A Candidate of New Insensitive High Explosive; MTNI

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1-methyl-2,4,5-trinitroimidazole (MTNI; **1**) was reinvestigated and fully characterized as a promising candidate of new insensitive high explosives. Compound **1** was synthesized from the imidazole (**2**), via 5 step reactions. According to our preliminary sensitivity tests, **1** was almost as insensitive as TNT. The explosive performances, i.e. detonation velocity, and C-J pressure, were evaluated theoretically, and were found to be comparable to those of RDX. In addition, owing to its low melting point, 82 ^{o}C, we believe that **1** is an excellent candidate of melt-castable explosives. The structure of **1** was characterized by X-ray diffraction. The crystal is orthorhombic; M = 434.23, *Pca2*$_1$, a = 8.6183(6) Å, b = 17.7119(12) Å, c = 10.6873(7) Å, Z = 4, V = 1631.38(19) Å^3, Dc = 1.768 g/cm^3. The structure was refined to *R* = 0.0278 for 3474 independent reflections with **I** > 4σ(*I*). The molecular structures calculated by high levels of ab initio and density functional theories were in good agreement with that observed by X-ray experiment.

Introduction.

In the last few decades, polynitroimidazoles have been investigated due to their properties as antibiotic, radiosensitizers and anti-protozoans [1,2,3].

Although these nitroimidazole derivatives were studied mainly for their pharmacological medicinal chemistry, they were seldom studied for their use in explosives and propellants application. However more recently these nitroimidazoles, as so-called “high energy density materials”, have attracted renewed attention due to their favorable detonation performances. 2,4-Dinitroimidazole is an example [4,5,6].

In the modern ordnance there is a strong requirement for explosives having good thermal stability, impact insensitivity and explosive performance. However, these requirements are somewhat mutually exclusive. Explosives having good thermal stability and impact insensitivity usually exhibit poor explosive performance, while most explosives with high performance are prone to be sensitive. 1,3,5-Triamino-2,4,6-trinitrobenzene (TATB) is currently employed for insensitive high explosive applications, but does not provide a sufficiently high power in order to replace RDX and HMX in some applications. Therefore, there is a continuing need for explosives that are powerful, yet resistant to accidental stimuli and sympathetic initiation.

Compound **1** was synthesized previously [7], but appear to have not been characterized fully. Thus, as a part of our program to search more powerful and less sensitive explosives and propellants, we succeeded to repeat synthesizing **1** and calculated its expected performance and discovered that the crystalline **1** is energetic for propellant and explosive applications based on the experimental results.

Results and Discussion.

a. Theoretical Calculation.

Table 1. Selected geometric parameters [a] of MTNI calculated at the B3LYP/6-31G** and BP86/6-31G** levels along with those observed by X-ray.

