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We have reinvestigated the synthesis of 1-methyl-2,4,5-trinitroimidazole (MTNI; **1**), and further characterized its physical properties. It is a promising candidate as an insensitive high explosive. Compound **1** was synthesized from the imidazole (**2**), *via* a 5-step sequence of reactions, and subjected to various sensitivity tests for explosives. The structure of **1** was characterized by X-ray diffraction. The crystal is orthorhombic; $C_4H_3N_5O_6$, $M = 217.11$, $Z = 8$, $Pca2_1$, $a = 8.6183(6) \text{ \AA}$, $b = 17.7119(12) \text{ \AA}$, $c = 10.6873(7) \text{ \AA}$, $V = 1631.38(19) \text{ \AA}^3$, $D_c = 1.768 \text{ g/cm}^3$. The structure was refined to $R = 0.0284$ for 3201 independent reflections with $I > 2\sigma(I)$. The molecular structures calculated by high levels of *ab initio* and density functional theories were in good agreement with those observed by X-ray experiment. According to our preliminary sensitivity tests, **1** was characterized to be intermediate in sensitivity between RDX and TNT. The explosive performances were evaluated theoretically, and were found to be comparable to those of RDX. In addition, owing to its low melting point ($82 \text{ }^\circ\text{C}$), **1** is believed to be an excellent candidate for inclusion in melt-castable explosives, and may lead to increased explosive power.

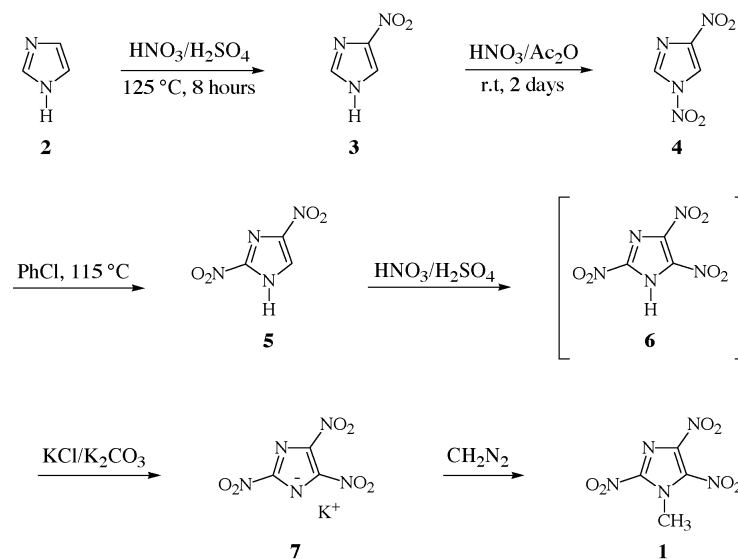
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Introduction.

In the last few decades, polynitroimidazoles have been investigated mostly due to their properties as antibiotics, radiosensitizers and anti-protozoans [1-3]. Although these nitroimidazole derivatives were studied extensively for their potential pharmacological uses, there were only a limited number of studies on applying them to explosives and propellants up to early 1990s. However, quite recently, these nitroimidazoles, as so-called 'high energy density materials', have attracted renewed attention due to their favorable explosive performance as well as improved safety characteristics. 2,4-Dinitroimidazole serves as a good example [4-6].

In modern ordnance, there is a need to have an explosive molecule, which is highly stable to thermal heating, substantially insensitive to impact, and highly powerful upon explosion. Unfortunately, these characteristics are quite often contradictory to each other. For instance, explosives showing 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 sufficiently high power to replace RDX (1,3,5-trinitro-1,3,5-triazacyclohexane) and HMX (1,3,5,7-tetranitro-1,3,5,7-tetraazacyclooctane)

Scheme 1



in most applications. Therefore, there is a continuing need for new explosives that are powerful, yet resistant to accidental stimuli and sympathetic initiation.

Compound **1** was synthesized previously [7], but appeared to have not been characterized fully. Thus, as a part of our program to search for more powerful and less sensitive explosives and propellants, our efforts toward full characterization of **1** were extended to a revisit of the synthesis, theoretical structural examination, and crystal structure analysis. Furthermore, based on both theoretical prediction and measurement of explosive properties, **1** appeared to be excellent as an energetic filler for propellants and explosives.

Results and Discussion.

a. Synthesis.

