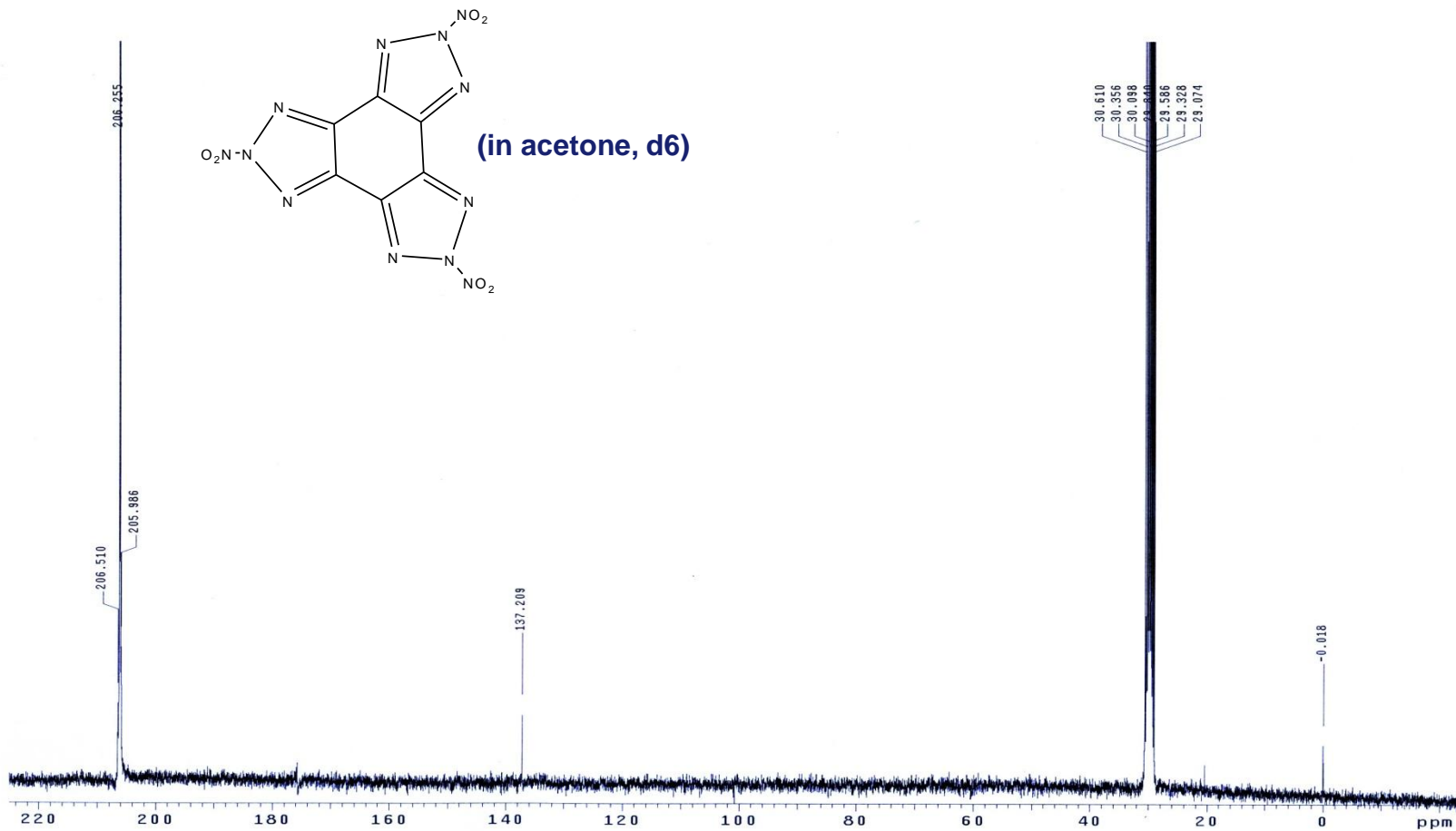
# Synthesis of Tris(nitrotriazolo)benzene, (TNTB)



