工學博士 學位論文

Synthesis of bisnitropyrazolylmethane and dialkyl-dinitro-imidazolium as candidates for new high energy materials

새로운 고에너지물질 후보물질로서 비스니트로피라졸릴메테인 및 디알킬디니트로이미다졸리움의 합성

2021年 2月

서울大學校 大學院
化學生物工學部
金 南 泰

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金 南 泰의 工學博士 學位論文을 認准함

2020年 12月

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Synthesis of bisnitropyrazolylmethane and dialkyl-dinitro-imidazolium as candidates for new high energy materials

A THESIS SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN ENGINEERING AT THE GRADUATED SCHOOL OF SEOUL NATIAONAL UNIVERSITY

February 2021

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ABSTRACT

The azole compounds substituted with nitro groups have a difficulty in that their explosive performance is improved but their nucleophilicity is decreased as electron-withdrawing nitro groups are additionally introduced. For this reason, it remains a challenging task to synthesize new high-energy materials (HEMs) via alkylation of the nitroazoles. In this thesis, the results of synthetic studies for new nitroazoles based HEMs are presented via their alkylation reactions using selected reagents with high electrophilicity or applying appropriate reaction conditions.

First, the *N*,*N'*-methylene bridged coupling reaction of 4-chloro-3,5-dinitro-1*H*-pyrazole (ClDNP) **1** was studied. ClDNP **1** is known to have a difficulty for coupling reaction due to its reduced nucleophilicity. Bis(4-chloro-3,5-dinitro-1*H*-pyrazol-1-yl)methane **2** was obtained in a yield of 79% under reaction conditions in which highly electrophilic diiodomethane was used excessively. It is expected that these reaction conditions of using the excess alkylation reagent could be applied to the

coupling reaction of the nitroazole-based material having reduced nucleophilicity. Compound **2** is expected to be a useful precursor of new HEMs because it is easy to change its reactive chloro groups with energetic functional groups. In fact, bis(4-azido-3,5-dinitro-1*H*-pyrazol-1-yl)methane **3** was obtained in 77% yield by substituting the chloro group of **2** with energetic azido group under mild reaction condition. Compound **3** is expected to be used as a new green primary explosive candidate as it has better thermal stability and explosive performance than DDNP (2-diazo-4,6-dinitrophenol), a widely used military primary explosive.

Second, the synthesis of 4,5-dinitro-*N*,*N'*-dialkylimidazolium cations was studied by quaternizing 4,5-dinitroimidazoles via alkylation reactions. In the research field of energetic ionic liquids (EILs), dinitroimidazoles have been reported to be unable to be quaternized due to the electron-withdrawing effect nitro groups substituted on them. In order to achieve this challenging task, it was necessary to select a more reactive alkylating reagent than methyl triflate. This challenge was

overcome by using Meerwien's reagents (R_3OBF_4) as more reactive alkylating reagents. As a result of quaternization reaction of 4,5-dinitro-1*H*-imidazole **4** and 1-methyl-4,5-dinitro-1*H*-imidazole **5** using triethyloxonium tetrafluoroborate ($Et_3O^+BF_4^-$), 1,3-diethyl-4,5-dinitro-1*H*-imidazol-3-ium tetrafluoroborate ([1,3-diEt-4,5-diNO_2-Im][BF_4]) **6** and 3-ethyl-1-methyl-4,5-dinitro-1*H*-imidazol-3-ium tetrafluoroborate ([3-Et-1-Me-4,5-diNO_2-Im][BF_4]) **7** were obtained. Newly obtained compounds **6** and **7** are expected to be used as precursors for new HEMs via metathesis reaction with energetic anions. In fact, two new HEMs candidates, 1,3-diethyl-4,5-dinitro-1*H*-imidazol-3-ium 2,4,5-trinitroimidazol-1-ide ([1,3-diEt-4,5-diNO_2-Im][2,4,5-triNO_2-Im]) **8**, 3-ethyl-1-methyl-4,5-dinitro-1*H*-imidazol-3-ium 2,4,5-trinitroimidazol-1-ide ([3-Et-1-Me-4,5-diNO_2-Im][2,4,5-triNO_2-Im]) **9** were also obtained via anion metathesis reaction with energetic 2,4,5-trinitroimidazolate anion. Compound **9** showed the promising properties as a new insensitive HEM because of its excellent insensitivity and more powerful explosive performance than those of TNT (2,4,6-trinitrotoluene).

Keywords: High-energy materials, Explosives, Primary explosives, Energetic ionic liquids, nitroazoles, alkylation reaction, Meerwein's reagents

Student number: 2017-31412

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

LIST OF SCHEMES

LIST OF ABBREVIATIONS

aq.	Aqueous
br	broad
BAM	Bundesanstalt für materialprüfung
calcd	calculated
CH_2Br_2	Dibromomethane
CH_2Cl_2	Dichloromethane
CH_2I_2	Diiodomomethane
d	doublet
DDNP	2-diazo-4,6-dinitrophenol
DMSO	Dimethylsulfoxide
DMF	*N*,*N*-Dimethylformamide
DSC	Differential scanning calorimetry
EDC	1,2-Dichloroethane
EA	Elemental analysis
EILs	Energetic ionic liquids
Equiv or eq.	Equivalent
EtOAc	Ethyl acetate
$Et_3O^+BF_4^-$	Triethyloxonium tetrafluoroborate
FAB	Fast atom bombardment
FT-IR	Fourier-transform infrared spectroscopy

g	gram(s)
H_2SO_4	Sulfuric acid
HBF_4	Tetrafluoroboric acid
HEMs	High-energy materials
HNO_3	Nitric acid
HRMS	High resolution mass spectra
Hz	hertz
IR	infrared (spectrum)
ILs	Ionic liquids
J	coupling constant(s)
Li_2CO_3	Lithium carbonate
$Me_3O^+BF_4^-$	Trimethyloxonium tetrafluoroborate
min	minute(s)
Mp	Melting point
NaN_3	Sodium azide
NMR	Nuclear magnetic resonance
NCS	N-chlorosuccinimide
THF	Tetrahydrofuran
TGA	Thermogravimetric analysis