Imidazole (**2**) was converted in good yield to 4-nitroimidazole (**3**) by following the procedure given by Bulusu and coworkers [6], where the mixed acid comprised of 70 % nitric acid and concentrated sulfuric acid was used. The yield of **3** depends on the reaction time and reflux temperature (Scheme 1).

The transformation of 4-nitroimidazole (**3**) into 1,4-dinitroimidazole (**4**) was achieved by treatment with acetyl nitrate (AcONO₂), which was generated in a mixed solution of acetic anhydride and fuming nitric acid in acetic acid *in situ* at low temperature [6]. Treatment for two days provided an excellent yield of **4**. Approximately 3 % of unreacted **3** was present as a major impurity, and was removed by extraction with methylene chloride. This compound **4** was thermally unstable at elevated temperatures (over 50 °C), and was labile to revert back to **3** by the dissociation of the nitro group at 1 position.

2,4-Dinitroimidazole (**5**) was prepared from **4** by thermal rearrangement in refluxing chlorobenzene [6]. In general, the synthesized **5** was contaminated with **3** in a small amount. It was probable that a very small portion of **4** was decomposed during the rearrangement resulting in the formation of **3**. Along with thermal decomposition mentioned above, the presence of **3** in **5** appeared to come from the contaminated **4**. To minimize **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 a mixed acid condition. Studies indicated that **6** was not stable enough to be isolated. Hence, the extracted ether solution of **6** was treated with saturated K₂CO₃/KCl solution to obtain potassium 2,4,5-trinitroimidazole (**7**) in good yield [8]. Although it was known that **6** could also be synthesized *via* 2,4,5-triiodoimidazole, we chose the route through 2,4-DNI (**5**) due to our previous experience in dealing with similar compounds.

Our target molecule **1** was synthesized by reacting **6**, which was regenerated from **7** by treating with hydrochloric acid, and then with diazomethane (CH₂N₂) in ether solution [7]. To make the diazomethane, Diazald (*N*-methyl-*N*-nitroso-*p*-toluenesulfonamide) was

purchased from Aldrich and used *in situ* [9]. When 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 probable that in the crude **6** the presence of impurities such as unreacted **5** might have affected the formation of the desired product.

b. Crystal Structure.

The structure of **1** consists of well-separated molecules with the closest intermolecular contact of 2.939(2) Å between N(1) and O(52'). Final atomic positional parameters for non-hydrogen atoms are shown in Table 1. The two molecules in the asymmetric unit have very similar structures as shown in Table 2. In the two molecules, 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°.

Table 1
Fractional Atomic Coordinates [a] and Equivalent
Displacement Parameters [b] for **1**

	x	y	z	U(eq)[c]
<i>(Molecule 1)</i>				
C(1) [d]	2534(2)	1416(1)	9136(2)	50(1)
C(2)	4934(2)	595(1)	8715(2)	34(1)
C(4)	6542(2)	1041(1)	9952(2)	34(1)
C(5)	5242(2)	1471(1)	10058(1)	34(1)
N(1)	4172(2)	1179(1)	9259(1)	35(1)
N(2)	4260(2)	142(1)	7716(1)	42(1)
N(3)	6340(1)	486(1)	9113(1)	35(1)
N(4)	7946(2)	1089(1)	10691(1)	40(1)
N(5)	4936(2)	2144(1)	10796(1)	43(1)
O(21)	3229(2)	423(1)	7099(1)	54(1)
O(22)	4810(2)	-488(1)	7566(2)	59(1)
O(41)	9014(2)	681(1)	10408(2)	64(1)
O(42)	7939(2)	1531(1)	11568(1)	54(1)
O(51)	5810(2)	2670(1)	10643(2)	60(1)
O(52)	3822(2)	2136(1)	11487(2)	69(1)
<i>(Molecule 2)</i>				
C(1')	7884(2)	3548(1)	2680(2)	50(1)
C(2')	5516(2)	4302(1)	1961(2)	38(1)
C(4')	3785(2)	3922(1)	3142(2)	39(1)
C(5')	5083(2)	3520(1)	3431(2)	37(1)
N(1')	6231(2)	3768(1)	2663(1)	37(1)
N(2')	6283(2)	4685(1)	928(2)	48(1)
N(3')	4063(2)	4417(1)	2217(2)	42(1)
N(4')	2231(2)	3849(1)	3646(2)	51(1)
N(5')	5336(2)	2915(1)	4318(2)	49(1)
O(21')	7312(2)	4348(1)	387(2)	64(1)
O(22')	5804(2)	5312(1)	670(2)	70(1)
O(41')	1355(2)	4375(1)	3540(2)	66(1)
O(42')	1921(2)	3253(1)	4145(3)	97(1)
O(51')	4779(3)	2975(1)	5338(2)	82(1)
O(52')	6070(2)	2370(1)	3934(2)	77(1)

[a] × 10⁴; [b] Unit : Å² × 10³; [c] Defined as one third of the trace of the orthogonalized U_{ij} tensor; [d] See Figure 1 for the numbering scheme.