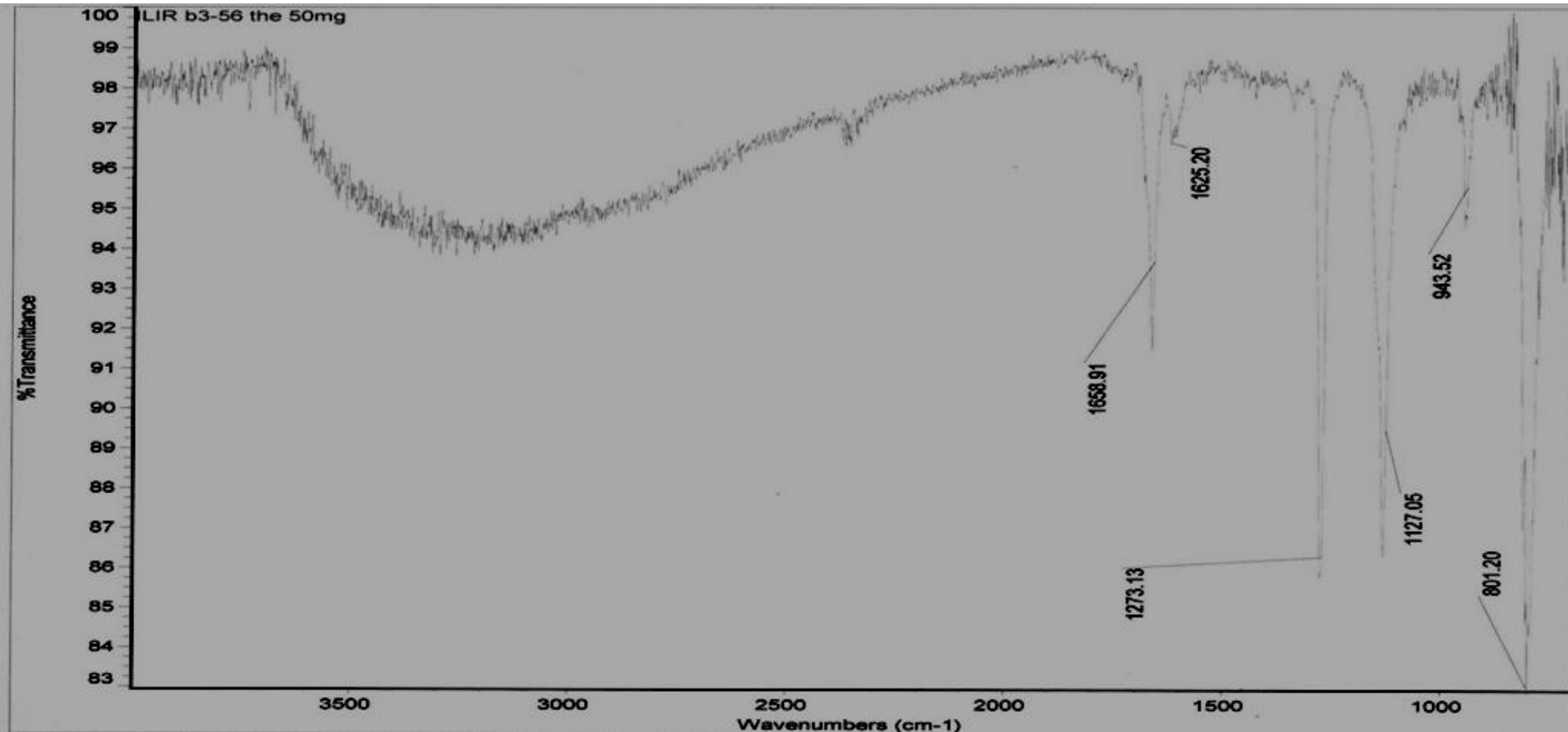
TNTB



# $^{13}\text{C}$ NMR of TNTB

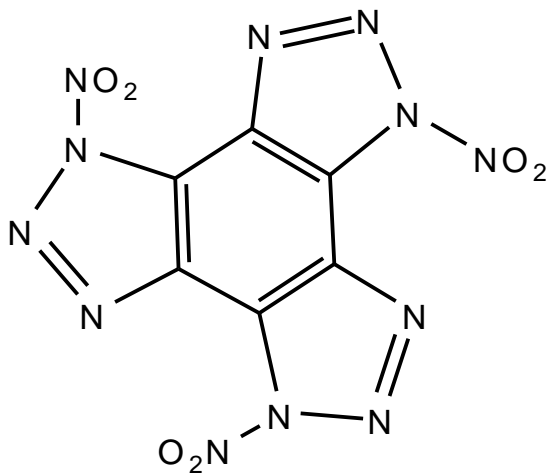


# IR of the Powder Form of TNTB

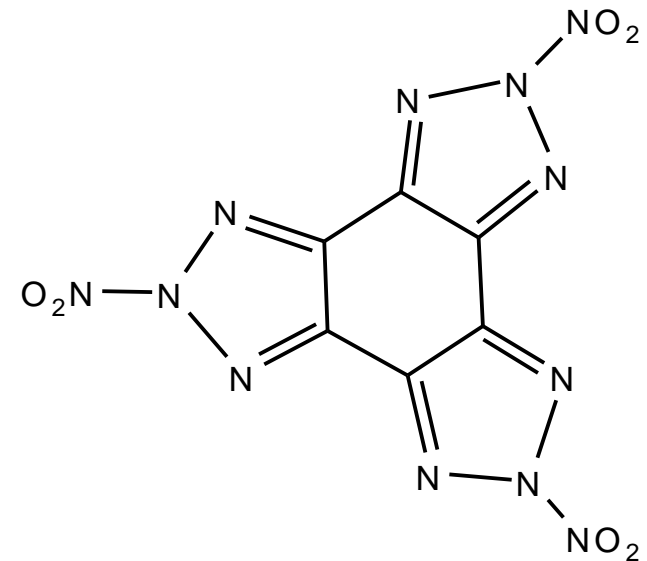


# TNTB Crystallization

TNTB crystallized out of acetone/water mixture.