Chapter I: Synthesis of bis(4-azido-3,5-dinitro-1H-pyrazol-1-yl)methane as a green primary explosive

Introduction

1. High-energy materials (HEMs)

High-energy materials (HEMs) are a general term for various explosives (explosives, propellants, pyrotechnics), and in recent years it is mainly used to refer to high performance explosives. HEMs have been developed in various forms since the first invention of black powder in China in the 7th century. Since the invention of nitroglycerin (NG) and dynamite using it, rapid development has been achieved.[1]

HEMs are classified into explosives, propellants and pyrotechnics according to the purpose of use. Among them, explosives refer to substances that rapidly release heat and pressure by causing a continuous exothermic decomposition reaction of their constituents themselves when triggered by specific external stimuli.[2] In general, the temperature generated during an explosion reaches 3000 to 5000 °C, and the volume

expansion by the generated gas is in the range of 12000 to 15000 times. These explosions occur within a few microseconds and are accompanied by shock waves and roaring sounds.

Explosives are classified into high explosives, low explosives, pyrotechnics, and civil explosives again according to their nature, and this paper focuses on the development of high explosives (Figure 1).[1,3] Depending on the intensity of the explosion, it is largely divided into high explosives (v_d = detonation velocity, v_d = 5000~10000 m s^{-1}) and low explosives (v_d = 300~3000 m s^{-1}). High explosives are subdivided into primary, secondary, and tertiary explosives according to their explosive properties and sensitivity.

Primary explosives are highly sensitive and easily explode even with weak external stimuli (impact, spark, friction, etc.). For this reason, it must be handled very carefully. They are mainly used in detonators, primers, and percussion caps. Representative explosives that are widely used are lead azide (LA), silver azide (SA) and mercury fulminate.

Secondary explosives are relatively insensitive to external shocks compared to primary explosives, but they cause very high explosive shocks when exploding. In order to detonate the secondary explosive, a small amount of the primary explosive is required as a detonator or booster.

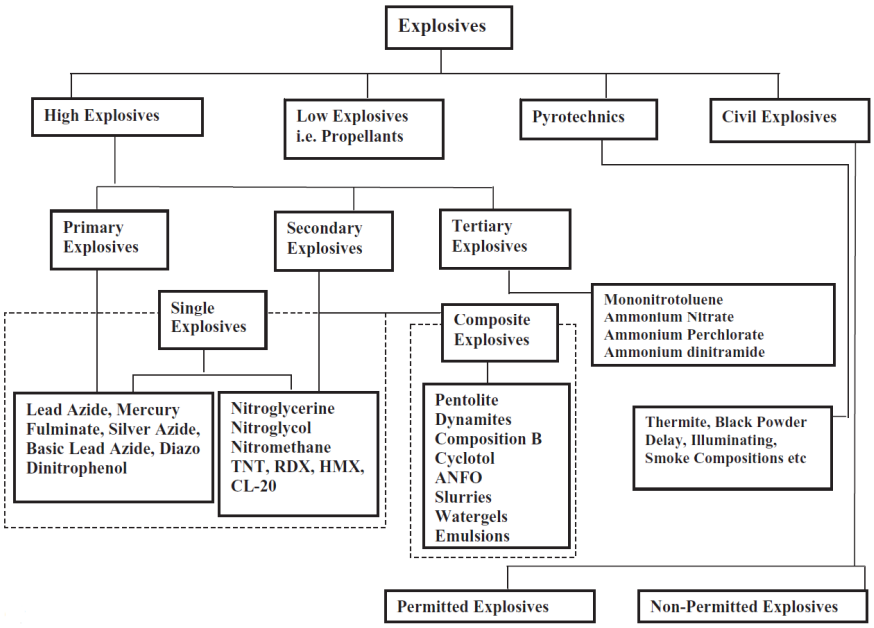


Figure 1. Classification of explosives according to nature of explosive.[1]

Pentaerythritol tetranitrate (PETN) is a representative benchmark explosive that distinguishes between primary and secondary explosives. Primary explosives are usually more sensitive than PETN.Another difference is that the primary explosive is detonated by burning while the secondary explosive is detonated by the shock wave.

2. Properties of explosives

Explosives are characterized by the heat of formation, heat of explosion, detonation velocity (D), detonation pressure (P), and impact sensitivity

of the compounds. Among them, the most commonly used indicators are the explosive velocity (v_d), the explosive pressure (P), and the impact sensitivity related to the stability of the compound. The explosive properties of representative explosives developed and used in recent years can be represented by a graph as shown in the figure below (Figure 2).[4] In general, it can be seen that the explosive performance of an explosive and its insensitivity have a trade-off relationship.

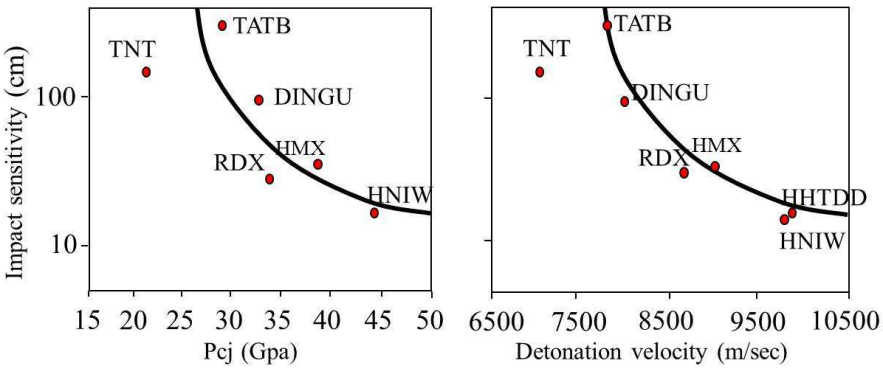


Figure 2. Relationship between explosive performances and sensitivity.