Table 2
Bond Lengths [a] and Angles [b] for **1** from X-ray Experiments

(1) Bond lengths

	(Molecule 1)	(Molecule 2)
C(1)-N(1) [c]	1.479(2)	1.477(2)
C(2)-N(3)	1.299(2)	1.298(2)
C(2)-N(1)	1.356(2)	1.355(2)
C(2)-N(2)	1.455(2)	1.454(2)
C(4)-N(3)	1.341(2)	1.343(2)
C(4)-C(5)	1.360(2)	1.361(2)
C(4)-N(4)	1.4474(19)	1.449(2)
C(5)-N(1)	1.359(2)	1.358(2)
C(5)-N(5)	1.453(2)	1.449(2)
N(2)-O(21)	1.212(2)	1.215(2)
N(2)-O(22)	1.223(2)	1.217(2)
N(4)-O(41)	1.210(2)	1.205(2)
N(4)-O(42)	1.221(2)	1.212(2)
N(5)-O(51)	1.2083(19)	1.195(2)
N(5)-O(52)	1.212(2)	1.225(2)

(2) Bond angles

	(Molecule 1)	(Molecule 2)
\angle N(3)-C(2)-N(1)	115.05(14)	115.56(15)
\angle N(3)-C(2)-N(2)	122.12(14)	121.68(15)
\angle N(1)-C(2)-N(2)	122.77(14)	122.61(15)
\angle N(3)-C(4)-C(5)	111.08(13)	111.22(15)
\angle N(3)-C(4)-N(4)	121.10(14)	119.76(15)
\angle C(5)-C(4)-N(4)	127.57(15)	128.94(15)
\angle C(4)-C(5)-N(1)	107.01(13)	107.04(14)
\angle C(4)-C(5)-N(5)	130.87(14)	131.24(16)
\angle N(1)-C(5)-N(5)	122.06(13)	121.68(15)
\angle C(2)-N(1)-C(5)	103.43(12)	103.22(13)
\angle C(2)-N(1)-C(1)	129.82(14)	128.99(15)
\angle C(5)-N(1)-C(1)	126.51(13)	127.59(15)
\angle O(21)-N(2)-O(22)	125.89(15)	126.04(17)
\angle O(21)-N(2)-C(2)	117.75(14)	117.63(15)
\angle O(22)-N(2)-C(2)	116.35(14)	116.31(16)
\angle C(2)-N(3)-C(4)	103.41(13)	102.96(14)
\angle O(41)-N(4)-O(42)	125.39(15)	125.18(17)
\angle O(41)-N(4)-C(4)	117.66(15)	118.38(16)
\angle O(42)-N(4)-C(4)	116.94(14)	116.44(15)
\angle O(51)-N(5)-O(52)	125.82(15)	125.71(18)
\angle O(51)-N(5)-C(5)	116.48(14)	118.05(17)
\angle O(52)-N(5)-C(5)	117.68(15)	116.20(17)

[a] Unit: Å; [b] Unit: degree; [c] See Figure 1 for the numbering scheme.

In Figure 1, it is shown that the three-nitro groups are substituted on C(2), C(4) and C(5) positions of the imidazole ring. The bonds of C(2)-N(2), C(4)-N(4) and C(5)-N(5) of the nitro groups are not coplanar with the imidazole ring and displaced -0.0975 Å, -0.0676 Å and 0.1100 Å from the imidazole ring, respectively. The 2-, 4- and 5-nitro groups are also twisted out of the imidazole plane by 24.2°, 9.8° and 39.5°, respectively. The bond lengths within the planar imidazole ring are similar to those of 2,4-dinitroimidazole [5]. As expected, the shortest C-N bond is C(2)-N(3) [1.2970(18) Å] which means a double bond localization and this is in good agreement with those reported in 2,4-dinitroimidazole [5] and 1,4-dinitroimidazole [10].