Or

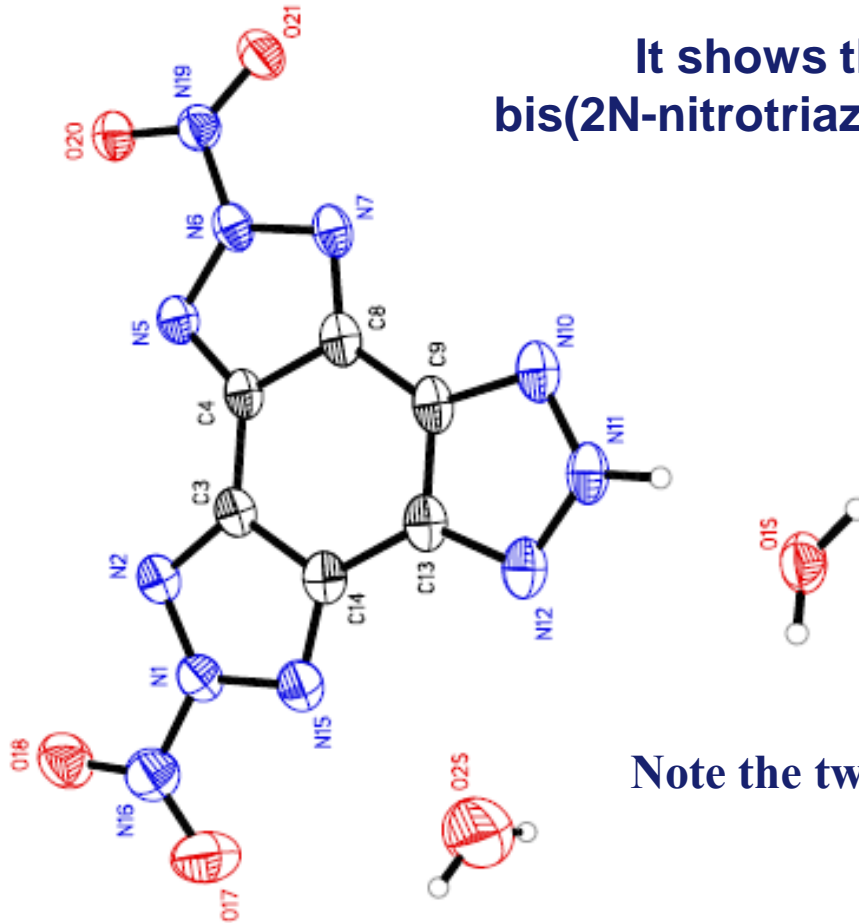


# Picture of the Crystals



# X-ray Crystallography