2.1. Explosophores

However, the explosive performance and sensitivity of explosives do not always have a trade-off correlation. There are many exceptions to the correlation of these explosive properties (for example, cases in which an

increase in explosive performance and a decrease in sensitivity have occurred when a specific energetic functional group in a specific explosive is changed). Reflecting these exceptions, recent research results tend to recognize the correlation between the explosive performance and sensitivity of explosives as a trend rather than as a defined correlation.[5]

Their trends show a lot of difference depending on the stability of organic compounds that make up the skeleton of HEMs, and the properties of explosophores, a functional group that imparts explosive properties. As representative frameworks for HEMs, azoles contain nitrogen or oxygen as well as carbon as heterocyclic compounds, so they have higher thermal stability, heat of formation, and density than their carbocyclic analogs composed of only carbon. In addition, they can have excellent stability due to their aromaticity. In organic chemistry, explosophores refer to functional groups that provide explosive properties to organic compounds. The term was first used in 1935 by V. Pletz, a Russian chemist.[6] Among the representative classifications (Table 1), Comparing the nitro ($-NO_2$) and azido ($-N_3$) groups, when the nitro group is introduced compared to the azido group, the explosive performance is greatly improved, but the sensitivity is relatively less. On the other hand, when the azido group is introduced, the explosive performance is improved, but the sensitivity is greatly increased. The

introduction of the azido group is preferred for the synthesis of primary explosives that require higher sensitivity using this difference in characteristics.

Table 1. Categories of explosophores.[7]

Category	Functional group	Remarks
I	$-NO_2$, $-ON=O$ and $-ONO_2$	Both inorganic and organic substances
II	$-N=N-$ and $-N^{-}=N^{+}=N^{-}-$	Inorganic and organic azides and diazo compounds.
III	$-R_nNX_m$	X = halogen
IV	$-C=N-O-$	Fulminates
V	$-OClO_2$ and $-OClO_3$	Inorganic and organic chlorates and perchlorates
VI	$-O-O-$ and $-O_3$	Inorganic and organic peroxides and ozonides
VII	$-C\equiv C-$	Acetylene and metal acetylides
VIII	M–C	Metal bonded with carbon in some organometallic compounds.

2.2. Detonation velocity

Detonation velocity (v_d), a property representing the performance of explosives, can be calculated through calculation if the chemical structural formula of the compound is known. The detonation velocity (v_d) of the compound consisting of C, H, N, and O can be calculated through the following empirical formula:[1]

v_d = (F - 0.26)/0.55 (eq. 2.2.1)

$$F = \frac{100}{MW}\left[n(O) + n(N) - \left(\frac{n(H)}{2n(O)}\right) + \left(\frac{A}{3}\right) - \left(\frac{n(B)}{1.75}\right) - \left(\frac{n(C)}{2.5}\right) - \left(\frac{n(D)}{4}\right) - \left(\frac{n(E)}{5}\right)\right] - G \quad \text{(eq. 2.2.2)}$$

v_d = detonation velocity

G, A = constant depend on physical state and structure

MW = molecular weight

n(O), n(N), n(H) = number of oxygen, nitrogen, hydrogen atoms

n(B) = number of oxygen atoms in excess of those already available to form CO_2 and H_2O

n(C) = number of oxygen atoms double bonded to carbon as in C=O

n(D) = number of oxygen atoms singly bonded directly to carbon in C-O-R linkage where R = H, NH_4 or C

n(E) = number of nitrate group as nitrate-ester or nitrate salt

The detonation velocity (v_d) and detonation pressure (P) can be

calculated by using the heat of formation of the compound or additional information of the detonation product:[8]

$$v_d = \mathrm{A}\sqrt{NM^{\frac{1}{2}}\,Q^{\frac{1}{2}}(1 + B\rho_0)} \quad , \quad P = K\,\rho_0{}^2 NM^{\frac{1}{2}}Q^{\frac{1}{2}} \qquad \text{(eq. 2.2.3)}$$

A, B, K = constants

N = moles of gaseous detonation products /g

M = average molecular weight of detonation gas product

Q = ΔH_0/g, chemical energy of the detonation reaction (cal/g)

ρ_0 = initial density of explosive (g/cm^3)

2.3. Sensitivity[9]

The usefulness of explosives lies in their ability to explode on demand. Depending on the explosive, the energy required for explosion has a wide range from weak external impact to strong impact by shock wave. Hence, the sensitivity of an explosive can be said to be the amount of energy the material must absorb in order to obtain a certain probability of causing an explosive reaction. In terms of sensitivity, primary explosives are explosives with the highest sensitivity. There is no strict standard to classify each explosive according to its sensitivity, but it is generally classified into primary and secondary explosives based on the sensitivity of PETN.

2.3.1. Impact sensitivity[9]

The most representative and well-known sensitivity of an explosive is its impact sensitivity. Impact sensitivity is obtained by measuring a critical point that can cause an explosion within a certain probability range by dropping a mass on an explosive sample. The critical point measured by this method is mainly expressed as the energy (J) applied to the sample or the height (cm) at which the mass was dropped. Impact sensitivity is the main physical property of explosives; however, it may have different values depending on the crystal shape of the sample.

2.3.2. Friction sensitivity[9]

Friction sensitivity is measured by applying a specific friction load to explosive samples. Although many explosives have been tested for a long period of time to measure frictional sensitivity, it is still a difficult challenge to interpret this phenomenon quantitatively. This is because not only the factors that influence the initiation of explosives, but also their correlations are quite complex. Measurement of friction sensitivity is carried out by placing an explosive material between two specific surfaces and then moving each side simultaneously or only one side under a specific load.

3. Requirements for new green primary explosives

Primary explosives are highly sensitive to external stimuli and often used as primers or detonators for initiating main charge. Traditional primary explosives such as lead azide (LA) and mercury fulminate (MF) have proven efficient production processes, production costs, and excellent performance. However, they usually contain heavy metal elements that are harmful to the environment and the health of users. These factors are emphasized in recent research on new explosives, and eco-friendly explosives composed of only carbon (C), hydrogen (H), nitrogen (N), and oxygen (O) are mainly being developed.[9]

DDNP (2-diazo-4,6-dinitrophenol) is a representative green primary explosive. However, its low explosive performance and lack of thermal stability limit its use in many cases (Figure 3).[10]

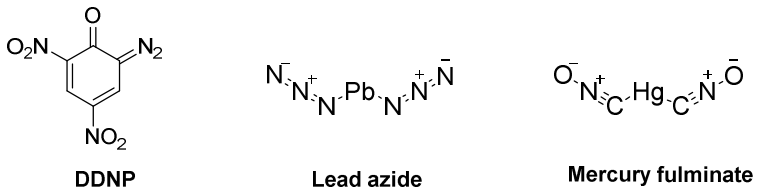
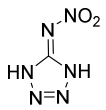


Figure 3. Representitive primary explosives.

