Defense Acquisition Program Administration

# Synthesis of Ethyl 5-tetrazolyldinitroacetate as a Key Intermediate for 5-Dinitromethyltetrazole or 5-Dinitromethylidene-1,4-dihydrotetrazole

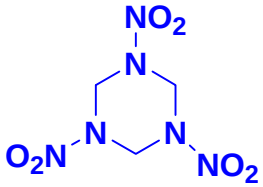
Kyoo-Hyun Chung,* Choong Hwan Lim,* Jin Rai Cho†

* High Energy Material Research Center, Department of Chemistry, Inha University
† Agency for Defense Development

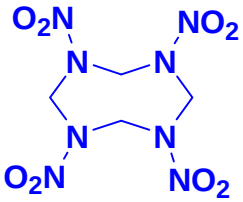
Agency for Defense Development

# Some molecular explosives

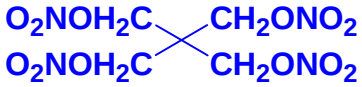

TNT




RDX

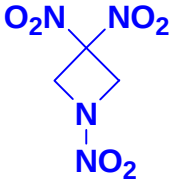



HMX

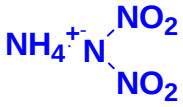



PETN

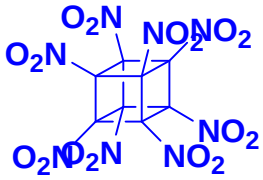

HNIW




TNAZ

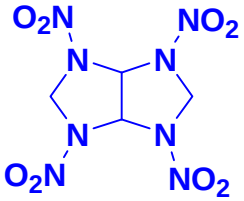



ADN



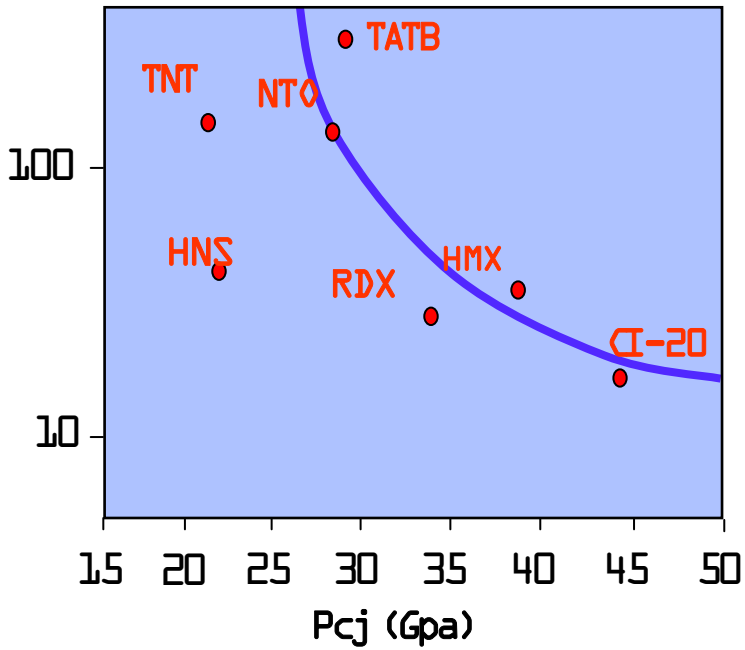

ONC

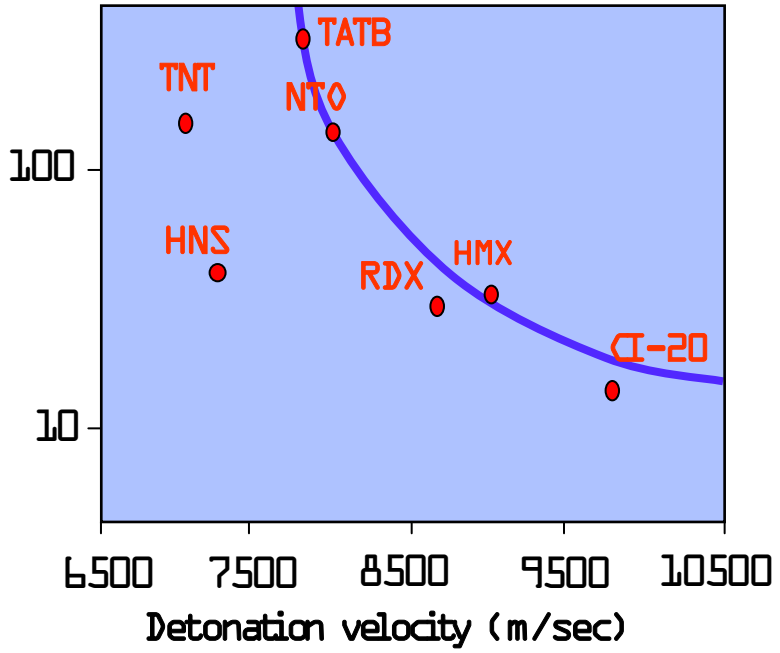

HpNC



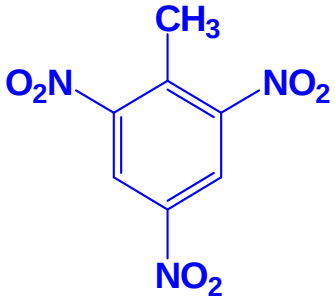

bicyclo-HMX

# Impact sensitivity vs Detonation properties

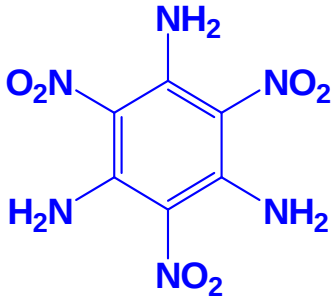


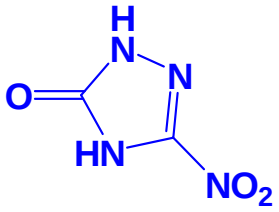