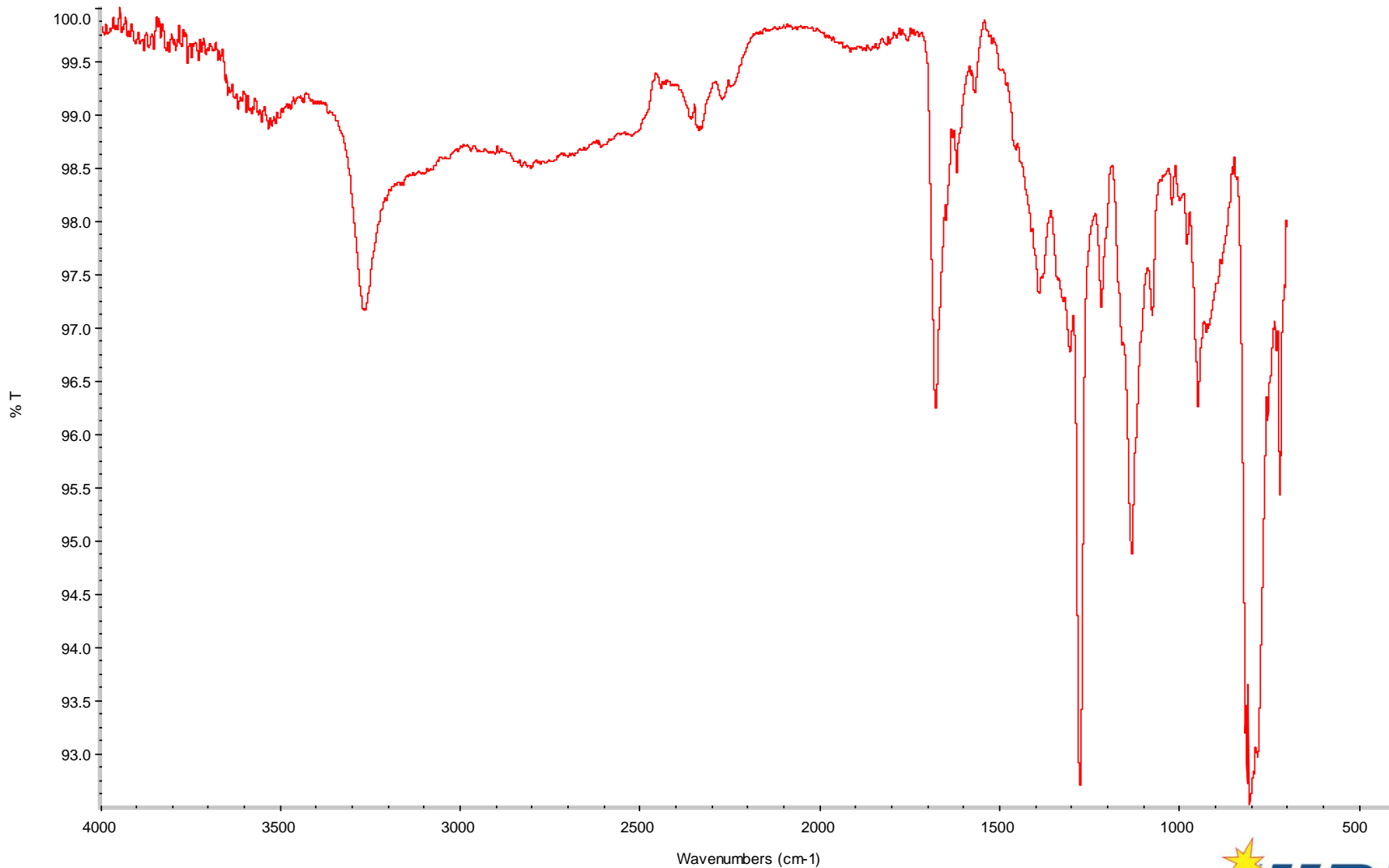
It shows the crystals are bis(2N-nitrotriazolo)triazolobenzene.