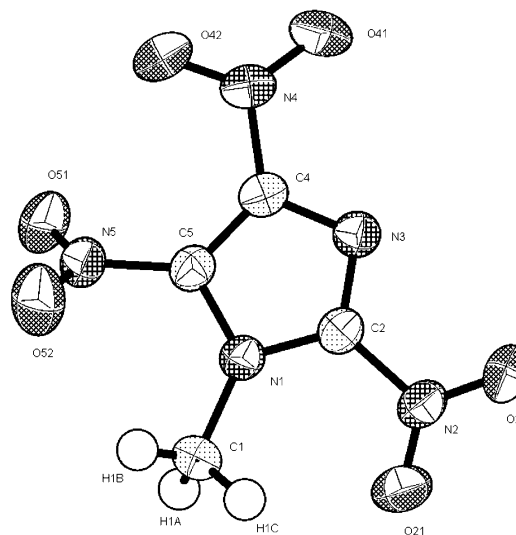


Figure 1. Molecular structure with atomic numbering scheme showing 50% probability displacement ellipsoids. H-atoms are drawn as small spheres of arbitrary radii.

c. Theoretical Studies on Molecular Structure and Explosive Performance.

The structure of **1** was fully optimized at the B3LYP/6-31G** and BP86/6-31G** levels by using the Gaussian-94 series of programs [11]. The important geometric parameters calculated at these levels are summarized in Table 3 along with those observed from X-ray experiments. As shown in Table 3, our calculated bond lengths and angles are in good agreement with those

Table 3

Selected Geometric Parameters [a] of **1** 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]
C(1)-N(1)	1.479	1.480	1.478
C(2)-N(3)	1.314	1.327	1.299
C(2)-N(1)	1.371	1.383	1.355
C(2)-N(2)	1.462	1.470	1.455
C(4)-N(3)	1.342	1.349	1.342
C(4)-C(5)	1.386	1.400	1.361
C(4)-N(4)	1.447	1.453	1.448
C(5)-N(1)	1.375	1.383	1.359
C(5)-N(5)	1.460	1.468	1.451
\angle N(3)-C(2)-N(1)	114.12	114.06	115.31
\angle N(3)-C(4)-C(5)	110.79	111.02	111.15
\angle C(4)-C(5)-N(1)	106.51	106.35	107.03
\angle C(2)-N(1)-C(5)	104.02	104.15	103.33
\angle C(2)-N(3)-C(4)	104.56	104.41	103.19

[a] Units are Å in bond lengths, degrees in bond angles; [b] Numbering scheme is shown in Figure 1; [c] Average values of two molecules in the asymmetric unit.

measured from X-ray experiments. According to this comparison of the geometries of the structures obtained from theoretical and X-ray experiments, we feel confident that further predictions of explosive performances can be made based on theoretical experiments.

By utilizing *ab initio* calculated structures and energies, we estimated the heat of formation in the solid phase, and the density. We used the 'group additivity method' developed by Stine [12] and by Ammon and coworkers [13] to estimate the density of **1**. Both methods calculated the density of **1** to be *ca.* 1.82-1.84 g/cc, which are 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.* [14,15] and correcting the sublimation energy [16].

The various explosive performances of **1**, computed by the Cheetah 2.0 program [17], are depicted in Figure 2 and compared with those of RDX which is one of the most commonly used explosives in recent military applications. As shown in Figure 2, the explosive performances were initially predicted to be quite comparable to those of RDX, when the density was computed by 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.

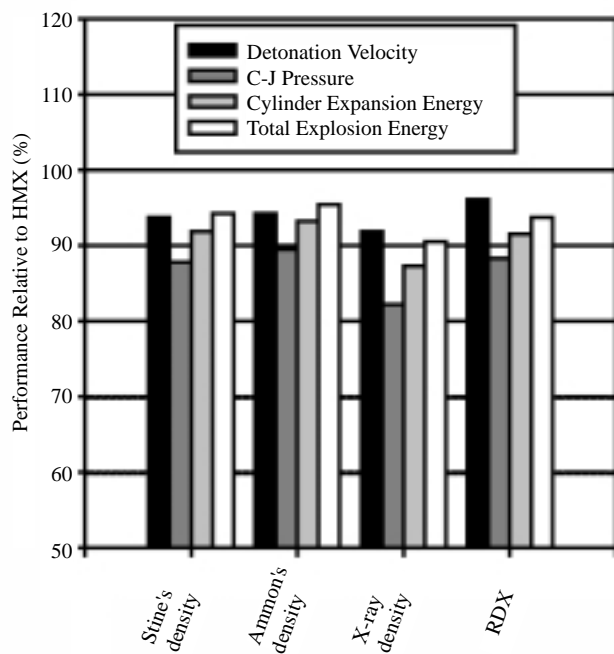


Figure 2. Explosive performances of **1** compared with those of RDX calculated by the Cheetah 2.0 program.

d. Characterization of Thermal Behavior and Sensitivities.