4. Superiority of bis(nitroazolyl)alkanes structure compared to its unsubstituted nitroazoles[11]

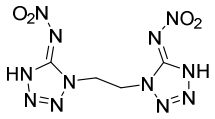
It has been empirically confirmed that nitroazoles of asymmetric structure have better explosive properties when they are synthesized into *N*,*N'*-alkane-bridged nitroazoles. This trend was investigated in bis(tetrazolyl)ethanes, previously reported high energy materials (Table 2). Except for the density, all physical properties of 1,2-bis(4,5-dihydro-5-nitroimino-1*H*-tetrazol-1-yl)ethane **B** were superior to those of unsubstituted 5-nitroiminotetrazole **A**. These differences in physical properties were estimated by the improved molecular structure symmetry of the *N*,*N'*-alkane-bridged derivative.

Table 2. Comparison of physical properties of unsubstituted 5-nitroiminotetrazole and *N*,*N'*-alkane-bridged derivative.



Compound **A**

4,5-Dihydro-5-(nitrimino)-1*H*-tetrazole



Compound **B**

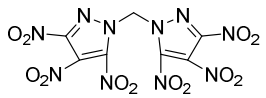
1,2-bis(4,5-dihydro-5-nitroimino-1*H*-tetrazol-1-yl)ethane

Compounds	T_d[a] (°C)	ρ[b] (g/cm^3)	P[c] (GPa)	v_d[d] (m/s)	IS[e] (J)	OB[f] (%)	ΔH_f[g] (kJ/mol)
Compound A	122	1.87	36.3	9173	1.5	-12.3	468.6
Compound B	194	1.86	38.2	9329	10	-39.1	

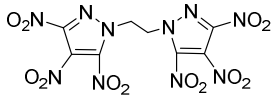
[a]Decomposition temperature, [b]Density (25 °C), [c]Detonation pressure, [d]Detonation velocity, [e]Impact sensitivity, [f]Oxygen balance, [g]Heat of formation.

5. Previous studies on the synthesis of bis(nitropyrazolyl)alkanes from nitropyrazoles

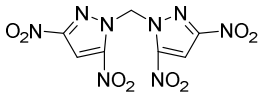
The synthesis of bis(3,4,5-trinitro-1*H*-pyrazol-1-yl)methane[12] and 1,2-bis(3,4,5-trinitro-1*H*-pyrazol-1-yl)ethane[13] have been reported, which are coupling two polynitropyrazoles through *N*,*N′*-alkyl-bridges. Each of these compounds have high explosive performances (detonation velocity, D), thermal stabilities (decomposition temperature, T_d) and relatively low impact sensitivities (IS) (Figure 4). In this regard, our group also synthesized B(3,5-DNP)M and B(3,4-DNP)M by coupling two isomeric dinitropyrazoles, and reported their predicted explosive performances.[14] These bis(dinitropyrazolyl)methanes have only two nitro groups in each pyrazole, so their explosive performances are slightly lower than that of bis(trinitropyrazolyl)methane/ethane. However, their thermal stability and insensitivity are remarkably high, so they are expected to be used as useful insensitive explosives.



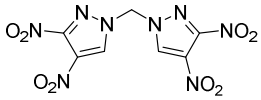
bis(3,4,5-trinitro-1*H*-pyrazol-1-yl)methane



1,2-bis(3,4,5-trinitro-1*H*-pyrazol-1-yl)ethane



bis(3,5-dinitro-1*H*-pyrazol-1-yl)methane
(**B(3,5-DNP)M**)

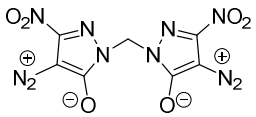


bis(3,4-dinitro-1*H*-pyrazol-1-yl)methane
(**B(3,4-DNP)M**)

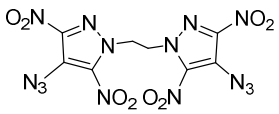
Figure 4. Reported bis(dinitropyrazole)s type secondary explosives.

6. Previous studies on the synthesis of bis(nitropyrazolyl)alkanes as primary explosives

Recently, the syntheses of bis(nitropyrazolyl)alkanes, compounds **C** and **D**, have been reported as candidates for new primary explosives (Figure 5).[12,13] Stable primary explosives with a symmetrical structure were obtained by coupling pyrazoles that were fully substituted with explosophores via an *N,N'*-alkane bridge. Despite their good physical properties, it is still difficult to simultaneously improve both the explosive performance and thermal stability. Therefore, the demand for the development of a better new green primary explosive will continue in the future.



Compound **C**
[bis(4-diazo-5-nitro-3-oxopyrazolyl)methane]

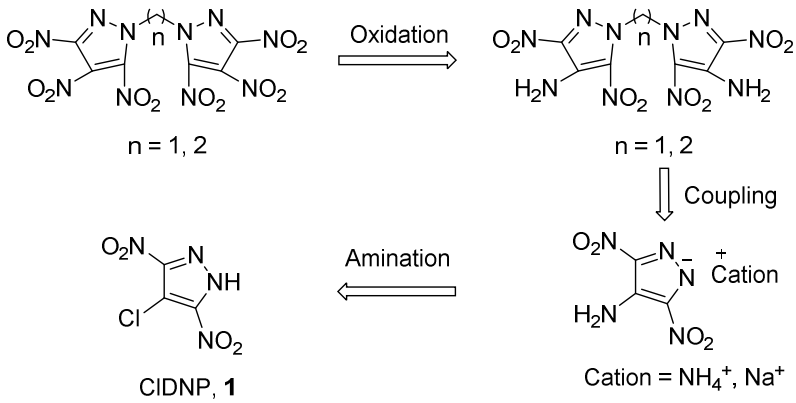


Compound **D**
[1,2-bis(4-azido-3,5-dinitro-1*H*-pyrazol-1-yl)ethane]

Figure 5. Reported bis(dinitropyrazole)s type primary explosives.