Note the two water molecules.

By Dr. Damon Parrish at NRL

# IR of Yellow Crystals



# What Happened?

**During crystallization decomposition takes place.**

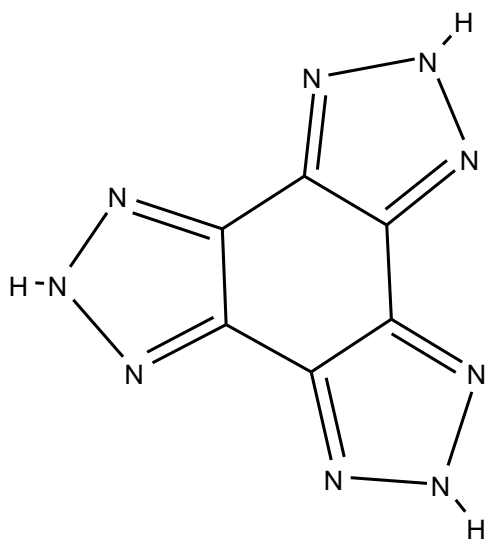
**When the powder or the crystal is kept in a closed vial, after a few days at room temperature a strong acidic smell develops.**

**The crystals are stable in the freezer.**

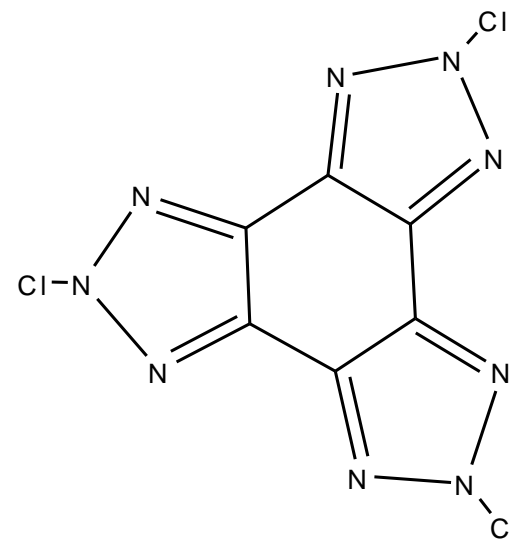
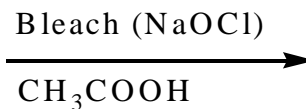
**Crystallization in the absence of water may form more stable crystals.**