# Insensitive explosives



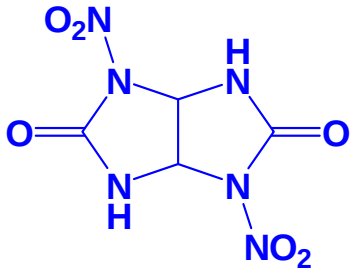

TNT



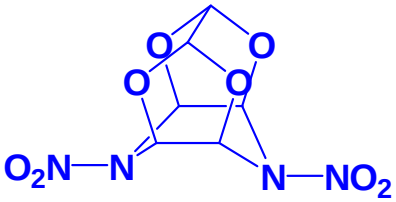

TATB



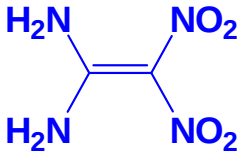

NTO




DINGU

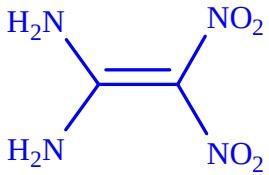



TOIW

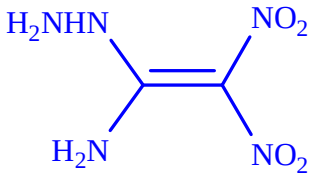


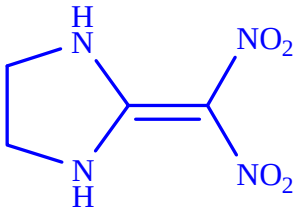

FOX-7

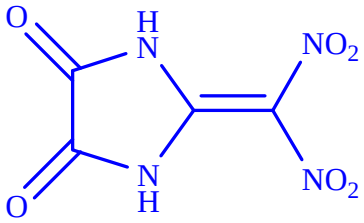
# Related compounds to FOX-7

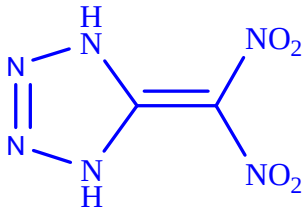


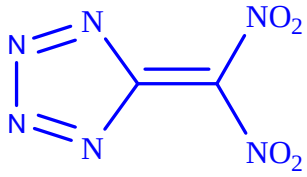

FOX-7



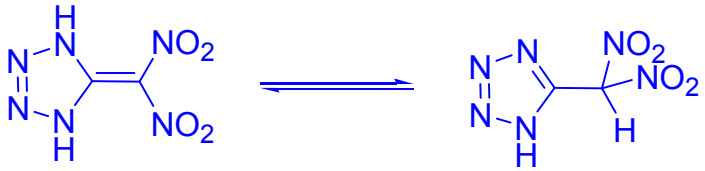



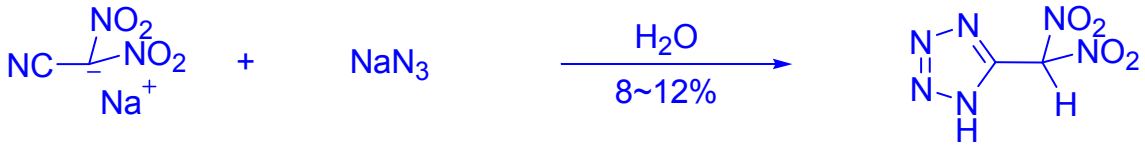



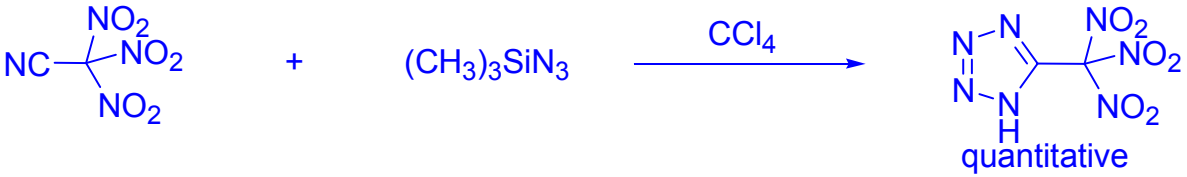



# Synthesis of 5-dinitromethyltetrazole (I)

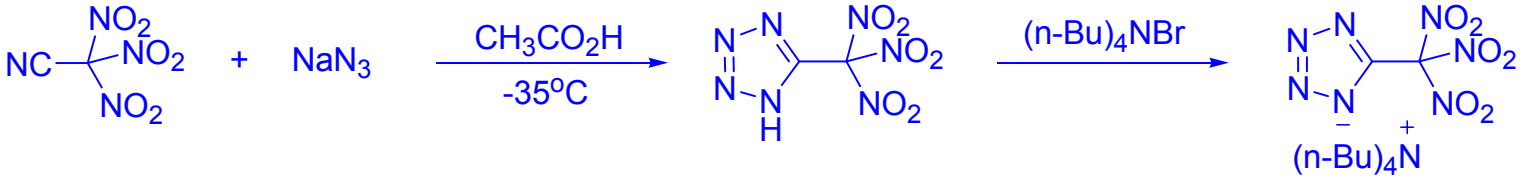




Einberg, F. *J. Org. Chem.*, **1964**, *29*, 2021-2024.



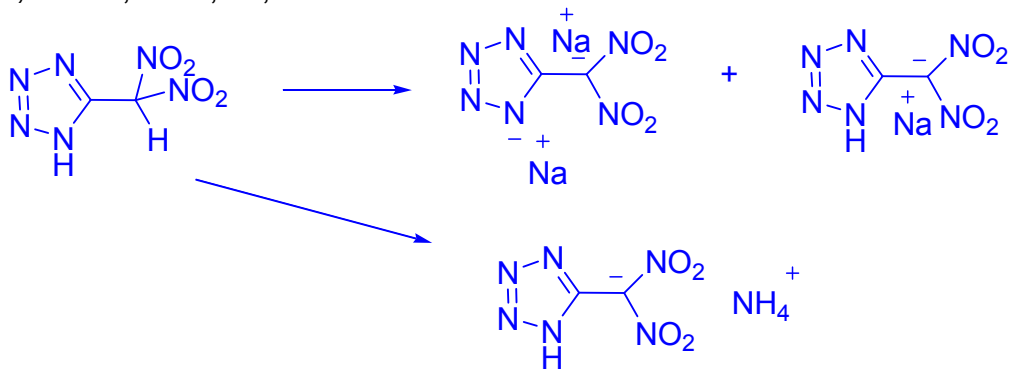

Grakauskas, V.; Albert, A. N. *J. Heterocyclic Chem.*, **1981**, *18*, 1477-1479.



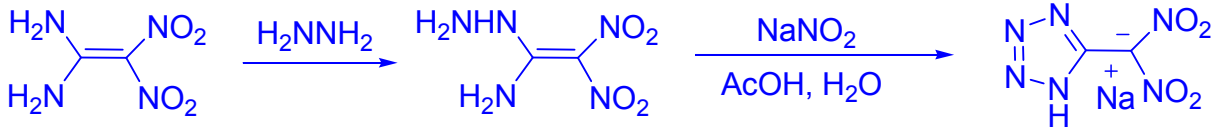
Shastin, A. V.; Godovikova, T. I.; Korsunshii, B. L. *J. Heterocyclic Chem.*, **1998**, *34*, 383.