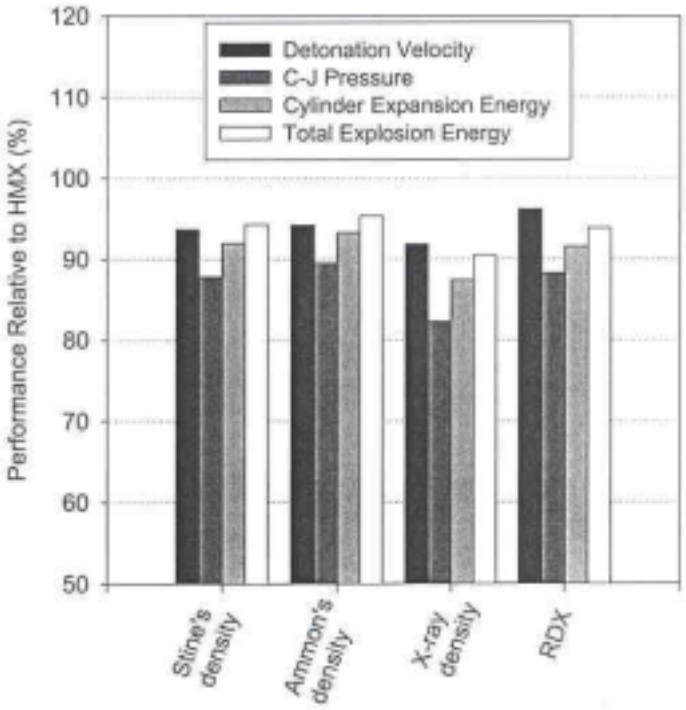
Geometric Parameters [b]	B3LYP/ 6-31G**	BP86/ 6-31G**	X-ray [c]
C1-N1	1.371	1.383	1.354
C1-N2	1.314	1.327	1.296
C3-N1	1.375	1.383	1.350
C2-C3	1.386	1.400	1.362
C2-N2	1.342	1.349	1.352
N1-C4	1.479	1.480	1.478
C1-N3	1.462	1.470	1.459
C2-N4	1.447	1.453	1.447
C3-N5	1.460	1.468	1.450
N2-C1-N1	114.12	114.06	115.47
N2-C2-C3	110.79	111.02	111.12
C1-N1-C3	104.02	104.15	103.23
C1-N2-C2	104.56	104.41	103.29
N1-C3-C2	106.51	106.35	106.90

[a] Units are in bond lengths, degrees in bond angles. [b] Numbering scheme is shown in Figure 2. [c] Average values of two molecules.

The structure of MTNI (**1**) was fully optimized at the B3LYP/6-31G** and BP86/6-31G** levels by using the Gaussian-94 series of programs [8]. The important geometric parameters calculated these levels were summarized in Table 1 along with those observed from X-ray experiments. As shown in Table 1, our calculated bond lengths and angles are in good agreement with those measured from X-ray experiments.

With utilizing ab initio calculated structures and energies, we estimated heat of formation in the solid phase and density. We used 'group additivity method' developed by Stine [9] and by Ammon and coworkers [10] to estimate the density of **1**. Both methods calculated the density of **1** to be ca 1.82-1.84 g/cc, which are indeed slightly higher than that observed by X-ray experiments, 1.768 g/cc. The heat of formation in the solid phase was estimated to be 40.7 kcal/mol by following the method developed by Politzer et al. [11,12] and correcting the sublimation energy [13].

Figure 1. Explosive performances of MTNI compared with those of RDX calculated by the Cheetah 2.0 program.