# N-Chlorination of TTB

## An Intermediate for Further Reactions



**TTB**

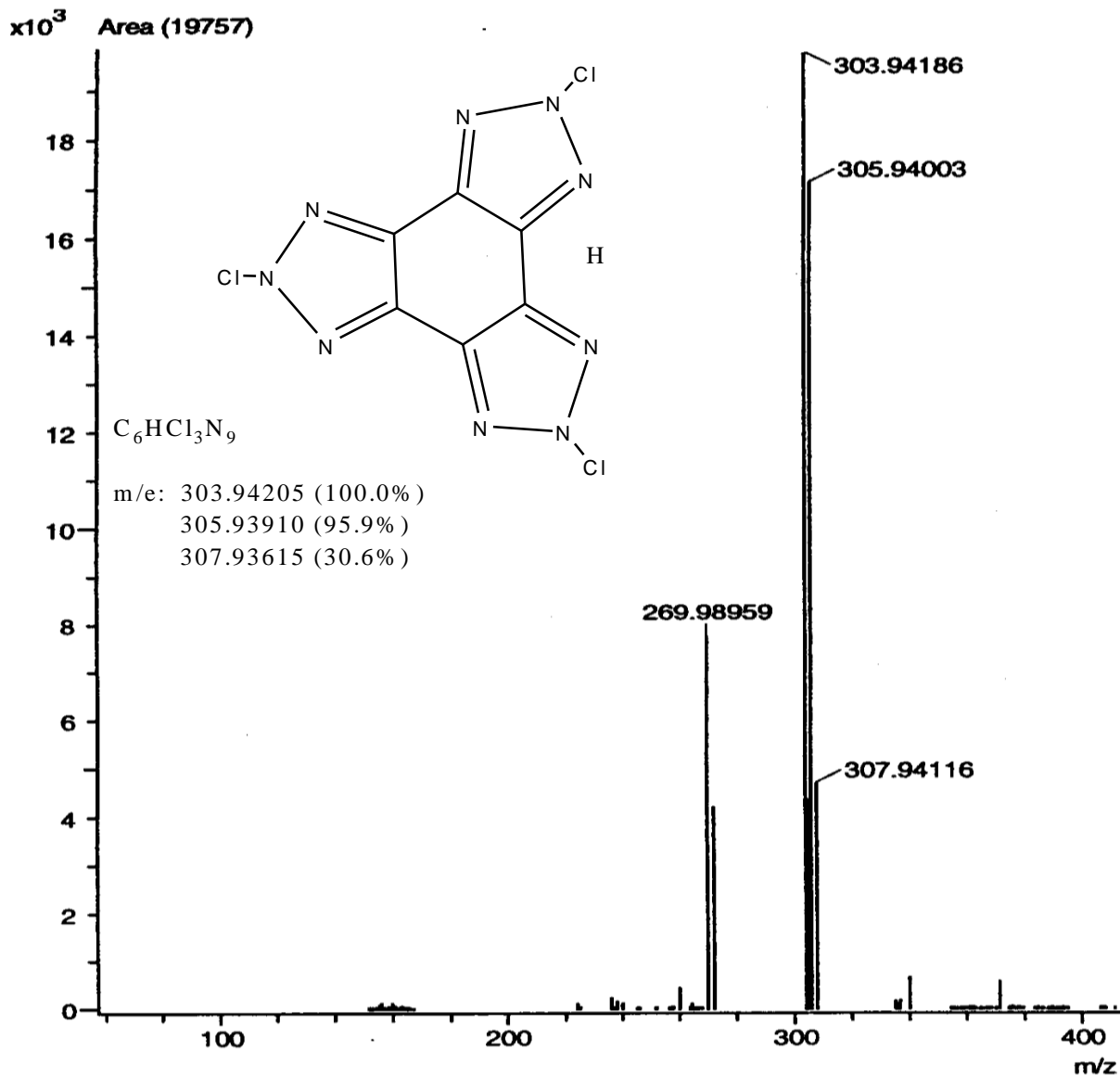


**TCTB**

**TCTB was found to be a very interesting molecule.**



# Mass Spectrum





# Some Properties of TCTB

Heat of formation (calculated by Joe Hooper at NSWCIHD to be 3900 kJ/kg) is 3.8 times higher than that of CL-20.

Holden calculation predicts a density of 1.94 g/cc.

Stable under ambient conditions. Rapidly decomposes at 211 °C.

Preliminary tests show it is not impact or friction sensitive.