# Synthesis of 5-dinitromethyltetrazole (II)


Terpigorev, A. N.; Tselinskii, I. V.; Makarevich, A. V.; Frolova, G. M.; Mel'nikov, A. A. *J. Org. Chem., USSR*, **1987**, *23*, 214-222.

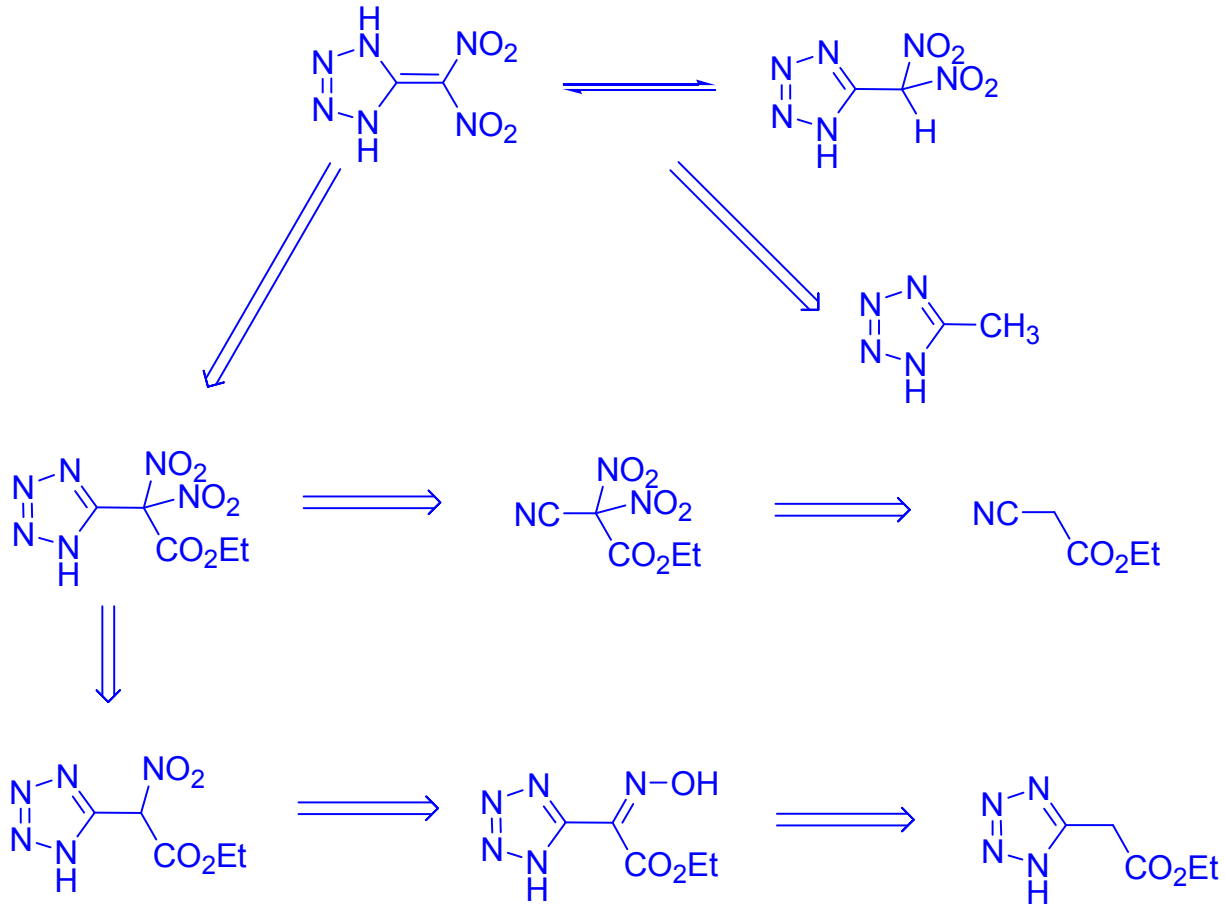



Einberg, F. *J. Org. Chem.,* **1964**, *29*, 2021-2024.

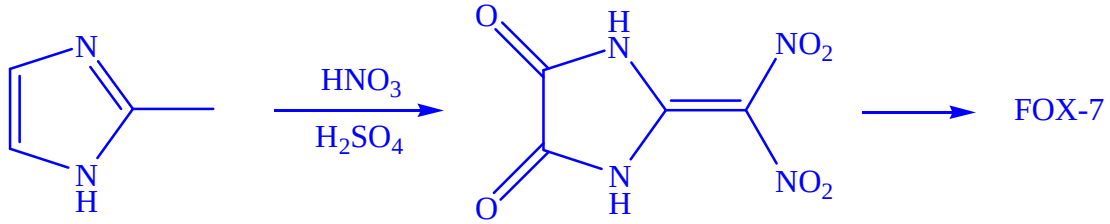



Katritzky, A. R.; Sommen, G. L.; Gromova, A. V.; Witek, R. M.; Steel, P. J.; Damavarapu, R. *Chem. Heterocycl. Comp.* **2005**, *41*, 111.

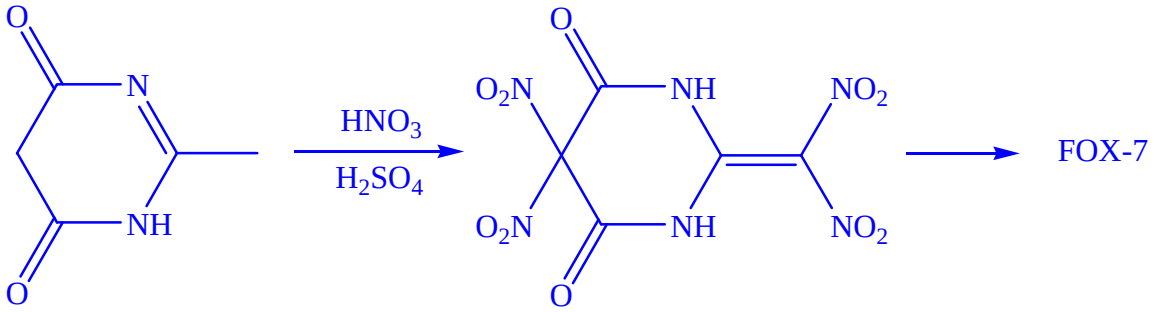
# Retrosynthetic analysis of 5-dinitromethylidene-1,4-dihydrotetrazole