We measured the melting point of **1** synthesized in our lab with a Differential Scanning Calorimeter (DSC), and found it to be 82 °C, which concurs with the result reported previously (see Figure 3). We also studied the thermal behavior by using a Thermogravimeter (TG). In the TG curve shown in Figure 4, Compound **1** started to evaporate at 190 °C and reached a peak at 280 °C, which indicated that **1** is thermally stable at least up to 190 °C.

The impact sensitivity of **1** was tested with a Julius Peter's Tester according to the procedure of MIL-STD-1751A, Method 1015. The test results are summarized in Table 4. The test was performed after drying the sample for 4 hours at 60 °C. At the time of the test, the room temperature was 22 °C and relative humidity was 68 %. The 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, **1** appears to be less sensitive to impact. When the friction sensitivity of **1** was also measured with Julius Peter's Tester according to the procedure of MIL-STD-1751A, Method 1024 under the same conditions, **1** was proved to be as insensitive as TNT to friction (Table 4).

We compared the density of **1** with those of other important explosives in Table 5. The density value measured by Archimedes method from the crystal of **1** at 25 °C is 1.752 g/cm³. According to our experimental result, the density of **1** is higher than that of Comp B, but slightly lower than that of RDX. When we carried out the calculations of explosive performance with the density value observed experimentally, **1** was predicted to have a performance value almost the same as RDX.

In conclusion, we believe that we have extended the horizon of nitroimidazole chemistry by examining various aspects of **1** carefully, *i.e.* synthesis, theoretical calculations, X-ray structure elucidation, and explosive performance. Since the explosive performance of **1** appears to be quite close to that of RDX, **1** may find itself to be one of the main explosive fillers for various warheads and ammunitions in the near future. Besides high explosive performance, it should be worthwhile to mention two other potential merits of **1**; (1) insensitiveness and (2) low melting point. Thus, **1** can be an excellent ingredient for explosive formulations with high power as well as great safety. In addition, since the melting point of **1** is almost as low as that of TNT, **1** is very easy to process to fill various shapes of warheads and ammunitions by casting melted slurries, which is not possible with other nitramine explosives whose melting points are much higher. If the economic issues are resolved, we may replace the modestly powerful TNT by **1** with greater power. Currently, we are optimizing the synthetic scheme of **1** and, at the same time, enhancing the production scale by working with a reaction calorimeter. These results will be presented in due course.