It is a new oxidizer.

It is hypergolic with PRIMARY LIQUID amines such as: aniline, hydrazine, diethylenetriamine and hydroxyethylethylenediamine.



# Hypergolic with Hydrazine



# Hypergolic with Hydrazine Cont'd



# Hypergolic with Hydrazine Cont'd





# Potential Applications

An initiator. IRFNA (Inhibited Red Fuming Nitric Acid) is used in rocket propulsion. IRFNA is “extremely corrosive”.

An oxidizing agent.

A chlorinating agent.

N-chloramines are used for wastewater treatment, disinfectant in military kitchen services, and in dishwashing compositions.

By analogy it should be a stronger reagent than the commercially available N-chlorotriazolobenzene.





# 1-Chlorobenzotriazole Has Commercial Uses

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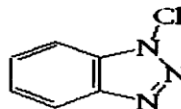
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## Product Details: 1-Chlorobenzotriazole (CBT)



Molecule: 1-Chlorobenzotriazole (CBT)  
Product Number: 1099  
CAS Number: [21050-95-3]

### Physical Properties


Chemical Formula: C<sub>6</sub>H<sub>4</sub>ClN<sub>3</sub>  
Mol. Wt.: 153.57  
Mp: 102-104°C  
Safety: Unique oxidizing and chlorinating agent

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<http://www.chemicalregister.com/1-Chlorobenzotriazole/Suppliers/pid107102.htm>

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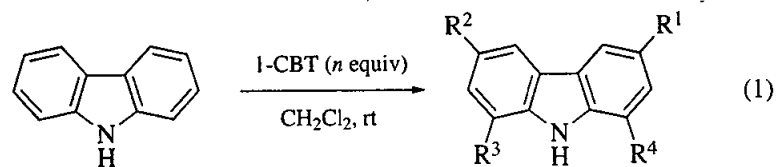
# 1-Chlorobenzotriazole Has Many Applications

**Table 1** Oxidation of Alcohols and Nitrogen Compounds by 1-Chlorobenzotriazole

Starting material	Solvent	Product	Yield (%)
Benzyl alcohol	CH <sub>2</sub> Cl <sub>2</sub>	Benzaldehyde <sup>a</sup>	70
1-Phenylethanol	CCl <sub>4</sub>	Acetophenone <sup>a</sup>	65
Cyclohexanol	CH <sub>2</sub> Cl <sub>2</sub>	Cyclohexanone <sup>a</sup>	70
Hydrazobenzene	CH <sub>2</sub> Cl <sub>2</sub>	Azobenzene	90
4,5-Diphenyl- pyrazolidin-3-one	CH <sub>2</sub> Cl <sub>2</sub>	<i>trans</i> -Stilbene	75
1-Aminobenzotriazole	CH <sub>2</sub> Cl <sub>2</sub>	Benzyne <sup>b</sup>	80

**Reaction with Sulfides.** Sulfides are efficiently oxidized to sulfoxides by 1-CBT in methanol or methylene chloride at -78 °C.<sup>3a</sup> The reaction is very fast and clean, giving no over-oxidation to sulfones as is often observed with peroxy acids (e.g. *m*-Chloroperbenzoic Acid). The performance of the reagent is comparable to *t*-butyl hypochlorite. This transformation has been used in the conversion of steroidal thioacetals to ketones.<sup>3b</sup> The intermediate formed between 1-CBT and sulfides

**Chlorination of Heteroaromatics.** Indoles and other nitrogen heterocycles are selectively chlorinated by 1-CBT in high yield. This procedure often succeeds where the standard reagent *t*-butyl hypochlorite fails.<sup>4</sup> Multiple equivalents of chlorine may be selectively incorporated simply by adjusting the initial amount of 1-CBT used (eq 1).<sup>4b</sup> The chlorination of some indoles is better effected by using 1-chloroisatin.<sup>4c</sup>