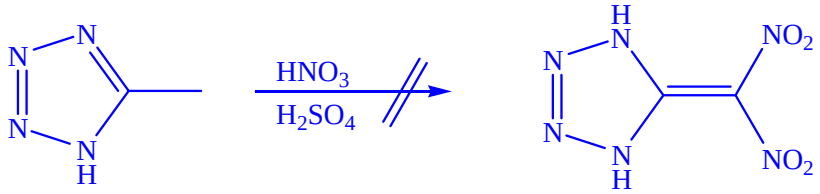
# Synthesis of dinitromethylidene from methyl



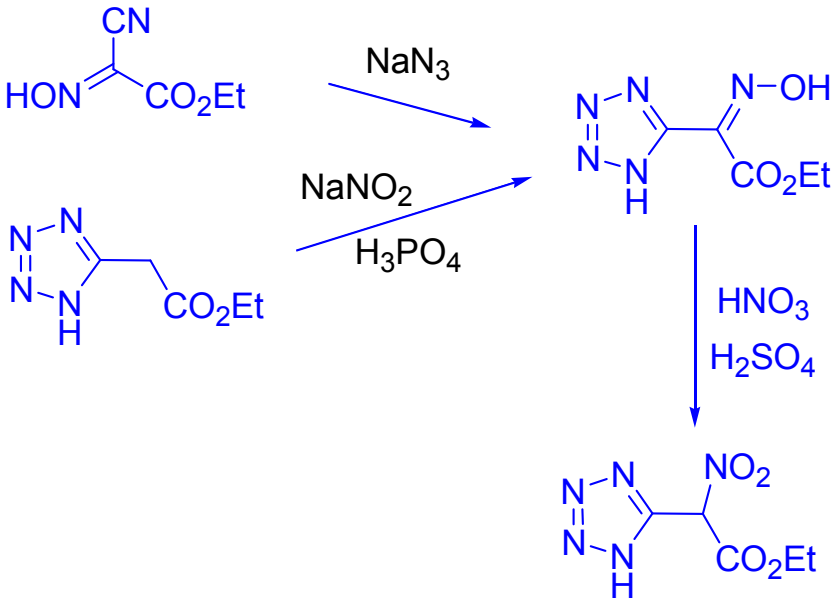

Latypov, N. V. ; Bergman, J.; Langlet, A.; Wellmar, U.; Bemm, U. *Tetrahedron*, **1998**, *54*, 11525.




Astrat'ev, A. A.; Dashko, D. V.; Mershin, A. Y.; Stepanov, A. I.; Urazgil'deev, N. *Russian J. Org. Chem.*, **2001**, *37(5)*, 729.



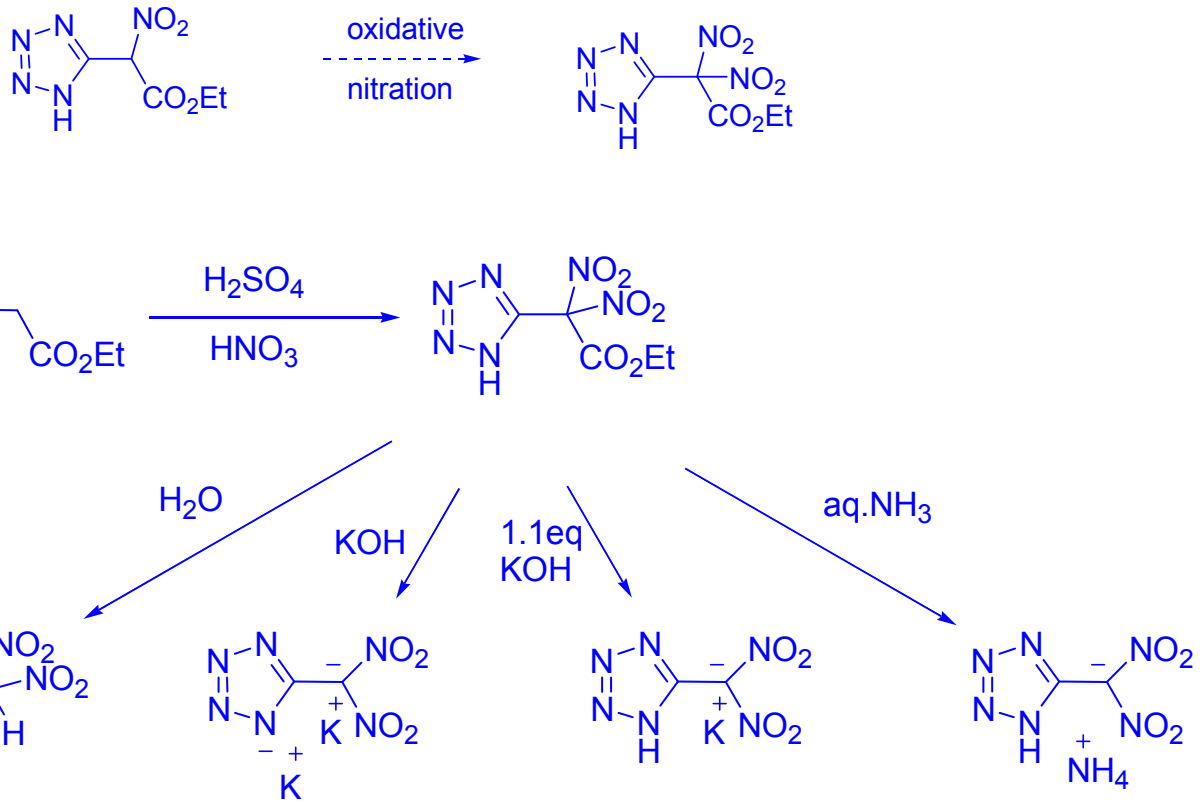
# Synthesis of oxime 5-dinitromethyltetrazolylacetate



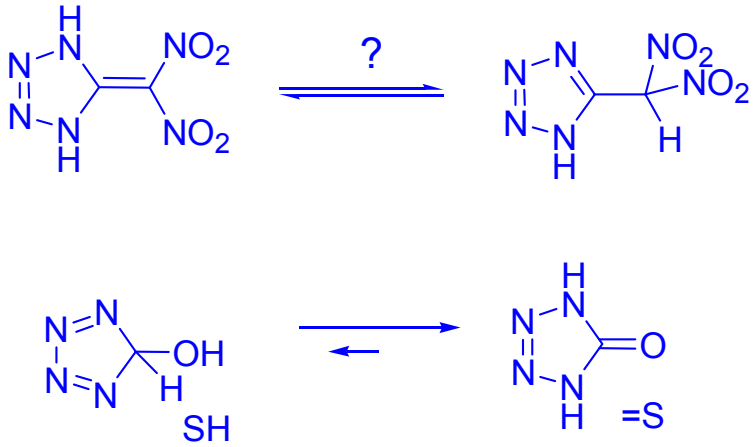

Lunn, W. H. W.; Schoepp, D. D.; Calligaro, D. O.; Vasileff, R. T.; Heinz, L. J.; Salhoff, C. R.; O'malley, P. J. *J. Med. Chem.*, **1992**, *35*, 4608-4612.