7. Previous studies on the synthesis of bis(nitropyrazolyl)alkanes from 4-chloro-3,4-dinitropyrazole 1

4-chloro-3,5-dinitropyrazole (ClDNP) **1** is attractive as a precursor of explosives because reacting 4-chloro-pyrazole with mixed acid (mixture of nitric acid and sulfuric acid) can introduce two nitro groups into the pyrazole ring via one step.[15] However, due to its low nucleophilicity, coupling to bis(nitropyrazolyl)s required high temperature and pressure reaction of **1** with aqueous ammonia solution to produce 4-amino-dinitropyrazole (LLM-116) salts for more reactivity.[12,13,15,16] This harsh reaction process has made it difficult to apply to industries (Scheme 1).

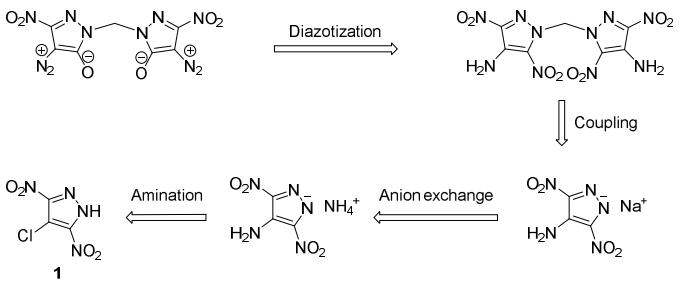


Scheme 1. Pathway for bis(polynitropyrazoles) from ClDNP **1**.

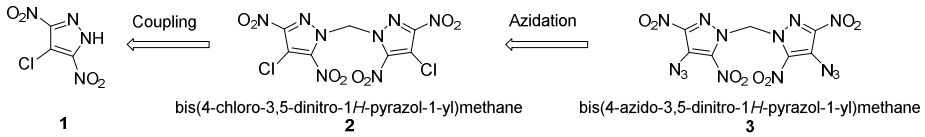
Results and Discussion

1. Synthetic strategy

After reviewing the previous studies on the synthesis of bis(nitropyrazolyl)alkanes, it was confirmed that if **1** can be directly copled, not only can the reaction step be reduced, but harsh reaction conditions can be avoided. From this point of view, a strategy to synthesize a new primary explosive by direct coupling of **1** was established (Scheme 2).



(A) Reported process: Coupling after aminatio of compound **1**



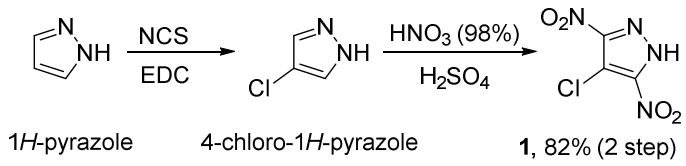
(B) New process: Direct coupling of compound **1**

Scheme 2. Synthesis of primary explosive from compound **1**.

To achieve this strategy, it is necessary to overcome the reduced nucleophilicity of **1** due to the substitution of the nitro and chloro groups, which are electron withdrawing groups. The careful selection of the reaction conditions enabled the coupling of **1** having the poor reactivity to produce **2** in a good yield. And the target compound **3** was produced by the double azidation reaction of **2** in one step. The detailed study results will be described in detail below.

2. Synthesis and characterization[18]

Compound **1** was prepared effectively in two steps from commercially available 1*H*-pyrazole with overall yield of 82% by modification of previously reported results (Scheme 3).[12,13,17]



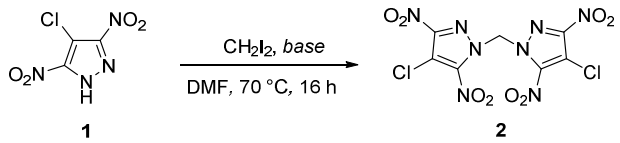
Scheme 3. Synthesis of compound **1** from 1*H*-pyrazole.

2.1. Initial screening results for coupling of ClDNP 1

To achieve the challenging coupling reaction of **1**, we have tested various reaction conditions using several bases and/or different dihalomethanes to produce *N*,*N*′-methylene bridged dinitropyrazoles. Between readily available dihalomethanes as a coupling agent, diiodomethane (CH_2I_2) was selected in the beginning because it is generally more reactive than dibromomethane (CH_2Br_2). DMF was also chosen for the reaction solvent among the polar reaction solvents screened; DMF, DMSO, and acetonitrile. When the theoretically equivalent amount of CH_2I_2 (0.5 eq.) was used (Table 3), the reactions did not proceed at all with potassium hydroxide as base or other alkali hydroxides such as NaOH, LiOH, and CsOH (entry 1-4). No reaction was also observed even with a stronger base, NaH (entry 5).

Only trace amount of **2** was observed with other alkali carbonates such as Na_2CO_3 or K_2CO_3 (entry 6, 7). On the other hand, the use of weaker base such as lithium carbonate (Li_2CO_3) yielded the expected product **2** after careful separation of the crude product mixture albeit in a poor yield (entry 9).

Table 3. Screening results for coupling of compound **1**.