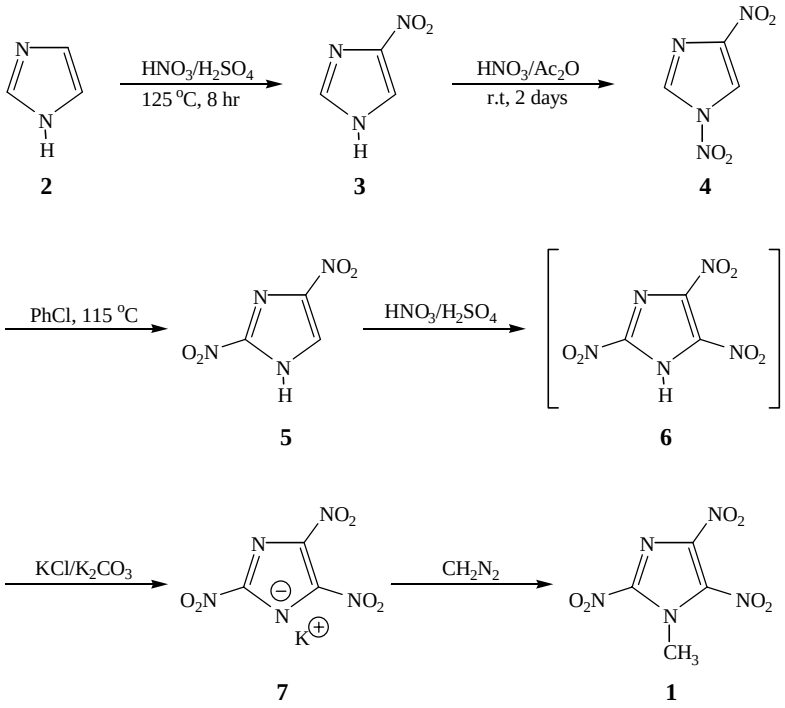


The various explosive performances of **1** computed by the Cheetah 2.0 program [14] are depicted in Figure 1 compared with those of RDX which is one of most commonly used explosives in recent military applications. As shown in Figure 1, the explosive performances were initially predicted to be quite comparable to those of RDX, when the density was computed by the group additivity methods. However, the explosive performances were calculated to be slightly inferior to those of RDX, when the crystal density measured by X-ray experiments was employed.

b. Synthesis.

Imidazole (**2**) was converted in good yield (46 %) to 4-nitroimidazole (**3**) by applying the literature procedure of Bulusu and coworkers [6], which uses mixed acid of 70 % nitric acid and concentrated sulfuric acid. The yield of **3** depends on the reaction time and refluxing temperature (Scheme 1).

Scheme 1.



The transformation of 4-nitroimidazole (**3**) into 1,4-dinitroimidazole (**4**) could be brought about by treatment with acetyl nitrate ($AcONO_2$), which could be generated in the mixed solution of acetic anhydride and fuming nitric acid in acetic acid *in situ* at low temperature [6]. It took two days to get excellent yield (95 %) of **4**. There are about 3 % of unreacted **3** as the major impurity, which can be removed by the extraction with methylene chloride. This compound **4** is so thermally unstable at the elevated temperature (over 50 °C) that nitro group of 1-position can be deleted to return to **3**.

2,4-Dinitroimidazole (**5**) was prepared from **4** by thermal rearrangement with refluxing in chlorobenzene [6]. The yield was 93 %. In general, the synthesized **5** were contaminated with **3** in a small amount. It is probably that very small portion of **4** might go back to **3** during the rearrangement. Along with above thermal decomposition, **3** in **5** can come from the contaminated **4**. To minimized **3** in **5**, it is important to get rid of **3** when making **4**.

The 3rd nitration to 2,4,5-trinitroimidazole (**6**) was performed in the mixed acid condition. As the intermediate of potassium 2,4,5-trinitroimidazolate (**7**), **6** was not stable enough that we could not isolate that. From the extracted ether solution of **6**, the solid of **7** was precipitated with the saturated K_2CO_3/KCl solution in good yield (60 %) [15]. It was reported that **6** could be manufactured via 2,4,5-triiodoimidazole, but we chose the route through 2,4-DNI (**5**).

Our target molecule, 1-methyl-2,4,5-trinitroimidazole (MTNI; **1**) was synthesized (36 %) when **6**, which was regenerated from **7** by treating with hydrochloric acid, was reacted with diazomethane (CH_2N_2) in ether solution [7]. To make the diazomethane, Diazald (*N*-methyl-*N*-nitroso-*p*-toluenesulfonamide) was purchased from the Aldrich and used *in situ* [16]. When the crude **6**, which was prepared from **5** and extracted with ether, was used to make **1** without converting to **7**, we failed to separate **1** from the product mixture. It is probably that in the crude **6**, there were lots of impurities such as unreacted **5**.

c. Crystal Structure.

All X-ray intensity data for compound **1** were collected with use of a Bruker SMART diffractometer equipped with a CCD area detector using Mo K_α radiation. Intensity data were corrected for Lorenz and polarization effects and were empirically corrected for absorption using

the ψ-scan method. Details on crystal and intensity data are given in Table 2.