Terpigorev, A. N.; Tselinskii, I. V.; Malsarevich,A. V.; Frolova, G. M.; Mel'nikov, A. A. *J. Org. Chem., USSR*, **1987**, *23*, 214-222.

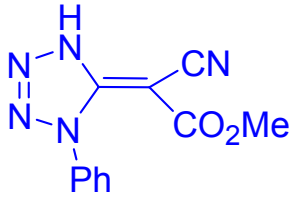
# Synthesis of 5-dinitromethyltetrazole and its salts



# Tautomerism of tetrazole-tetrazoline



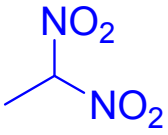

Butler, R. N. *Comp. Heterocycl. Chem., 1st ed*n **198**4, *5*, 791.



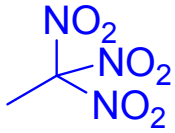

Saalfrank, R. W.; Fischer, M.; Wirth, U.; Zimmermann, H. *Angew. Chem., Int. Ed. Engl. 1987*, *2*6, 1218.

# $NO_2$ stretching


1558(asym)
1368(sym)

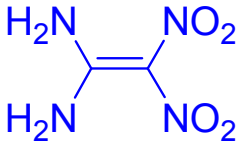



1587(asym)
1337(sym)




1595(asym)
1304(sym)


1527
1353

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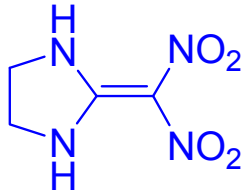
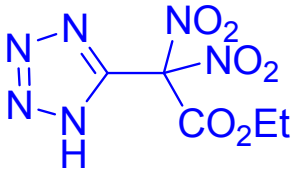
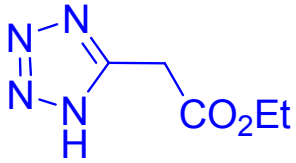



1565
1500

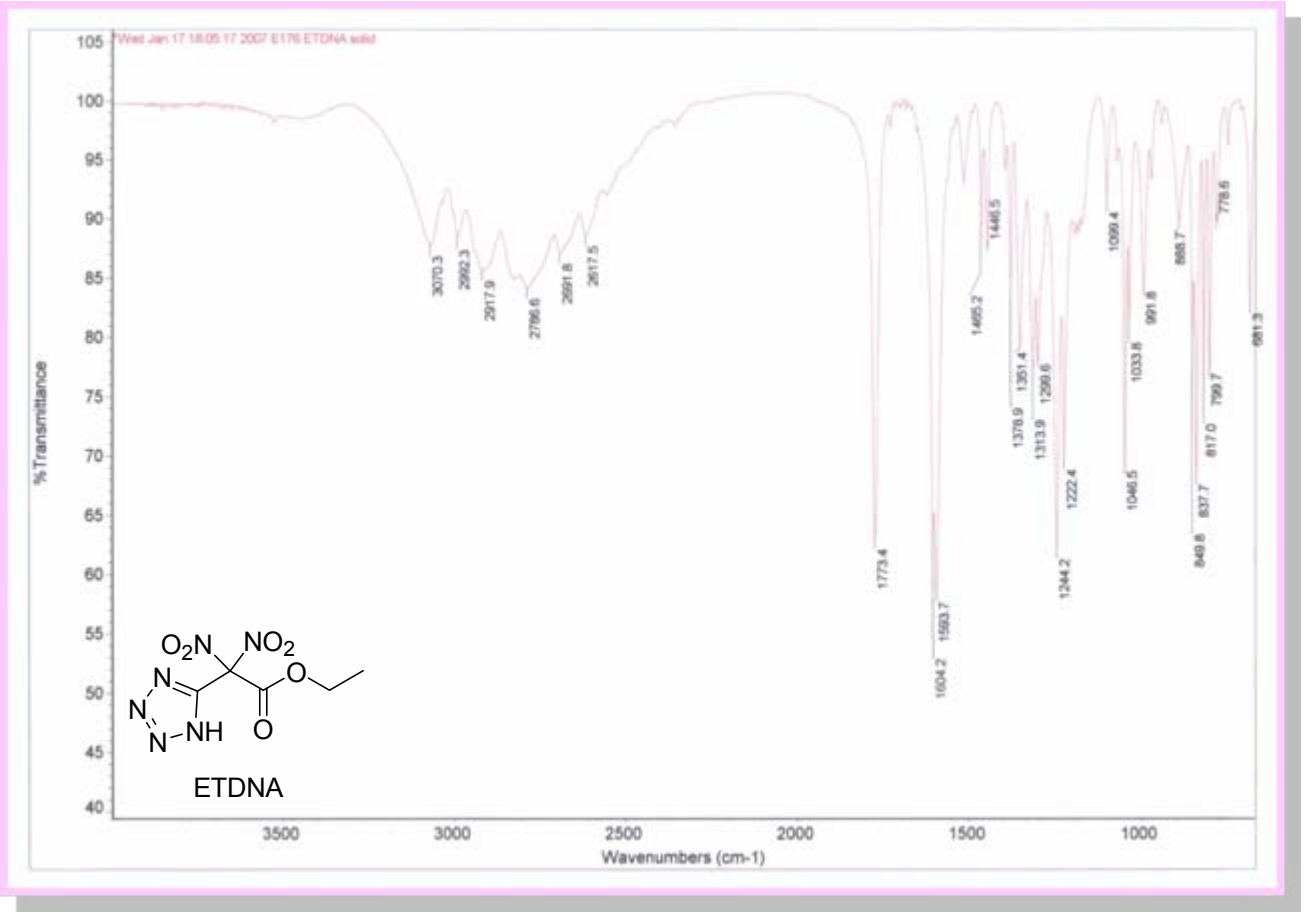



1593




1394

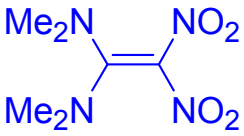
# IR of ETDNA


%Transmittance
Wavenumbers (cm-1)
3500
3000
2500
2000
1500
1000
105
100
95
90
85
80
75
70
65
60
55
50
45
40
3070.3
2992.3
2917.9
2786.6
2691.8
2617.5
1773.4
1604.2
1593.7
1485.2
1446.5
1378.9
1351.4
1313.9
1299.6
1244.2
1222.4
1099.4
1046.5
1033.8
991.8
868.7
849.8
837.7
817.0
799.7
778.6
681.3
O2N
NO2
N
N
NH
O
O
ETDNA