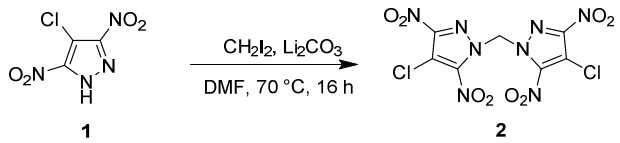
Entry	Reagent (eq.)	Base (eq.)	Yield (%)[a]
1	CH_2I_2 (0.5)	NaOH (1.0)	No reaction[b]
2	CH_2I_2 (0.5)	KOH (1.0)	No reaction[b]
3	CH_2I_2 (0.5)	$CsOH{\cdot}H_2O$ (1.0)	No reaction[b]
4	CH_2I_2 (0.5)	$LiOH{\cdot}H_2O$ (1.0)	No reaction[b]
5	CH_2I_2 (0.5)	NaH (1.0)	No reaction[b]
6	CH_2I_2 (0.5)	Na_2CO_3 (1.0)	Trace [b]
7	CH_2I_2 (0.5)	K_2CO_3 (1.0)	Trace [b]
8	CH_2I_2 (0.5)	Cs_2CO_3 (1.0)	No reaction [b]
9	CH_2I_2 (0.5)	Li_2CO_3 (1.0)	3

[a] Determined by $^{1}H/^{13}C$ NMR after purification
[b] Determined by ^{1}H NMR after extracted crude

2.2. Screening results of optimized reaction conditions for the synthesis of compound 2

According to the initial screening results, additional screening experiments were attempted to improve the reactivity of Li_2CO_3, a base that showed a desired result. The base was fixed with Li_2CO_3 and the amount of CH_2I_2 was gradually increased (Table 4). As a result, significant increases in yield were confirmed from 5 to 15 equivalents (entry 3-5). The yield increased up to 79% as the amount of Li_2CO_3 used increased, which is thought to be due to the its low solubility in DMF solvent (entry 6).

Table 4. Optimization studies for the synthesis of compound **2**.



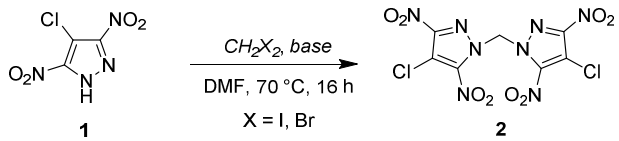
Entry	CH_2X_2 (eq.)	Base (eq.)	Yield (%)
1	CH_2I_2 (0.5)	Li_2CO_3 (1.0)	3
2	CH_2I_2 (2.0)	Li_2CO_3 (1.0)	5
3	CH_2I_2 (5.0)	Li_2CO_3 (1.0)	37
4	CH_2I_2 (10.0)	Li_2CO_3 (1.0)	54
5	CH_2I_2 (15.0)	Li_2CO_3 (1.0)	68
6	CH_2I_2 (15.0)	Li_2CO_3 (2.0)	79

2.3. Results of additional screening experiments to synthesize compound 2

Additional experiments were conducted to confirm the tendency of the coupling reaction of **2**. The reaction was studied using other bases and a coupling reagent by applying the reaction conditions optimized via the above experiments (Li_2CO_3 as a base and excess CH_2I_2 as a coupling reagent, respectively).

As a result of the experiment, in the reaction using Cs_2CO_3 as a base, the target material **2** could not be obtained at all (Table 5, entry 1). In the reaction using Na_2CO_3 and K_2CO_3 as bases, which confirmed the synthesis of a trace amount of target material in the initial screening experiments, compound **2** was obtained only with a low yield (entry 2, 3). When CH_2Br_2 was used as the coupling reagent under optimized conditions, low yields (27%) were obtained as expected (entry 4).

Table 5. Additional screening results of ClDNP **1** coupling.

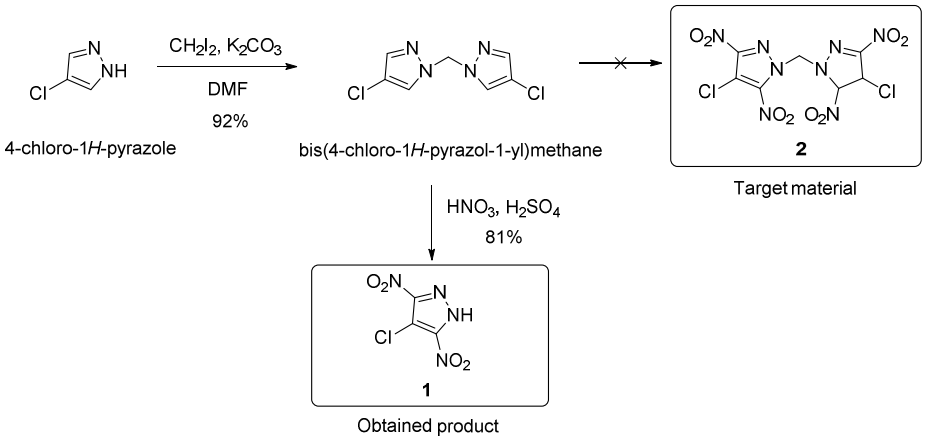


Entry	CH_2X_2 (eq.)	Base (eq.)	Yield (%)
1	CH_2I_2 (15.0)	Cs_2CO_3 (2.0)	No reaction
2	CH_2I_2 (15.0)	Na_2CO_3 (2.0)	26
3	CH_2I_2 (15.0)	K_2CO_3 (2.0)	27
4	CH_2Br_2 (15.0)	Li_2CO_3 (2.0)	27

2.4. Experimental results to synthesize compound 2 via an alternative route

An alternative route was also investigated to synthesize compound **2** via a coupling reaction with 4-chloro-1*H*-pyrazole first, followed by a nitration reaction (Scheme 4).

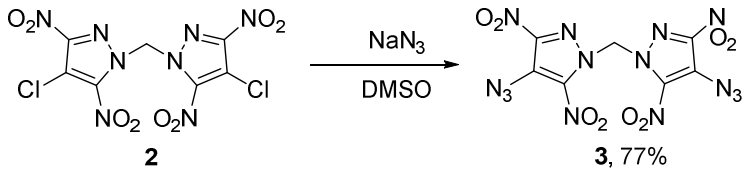
In the first step, bis(4-chloro-1*H*-pyrazol-1-yl)methane was readily obtained via the coupling reaction of 4-chloro-1*H*-pyrazole. However, unfortunately, in the nitration reaction of bis(4-chloro-1*H*-pyrazol-1-yl)methane, only ClDNP **1** could be obtained instead of the target material **2**. The cause of these results is thought to be due to its *N*,*N* acetal structure, which is vulnerable to moisture and strong acids.