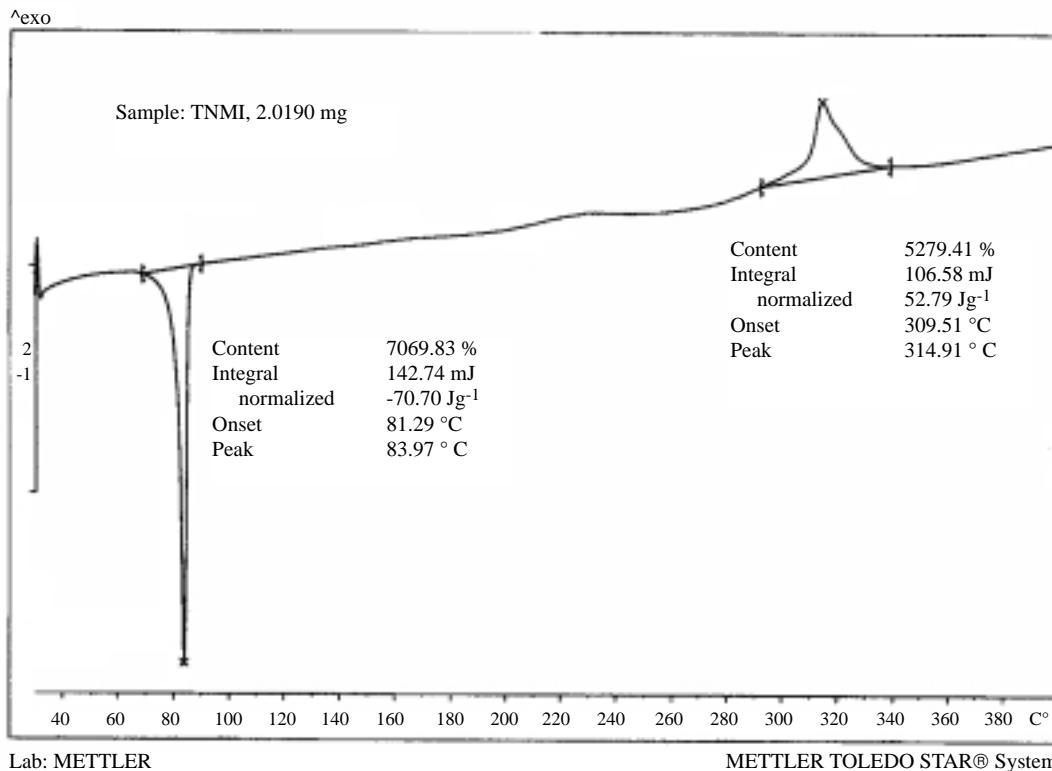


Figure 3. DSC curve of 1.

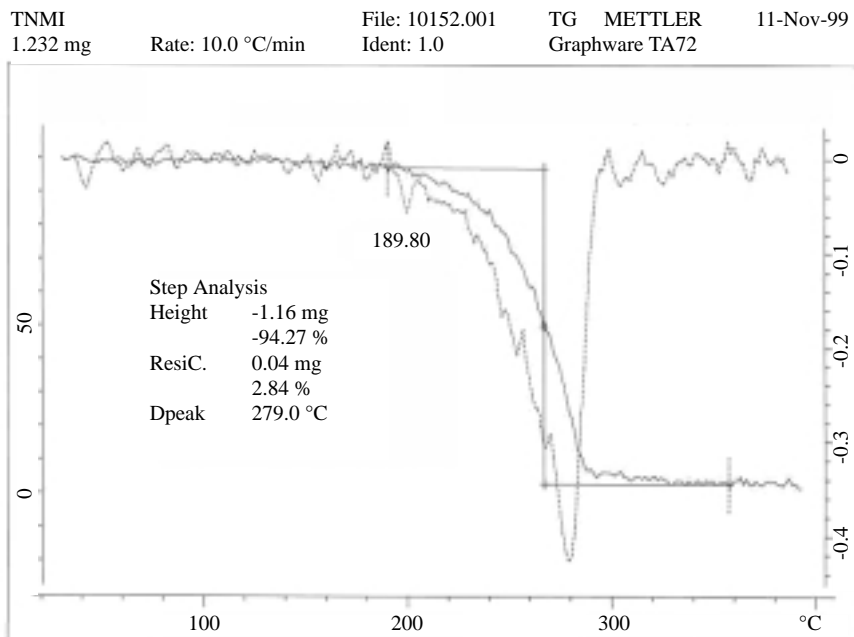


Figure 4. TG curve of 1.

Table 4
Impact and Friction Sensitivities [a] of **1** Summarized
along those of some other Important Explosives

Explosives	Impact	Friction
(Experimental values)		
1	14.6	N.R.
HMX (Class 1) [b]	5.4	11.6
(Literature values)		
TNT [c]	47.0	N.R.
Comp B [d]	19.8	29.1
RDX	7.4	16.1
HMX	6.5	10.6
PETN [e]	4.8	4.5

[a] Units in J; [b] Experiments were performed at the same time and same testers with **1**; [c] 2,4,6-Trinitrotoluene; [d] An explosive composition with 39.5 % of TNT, 59.5 % of RDX, and 1 % of wax; [e] Pentaerythritol tetranitrate.

Table 5
Density Values [a] of **1** Summarized along those
of with some other Important Explosives

Explosives	Density	Remark
1	1.768	calculated from the crystal data
	1.752	measured
(Literature values)		
TNT	1.65	
Comp B	1.72	
RDX	1.80	
HMX	1.89	
PETN	1.76	

[a] Unit in g/cm³.

EXPERIMENTAL

Melting points and decomposition temperatures were determined on a Differential Scanning Calorimeter, DSC 30 or DSC 821^e from Mettler Toledo. The thermogravimetric analyses were performed on a TG 50 from Mettler. In general, the rate of increase in temperature was 10 °C/minute. NMR spectra were obtained on a 200 MHz BRUKER AC 200 using deuteriochloroform, deuterioacetone, or deuteriodimethyl sulfoxide as solvent. Chemical shifts (δ) are given in ppm relative to tetramethylsilane ($\delta = 0$) for spectra run in deuteriochloroform ($\delta = 7.24$), deuterioacetone ($\delta = 2.04$), or deuteriodimethyl sulfoxide ($\delta = 2.49$ and 39.5). C, H and N elemental analyses were obtained from CHNS-O E.A. 1108 of Carlo Erba Instruments.