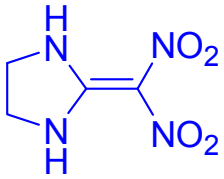
# IR of TDNM


%Transmittance
Wavenumbers (cm-1)
3214.3
2470.8
2359.3
1585.3
1523.8
1463.0
1402.3
1351.8
1330.2
1216.3
1071.6
1048.5
1018.5
995.9
834.6
782.8
754.1
711.9
669.5
TDNM

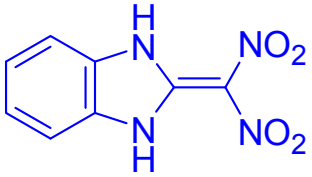
# UV absorption in MeOH



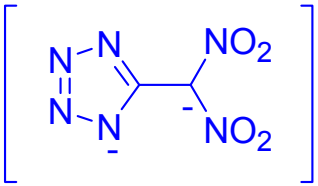
264, 302, <u>340</u>



<u>280</u>, 295, 330

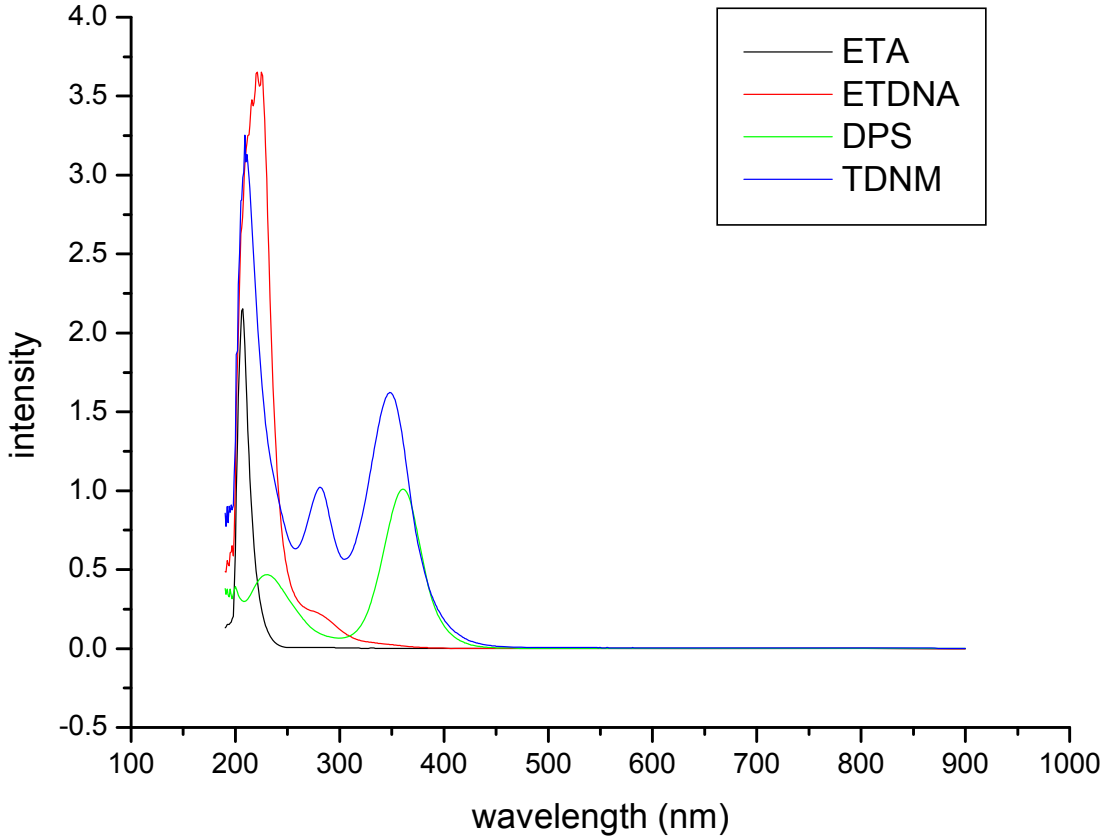


240, 320, <u>335</u>

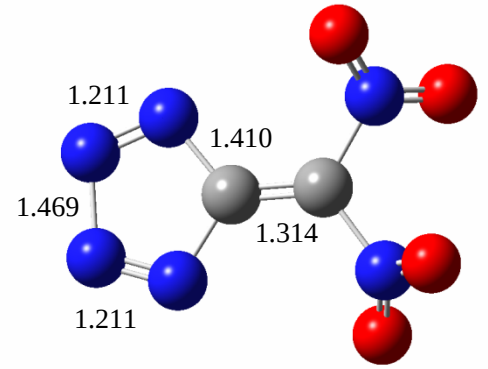


$2K^+$ 362 (in water)

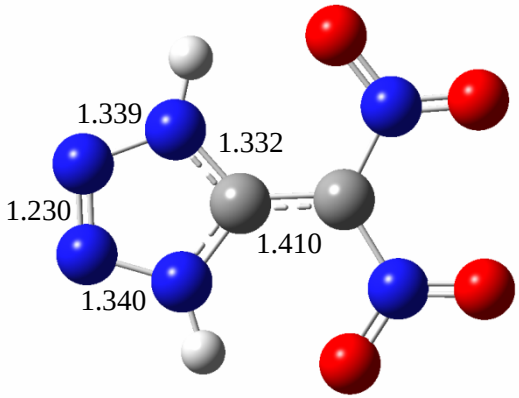
# UV-Vis of tetrazole derivatives



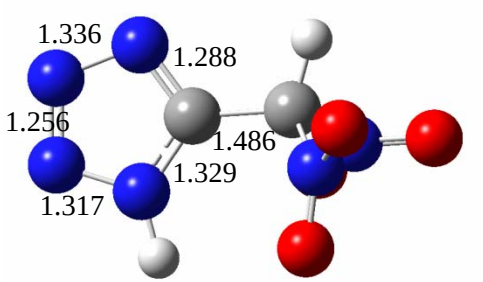
# RHF/6-31G(d) calculations



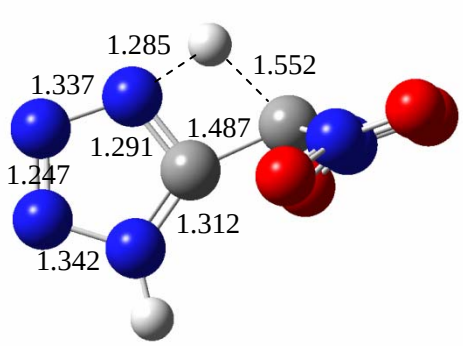

E=-701.43353 H




E=-702.70106 H (0.0 kcal/mol)