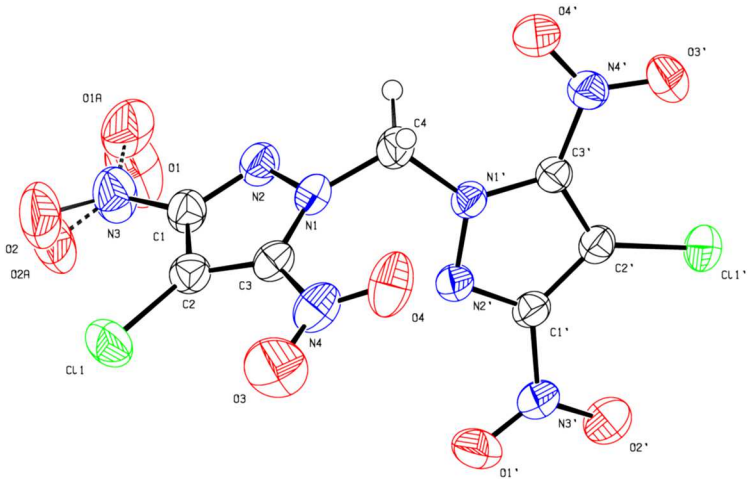
Scheme 4. Experimental results for an alternative route to synthesize compound **2**.

2.5. Synthesis of compound 3 via double azidation of compound 2

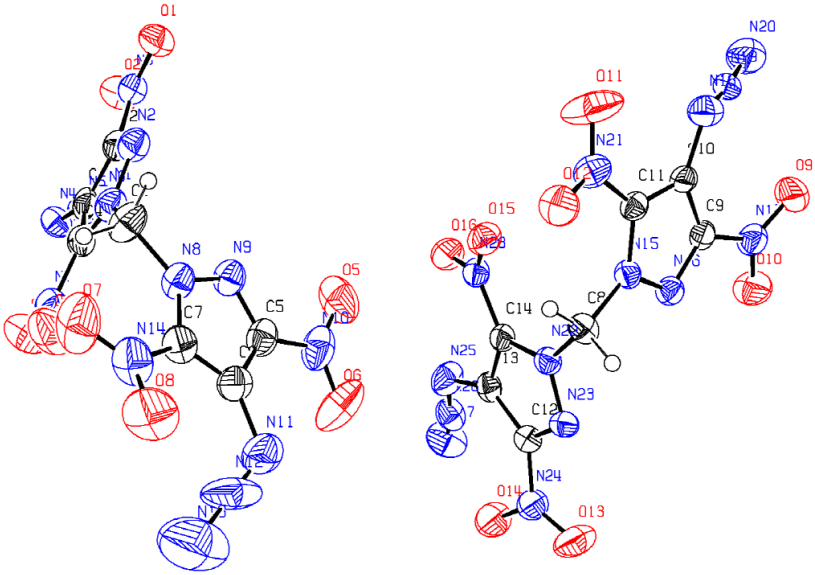
The novel coupled product with a methylene bridge, bis(ClDNP) **2**, was then reacted with sodium azide at room temperature to yield **3**, which introduced the azido group at the C-4 position of both dinitropyrazoles in one step (Scheme 5). As a result, **3** was obtained in a good yield of 77% under mild conditions. The structures of compounds **2** and **3** were confirmed by single-crystal X-ray diffraction analyses (Figure 6).



Scheme 5. Double azidation of compound **2**.



(A)



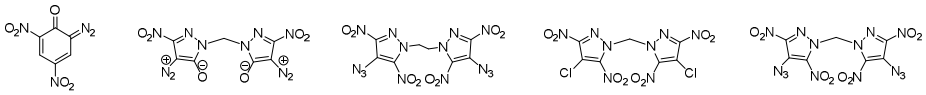
(B)

Figure 6. Single-crystal X-ray structure of compound **2** (A) and **3** (B).

3. Physical properties investigation[18]

Both new compounds, **2** and **3**, were characterized for their thermal stabilities, explosive performances and sensitivities (Table 6). Both compounds showed higher thermal stability (T_d, **2,** 345 °C; **3,** 159 °C) than that of DDNP (142 °C). High thermal stability is one of the most important properties of explosives as it allows safer processing and long-term storage under various operating conditions.

Table 6. Physical properties of **2** and **3** compared to other primary explosives.



DDNP Compound C Compound D 2 3

Compounds	T_d[a] (°C)	ρ[b] (g/cm^3)	OB[c] (%)	ΔH_f[d] (kJ/kg)	P[e] (GPa)	v_d[f] (m/s)	IS[g] (J)	FS[h] (J)
DDNP[19]	142	1.76	-61	630	24	7290	1	5
Compound C[12]	226	1.73	-45	1543	26	8016	1.5	40
Compound D[13]	135	1.76	-38	2390	31	8558	3	60
2	345	1.82	-28	-773	20	7134	6	353
3	159	1.76	-27	1954	30	8459	2	33

[a]Decomposition temperature
[b]Density (25 °C).
[c]Oxygen balance ($C_aH_bO_cN_d$; $(c\text{-}2a\text{-}b/2)1600/M_w$).
[d]Heat of formation.
[e]Detonation pressure.
[f]Detonation velocity.
[g]Impact sensitivity.
[h]Friction sensitivity.
Explosive performances (heat of formation, detonation pressure, and detonation velocity) were calculated by Explo5 computation.[20], Sensitivities were obtained from BAM testers.

The calculated oxygen balance (OB) values of the new compounds are better (**2**, -28%; **3**, -27%) than that of DDNP (-61%) and those of recently reported potential primary explosives, compounds **C** and **D** (**C,** -45%; **D,** -38%). The closer the OB value is to zero, the better it is as a green explosive, because it minimizes the emission of harmful gases such as carbon monoxide and/or nitrogen oxides (NO_x) by incomplete combustion during explosion. In addition, the sensitivity and explosive performance of an explosive are known to be closely related its oxygen balance. As expected, compound **3** having one less methylene bridge than that of compound **D** shows its OB value by a difference of more than 10% than that of compound **D**.

Sensitivity is an important factor in determining the category of explosives. Compound **2** (IS = 6 J; FS = 353 J) is relatively insensitive to impact and friction due to the introduction of a non-explosophore group, the chloride, which would make compound **2** be a useful precursor for further applications. On the other hand, the impact and friction sensitivities of compound **3** (IS = 2 J; FS = 33 J) are a little less than those of DDNP (IS = 1 J; FS = 5 J) but comparable to those of the recently reported bis(nitropyrazolyl)alkanes **C** (IS = 1.5 J; FS = 40 J) and **D** (IS = 3 J; FS = 60 J).