4-Nitroimidazole (**3**).

In a 1 L round-bottomed-3-neck flask equipped with a thermometer and a dropping funnel, 100 g of imidazole (**2**) (1.47 mole) was charged. To the above flask, 400 mL of 70 % nitric acid was added dropwise over 30 minutes at room

temperature. When the reaction mixture turned transparent, the solution was cooled to 5 °C. With stirring, 200 mL of 100 % sulfuric acid was added slowly over 1 hour. After being refluxed for 8 hours at 125 °C (bath temperature: 145 °C), the reaction mixture was cooled to room temperature. When the product mixture was poured over crushed ice (3 kg), **3** was precipitated as a white powder. When the mixture was still cold, **3** was filtered quickly, washed with cold water, and dried to obtain 76.5 g (46 %) of **3**. The structure was confirmed with DSC, ¹H- and ¹³C-NMR, and CHN analysis. mp 308 °C (on DSC); ¹H-NMR (dimethyl sulfoxide-d₆): δ (ppm) 7.8 (s, 1H, C₂H), 8.3 (s, 1H, C₅H), 13.2 (br, 1H, NH); ¹³C-NMR (dimethyl sulfoxide-d₆): δ (ppm) 119.2 (C₅), 136.0 (C₂). (The peak of C₄ was not detected.)

Anal. Calcd. for C₃H₃N₃O₂ (mw 113.08): C, 31.87; H, 2.67; N, 37.16. Found: C, 31.60; H, 2.36; N, 36.9.

1,4-Dinitroimidazole (**4**).

To 113.7 mL of acetic acid (1.99 mole) placed in a 500 mL 3-necked round-bottom flask was added 50 g of **3**, and the mixture cooled to 0 °C. To the stirred mixture, 100 % nitric acid (36.4 mL, 0.91 mole) was added dropwise slowly over 30 minutes. The reaction temperature was controlled between 0 to 15 °C. Acetic anhydride (84.6 mL, 0.90 mole) was added over 30 minutes to 1 hour at room temperature. After stirring for 2 days at room temperature, the product mixture was poured over crushed ice (900 g) to precipitate **4** as a white powder. When the mixture was still cold, **4** was filtered quickly, washed with cold water to remove trace acid, and dried to obtain 43.2 g of **4**. There are still large amounts of **4** in the acidic aqueous solution. This material was isolated by filtration, from which 23.1 g of **4** was recovered by extraction with methylene chloride. The total yield was 95 %. The synthesized **4** contained about 3 % of **3** typically. Because **3** is hardly soluble in methylene chloride, most of **3** can be removed easily using methylene chloride. The structure of **4** was confirmed with DSC, ¹H- and ¹³C-NMR; mp 92 °C (by DSC); ¹H-NMR (dimethyl sulfoxide-d₆): δ (ppm) 9.0 (s, 1H, C₂H), 9.4 (s, 1H, C₅H); ¹³C-NMR (dimethyl sulfoxide-d₆): δ (ppm) 115.5 (C₅), 132.5 (C₂). (The C₄ resonance was not detected.)

2,4-Dinitroimidazole (**5**).

Compound **4** (30.0 g, 0.19 mole) in 250 mL of chlorobenzene was placed in a 1 L flask and refluxed overnight at 115 °C. When the reaction mixture was cooled to room temperature, **5** was precipitated. Filtration and drying gave 27.82 g of **5** (93 %). The structure was confirmed with ¹H- and ¹³C-NMR, and CHN analysis; ¹H-NMR (dimethyl sulfoxide-d₆): δ (ppm) 8.6 (s, 1H, C₅H), 14.5 (br, 1H, NH); ¹³C-NMR (dimethyl sulfoxide-d₆): δ (ppm) 123.1 (C₅), 144.0 (C₂). (The C₄ resonance was not detected.)

Anal. Calcd. for C₃H₂N₄O₄ (mw 158.07): C, 22.80; H, 1.28; N, 35.44. Found: C, 23.20; H, 1.16; N, 35.10.

Potassium 2,4,5-Trinitroimidazolate (**7**).