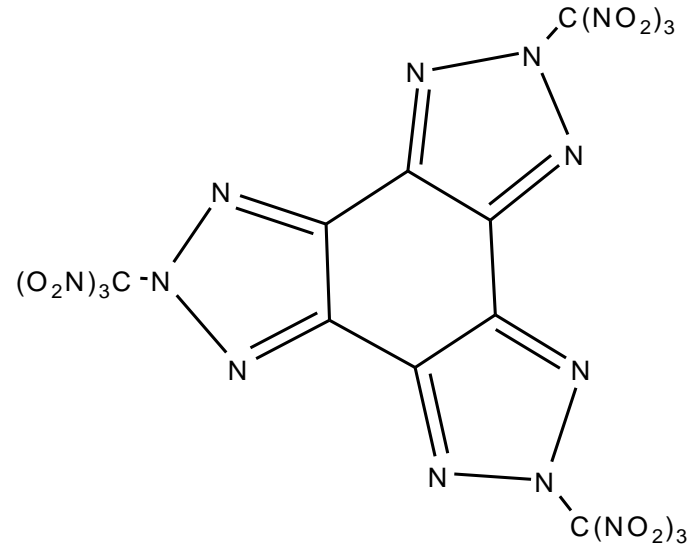
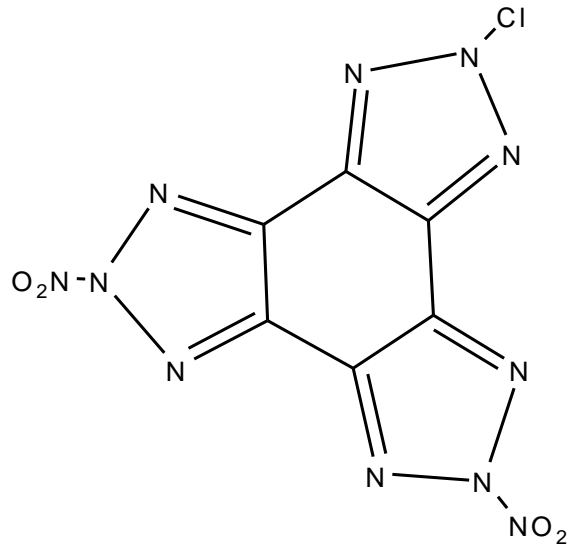
1-CBT (mol equiv)	Product	Yield (%)
1	R <sup>1</sup> = Cl; R <sup>2</sup> , R <sup>3</sup> , R <sup>4</sup> = H	79
2	R <sup>1</sup> , R <sup>2</sup> = Cl; R <sup>3</sup> , R <sup>4</sup> = H	64
4	R <sup>1</sup> , R <sup>2</sup> , R <sup>3</sup> , R <sup>4</sup> = Cl	61

**Other Applications.** The title reagent has been shown to undergo ready addition to alkenes, giving 1,2- and 2,2-chloroethylbenzotriazoles,<sup>6</sup> as well as to effect  $\alpha$ -chlorination of ketones.<sup>1</sup> 1-CBT has also been used in the preparation of other benzotriazole derivatives (1-nitro-, 1-bromo-, and 1-iodobenzotriazoles),<sup>7,8</sup> as well as the selenium transfer reagent bis(1-benzotriazolyl) selenide.<sup>9</sup>

M. P. Braun and C. R. Johnson, 1-Chlorobenzotriazole, in *The Encyclopedia of Reagents, L. Paquette, Ed., John Wiley & Sons Limited, 1995.*



# Compounds of Interest



# Conclusions

- **Novel nitro tristriazolobenzenes were made.  
One structure was confirmed by X-ray crystallography.**
- **Tris(chlorotriazolo)benzene was made.  
It has hypergolic properties.**
- **Tris(chlorotriazolo)benzene has potential commercial applications as an oxidant, a disinfectant and an energetic hypergolic agent!**



# Acknowledgments

**The ILIR program for the funding.**

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**Stanley Caulder**

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# IR Comparison