Table 2. Crystal data and experimental details

Crystal data

$\boldsymbol{C}_8\boldsymbol{H}_6\boldsymbol{N}_{10}\boldsymbol{O}_{12}$	Mo K_α
M_r = 434.23	=0.71073
Orthorhombic	Z=4
$Pca2_1$	T=296(2) K
a=8.6183(6)	=90.00°
b=17.7119(12)	=90.00°
c=10.6873(7)	γ=90.00°
V=1631.38(19)	Cell parameter from 20 reflections
μ=0.167 $^{-1}$mm	Yellow
Dc = 1.768 g/cm^3	

Data collection

Bruker SMART CCD

h= –11 11	θ_{max} = 27.53°
k= –23 23	θ_{min} = 1.15°
l= –13 13	$\boldsymbol{I} > 4\,\sigma(\boldsymbol{I})$
3741 measured reflections	3474 independent reflections

Refinement

R1=0.0278	$\Delta\rho_{max}$ = 0.16 e^{-3}
ωR2=0.0782	$\Delta\rho_{min}$ = –0.15 e^{-3}
S(GooF)=1.061	sigma $\boldsymbol{I}$ /net $\boldsymbol{I}$ =0.0449
F(000)=880	

$\omega = 1/[\sigma^2(\boldsymbol{F}_0^2)+(0.0373P)^2+0.0817\,P]$

where $P=[\,\boldsymbol{F}_0^2+2\,\boldsymbol{F}c^2]/3$

Extinction method: SHELXTL Extinction coefficient: 0.0032(11)

The crystal of compound **1** was grown in ethanol solution at room temperature. A yellow crystal of **1**, irregularly shaped, of approximate dimensions 0.45x0.50x0.56 mm^3, was used for crystal and intensity data collection. The crystal structure of **1** was solved by direct method with SHELXTL [17] and refined by full-matrix least squares on $\boldsymbol{F}^2$ with anisotropic displacement parameters for all non-H atoms. All H-atoms were generated in idealized positions and refined in a riding model.

The molecular structure and atom labeling are shown in Figure 2, the packing of the molecule in the crystal lattice is illustrated in Figure 3.

The results indicate that three nitro groups are coordinated with imidazole and the coordinated bond lengths are between 1.4471 and 1.4594 Å. The bond lengths from methyl to imidazole are N1-C4(1.480 Å) and N11-C14(1.475 Å). All of these are typical coordinated bond lengths.

According to the calculation, the equations of the planes of two imidazole rings are as follows:

$$-2.9071x + 10.7164y - 7.7078z = -3.0220 \quad (1)$$

$$2.1957x - 12.2853y - 7.2009z = -3.2085 \quad (2)$$

The dihedral angle between planes (1) and (2) is 88.9°.

Figure 2. Molecular structure with atomic numbering scheme showing 50 % probability displacement ellipsoids.
H-atoms are drawn as small of arbitrary radii.

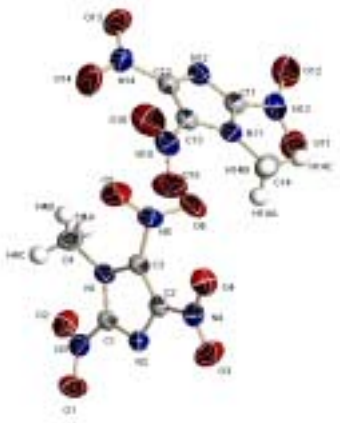
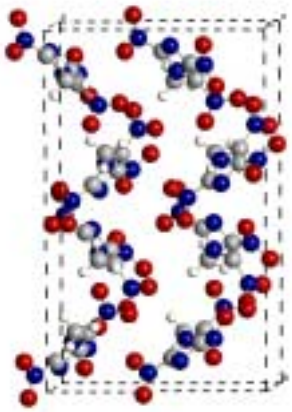


Figure 3. The perspective view of the unit cell of **1** along the a-axis.



d. Test and Evaluation.

The melting point of synthesized **1** was measured with DSC (Differential Scanning Calorimeter) and proved to be exactly correspondent with the reported data, 82 ^{o}C (Figure 4). This fact means that **1** can be utilized as an ingredient of the melt-castable explosives.