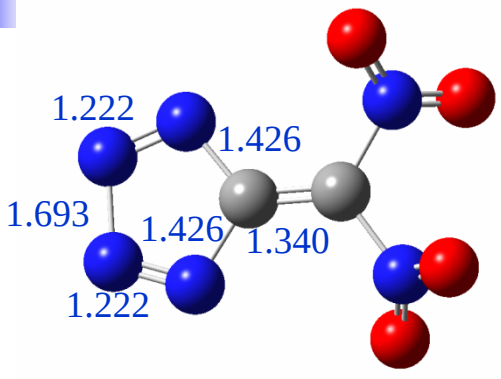



E=-702.69985 H
(0.75 kcal/mol)

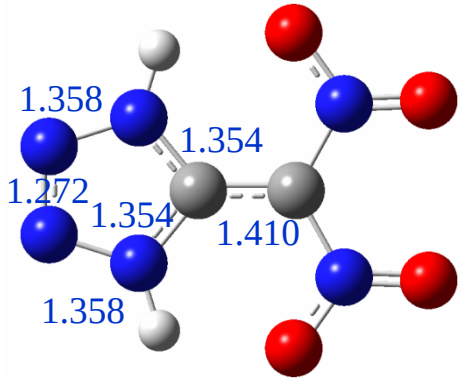



E=-702.57955 H (76.24 kcal/mol)

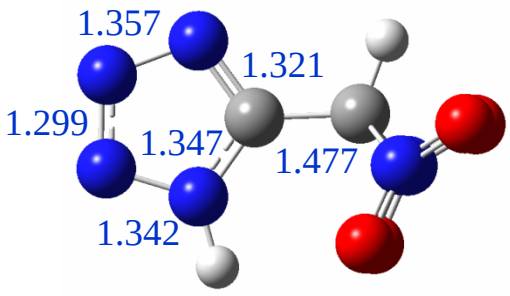
# B3LYP/6-31G(d) calculations



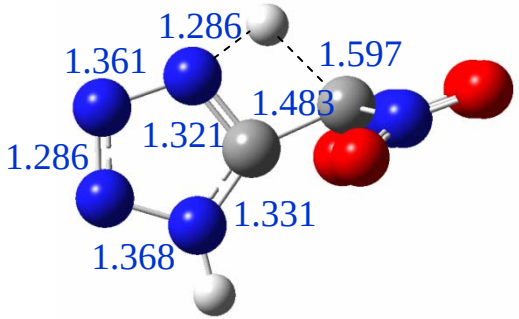

E=-705.24311 H




E=-706.54601 H
(0.00 kcal/mol)

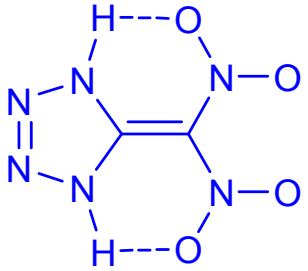


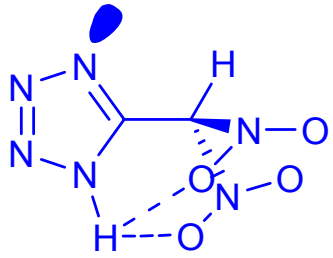

E=-706.53978 H
(3.90 kcal/mol)




E=-706.44411 H
(63.94 kcal/mol)