In a 250 mL round bottom flask, **5** (12.13 g, 0.077 mole) and 100 % nitric acid (38.5 mL, 0.962 mole) were placed and refluxed for 5 minutes in a preheated oil bath at 100 °C. After cooling to room temperature, 100 % sulfuric acid (54.7 mL, 1.03 mole) was added dropwise and the resulting mixture was refluxed again for 15 minutes. The reaction mixture was cooled to room temperature, and poured over crushed ice (400 g). The

pH of aqueous solution was controlled between 0.5 and 1.0 using saturated sodium bicarbonate solution, and the aqueous solution was then extracted 5 times with ether. The combined ether extracts were dried over anhydrous magnesium sulfate to obtain a dry ether solution of 2,4,5-trinitroimidazole (**6**). The above ether solution of **6** was neutralized with the saturated K_2CO_3/KCl (50:50) until the evolving of CO_2 gas ceased. The resultant precipitate was filtered then washed with a minimal amount of water and vacuum dried. This afforded orange colored powder of **7** (11.03 g, 60 %). This compound could not be identified with 1H - and ^{13}C -NMR, and CHN analysis. Only the decomposition temperature, 231 °C, could be measured on the DSC. The synthesized compound was proved to be **7** by the ultimate success in making **1** using **7**.

1-Methyl-2,4,5-trinitroimidazole (MTNI) (**1**).

Compound **7** (4.8 g, 0.020 mole) was dissolved in 120 g of hydrochloric acid (1:1) to regenerate **6**. The aqueous solution was extracted with ether 4 times and methylated with diazomethane. To obtain diazomethane, Diazald from Aldrich was utilized by the known method [9]. The resultant ether solution was dried and evaporated to give 1.57 g of 1-methyl-2,4,5-trinitroimidazole (36 %). The structure was confirmed with DSC, 1H - and ^{13}C -NMR, CHN analysis, and X-ray crystallography; mp 82 °C (on DSC); 1H -NMR (acetone- d_6): δ (ppm) 4.4 (s, 3H, CH_3); ^{13}C -NMR (acetone- d_6): δ (ppm) 37.7 (CH_3), (The peaks of imidazole ring C were not detected.).

Anal. Calcd. for $C_4H_3N_5O_6$ (mw 217.10): C, 22.13; H, 1.39; N, 32.26. Found: C, 22.60; H, 1.78; N, 32.00.

X-Ray Structure Determination.

A yellow crystal of **1**, grown in ethanol solution at room temperature, of approximate dimensions $0.45 \times 0.50 \times 0.56$ mm³, was used for data collection. Diffraction experiment was performed on a Bruker SMART diffractometer equipped with a CCD area detector using Mo K_{α} radiation ($\lambda = 0.71073$ Å).

The crystal structure of compound **1** was found to be orthorhombic, which belongs to space group $Pca2_1$ with crystallographic parameters of $a = 8.6183(6)$ Å, $b = 17.7119(12)$ Å, $c = 10.6873(7)$ Å, $V = 1631.38(19)$ Å³, $M = 217.11$, $Z = 8$, $\mu = 0.167^{-1}$ mm, $F(000) = 880$ and $D_c = 1.768$ g/cm³. The unit cell parameters were refined by a least-squares fit of the setting angles of 20 reflections in the range $0 < \theta < 28^\circ$. A total of 3741 measured reflections were obtained in the range of $2.3 < 2\theta < 55^\circ$, out of which 3201 independent reflections with $I > 2\sigma(I)$ were used for the determination and refinement of the crystal structure of **1**. Intensity data were corrected for Lorentz and polarization effects and were empirically corrected for absorption using the psi-scan method.

The crystal structure of **1** was solved by direct method with SHELXTL [18] and refined by full-matrix least squares on F^2 with anisotropic displacement parameters for all non-hydrogen atoms. All hydrogen-atoms were generated in idealized positions and refined in a riding model. The function minimized was $wR = \{ \sum [w(F_0^2 - Fc^2)]^2 / \sum [(F_0^2)^2] \}^{1/2}$. w , the weight of each reflection, was defined as $1 / [\sigma^2(F_0^2) + (0.0537P)^2 + 0.0340P]$, where $\sigma^2(F_0^2)$ came from counting statistics and $P = [F_0^2 + 2Fc^2] / 3$. The final R and weighted R factors were 0.0284 and 0.0795, respectively. The number of parameters refined was 273 and goodness of fit was 1.058.

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