1 starts to evaporate at 190 ^{o}C and reaches peak at 280 ^{o}C on TG (Thermogravimeter) (Figure 5). From this result, we know that **1** is thermally stable up to 190 ^{o}C.

Figure 4.

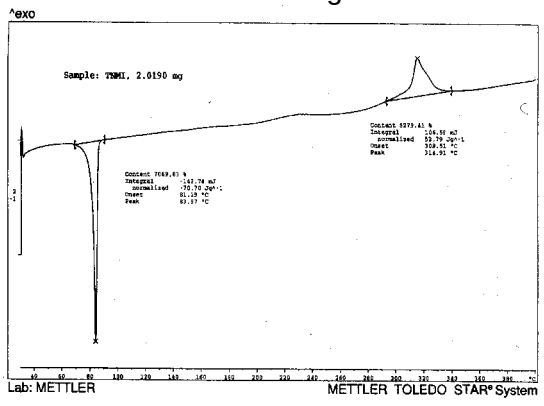
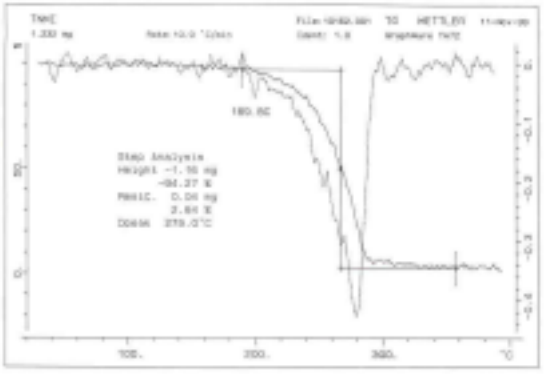


Figure 5.



The impact sensitivity of **1** was tested at Julius Peter's Tester (Table 3). The test was performed after drying for 4 hours at 60 ^{o}C. At that time, the room temperature was 22 ^{o}C and relative humidity was 68 %. As the result, 50 % probability detonating impact energy of **1** was 14.6 J whereas that of HMX, class 1, was 5.4 J. It is expected that the impact sensitivity level of **1** is similar with that of Comp B. From these data, we guessed **1** might be insensitive.

When friction sensitivity of **1** was also measured with Julius Peter's Tester at the same condition, **1** was proved to be as insensitive as TNT at the friction (Table 3).

Table 3.

Explosives	Impact (Energy; J)	Friction (Energy; J)	Remark
TNT	47.0	N.R.	
Comp B	19.8	29.1	
RDX	7.4	16.1	
HMX	6.5	10.6	
PETN	4.8	4.5	
MTNI (**1**)	14.6	N.R.	
HMX (CL 1)	5.4	11.6	* Tested on the same day with **1**.

In Table 4, there are the density data of several explosives including **1**. The measured density of crystal of **1** at 25 ^{o}C is 1.752 g/cm^{3}. From the experimental result, we knew that the density of **1** is higher than that of Comp B and slightly lower than that of RDX. So it is expected that **1** may have the performance value similar with that of RDX.

Table 4.

Explosives	Density (g/cm^{3})	Remark
TNT	1.65	
Comp B	1.72	
RDX	1.80	
HMX	1.89	
PETN	1.76	
MTNI (**1**)	1.768	* Crystal
	1.752	* Measured

MTNI (**1**) was synthesized successfully, its sensitivities were measured, and performance was calculated. Although the performance of **1** appears, at best, to be close to those of RDX, we believe that there are two possible merits to pursue the explosive formulations with **1**; (1) insensitiveness and (2) low melting point. If MTNI (**1**) is significantly less sensitive than RDX, it can be a good ingredient for insensitive explosives. Since the melting point of **1** is quite close to TNT, it also will be a good candidate to be used in melt-castable explosives and to replace TNT. We know that **1** is much more powerful than TNT.

Preliminary scale-up of **1** using Reaction Calorimeter will be performed in the near future.

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