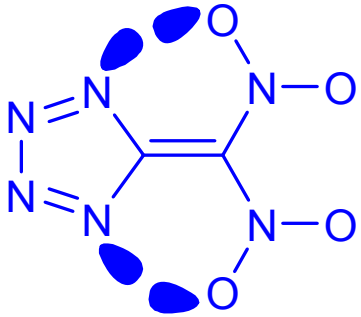
# Energy difference of tautomers



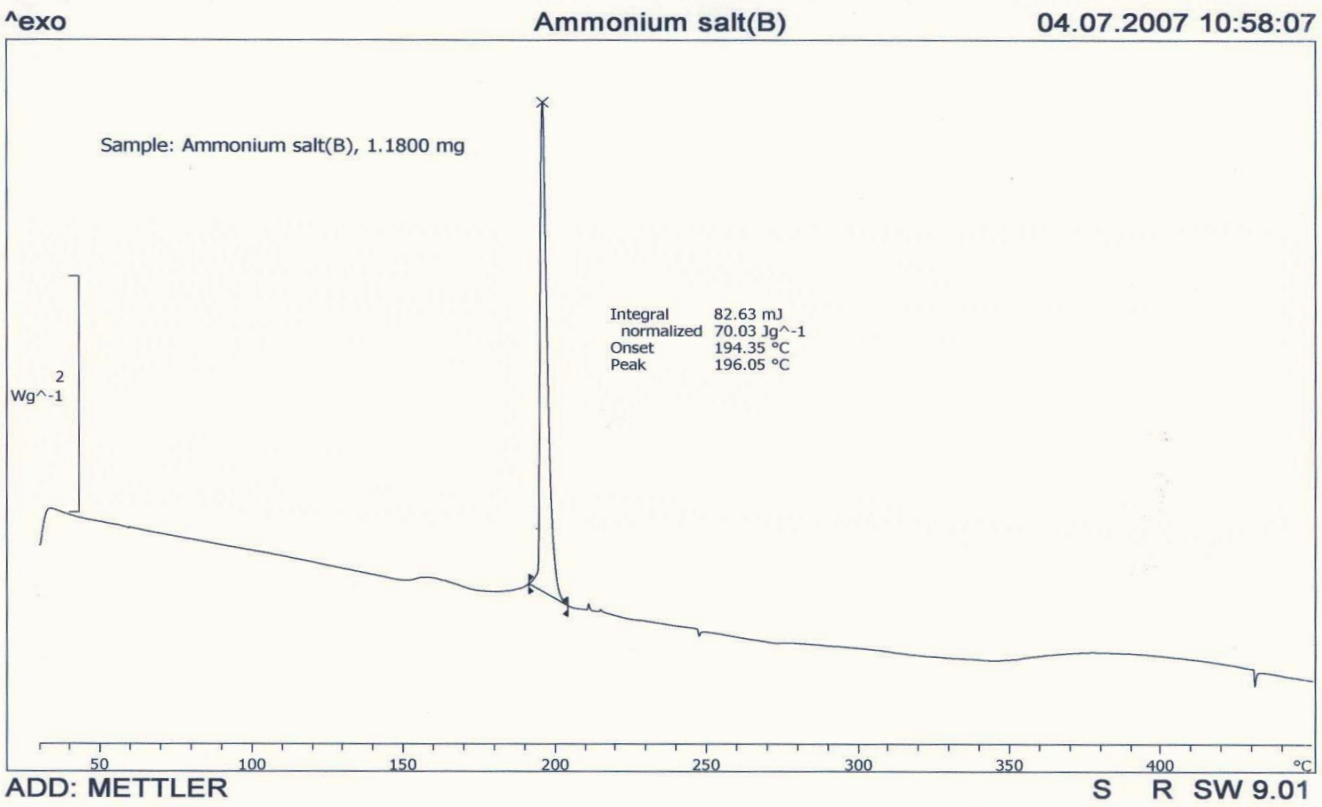


**a) RHF/6-31G(d) calculation ΔE=0.75 kcal/mol**

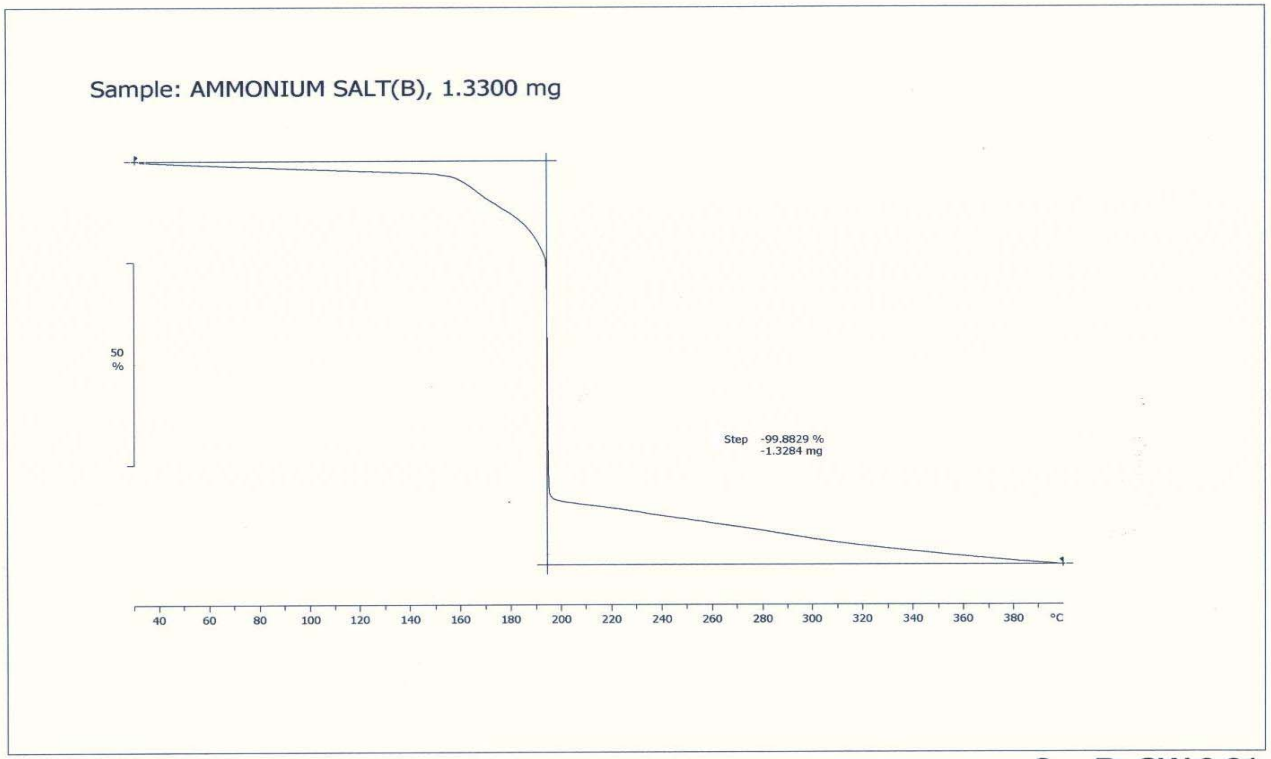
**b) B3LYP/6-31G(d) calculation ΔE=3.90 kcal/mol**



# DSC of ATDNM


^exo
Ammonium salt(B)
04.07.2007 10:58:07
Sample: Ammonium salt(B), 1.1800 mg
Integral 82.63 mJ
normalized 70.03 Jg^-1
Onset 194.35 °C
Peak 196.05 °C
2
Wg^-1
50
100
150
200
250
300
350
400
°C
ADD: METTLER
S R SW 9.01

# TGA of ATDNM


Sample: AMMONIUM SALT(B), 1.3300 mg
50
%
Step -99.8829 %
-1.3284 mg
40 60 80 100 120 140 160 180 200 220 240 260 280 300 320 340 360 380 °C
ADD: METTLER
S R SW 9.01

# Conclusion

- 5-Dinitrotetrazole was readily prepared from ethyl 5-tetrazolylacetate, via ethyl 5-tetrazolyldinitroacetate.

- 5-Dinitroterazole exists in the mixture of tetrazole and tetrazoline, because of small energy difference.

# High Energy Research Center

- Established in Inha University, Incheon, Korea
- Sponsored by Defense Acquisition Program Administration
  & Agency for Defense Development
- Period : 2004. 3. 16 - 2012. 12. 31 (9 years)
  25 Research topics
  1st period : 2004 - 2006
  2nd period : 2007 - 2009
  3rd period : 2010 - 2012
- Participant : University Professor and
  Researcher of Private company
- Three Research Divisions

# Division I

## Design and Synthesis Research

- Design techniques of explosive molecules
- Synthesis of polycyclic molecular explosives and oxidizers with high density and insensitivity
- Design and synthesis of high energetic binder system containing molecular explosives
- Crystallization and characterization of energetic materials
- Synthetic method of high energetic and high dense cyclic hydrocarbons
- Polyphosphazene elastomer and its synthesis
- Design and characterization of nitrogen cluster compounds
- Synthesis of nanocomposites of HEM with nanostructured materials

# Division II & III

## Energy Conversion Phenomenon Analysis Research

- Three dimensional numerical study for shaped charger
- Numerical modeling of energy conversion processes in high-temperature flows
- Numerical analysis of interior ballistics
- Mechanism analysis and power increasing methods for EMP generators
- Analysis of the effects on the semiconductors by EMP
- Measurement technique of solid propellant burning rates using ultrasound

## Rheological Property Research

- Rheological characteristics and extrudability of highly viscous energetic materials
- Composition research of silicone rubber
- Characteristics of nano aluminum slurry fuel
- Surface modification of high energy material using supercritical fluid

# Acknowledgement


- Defense Acquisition Program Administration
- Agency for Defense Development