Based on the measured and calculated properties, the explosive performances of the new compounds are calculated using EXPLO5

computation.[20] The calculated detonation velocity and pressure of **2** (v_d = 7134 m s^{-1}, P = 20 GPa) are somewhat insufficient to be used as an explosive. Nevertheless, it contains the rather reactive chloro groups with which various energetic groups can be introduced, and thus it could be valuable as a precursor for new explosives.[14] Meanwhile, the explosive properties of **3** (v_d = 8459 m s^{-1}, P = 30 GPa) not only exceed a widely used primary explosive, DDNP (v_d = 7290 m s^{-1}; P = 24 GPa), but also are comparable to those of compounds **C** (v_d = 8016 m s^{-1}; P = 26 GPa) and **D** (v_d = 8558 m s^{-1}; P = 31 GPa) with the similar molecular skeleton.

Conclusion

In summary, we have succeeded for the first time in the coupling reaction of readily available ClDNP **1** with the *N*,*N*'-methylene bridge to produce compound **2** that could be a useful intermediate for new explosives since it contains the chloro groups with high substitution reactivity. In fact, the double azidation reaction of **2** was achieved effectively in one step to give a novel compound **3** under mild conditions. Some physical properties of compound **3** were characterized, which showed its potential to be a new green primary explosive. Its explosive properties are comparable to those of the recently reported bis(nitropyrazolyl)alkane type primary explosives, compounds **C** and **D**, and more desirable than those of a currently used green primary explosive, DDNP.

Experimental Details[18]

1. Caution

We have carefully scaled-up for the synthesis of all the compounds after the synthesis on the mmole scale to avoid any dangerous situations. However, these compounds are potentially explosives, so unexpected explosions are always possible. In particular, compound **3** is highly sensitive, so care should be taken to avoid exposure to any scratches, shocks or high temperatures. Appropriate protective equipments and experiment tools (safety glasses, face shield, explosion proof clothing, Teflon spatula, etc.) will be necessary when handling these compounds. It is also recommended to handle only small amounts of compounds.

2. General Methods

All reagents were purchased commercially and used as received. Nuclear magnetic resonance (NMR) spectra were recorded on Bruker Avance III 400 FT-NMR (^{1}H at 400 MHz and ^{13}C at 100 MHz). Infrared spectra were recorded on a PerkinElmer FT-IR spectrometer by attenuated total reflection (ATR) spectroscopy (400–4000 cm^{-1} range). Elemental analyses were carried out using a Flash2000 (Thermo Fisher Scientific) elemental analyzer. High resolution mass spectra were

measured on JEOL JMS-6890. Decomposition and melting temperature (onset) were measured by differential scanning calorimetry (DSC, Mettler Toledo DSC 3, at a scan rate of 10 °Cmin^{-1}). Single-crystal X-ray diffraction data were collected using a Bruker D8 Venture and a PHOTON II 14 detector in the Western Seoul Center of Korea Basic Science Institute. Sensitivities were measured using standard Bundesanstalt für materialprüfung (BAM) testers (impact sensitivity: BAM impact test method, friction sensitivity: BAM friction test method) in the Agency for Defense Development.

Bis(4-chloro-3,5-dinitro-1*H*-pyrazol-1-yl)methane (2): ClDNP **1** (0.20 g, 1.0 mmol) and Li_2CO_3 (0.15 g, 2.0 mmol) were added to dimethylformamide (DMF, 2 mL), the resulting mixture was stirred at room temperature for 15 minutes. Diiodomethane (CH_2I_2, 4.17 g, 15.6 mmol) was added dropwise to the mixture in one portion. The reaction mixture was heated for 8 h at 70 °C in an oil bath. After cooling to room temperature, the reaction mixture was diluted with EtOAc (50 mL) and water (50 mL). A small amount of aqueous sodium thiosulfate solution was added to remove iodine. The mixture was extracted with EtOAc (3 x 50 mL). The organic layer was dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The concentrate was purified by silica gel column chromatography (4:1 hexane/EtOAc) to give **2** as sticky yellow solid. Recrystallization from isopropyl alcohol gave pure **2** as a yellow crystalline solid (0.16 g, 79%). Mp 167 °C; ^{1}H NMR (Acetone-d_6) δ 7.64 (s, 2H); ^{13}C NMR (Acetone -d_6) δ 151.2, 144.2, 108.7, 68.6; IR (ATR) 1562, 1511, 1440, 1323, 1263, 1222, 1140, 1073, 1003, 885, 805, 765, 710, 611 cm^{-1}; EA (%) calcd for $C_7H_2Cl_2N_8O_8$ (397.04): C 21.18, H 0.51, N 28.22; found: C 20.94, H 0.54, N 27.97; HRMS (FAB) calcd for $C_7H_1N_8O_8Cl_2$, $[M-H]^+$ 394.9294, found 394.9294.

Bis(4-azido-3,5-dinitro-1*H*-pyrazol-1-yl)methane (3): Compound **2** (0.20 g, 0.50 mmol) was dissolved in dimethylsulfoxide (DMSO, 4 mL), then sodium azide (NaN_3, 0.070 g, 1.0 mmol) was added to the mixture. The reaction mixture was stirred for 8 h at room temperature. The reaction mixture was diluted with EtOAc (50 mL) and water (50 mL). The solution was extracted with EtOAc (3 x 50 mL). The combined organic layers were dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The concentrate was purified by silica gel column chromatography (4:1 hexane /EtOAc) to give **3** as sticky yellow solid. Recrystallization from isopropyl alcohol gave pure **3** as a yellow powder (0.16 g, 77%). Mp 136 °C; ^{1}H NMR (Acetone-d_6) δ 7.64 (s, 2H); ^{13}C NMR (Acetone-d_6) δ 151.2, 144.2, 108.7, 68.6; IR (ATR) 2137, 1571, 1513, 1443, 1389, 1318, 1264, 1223, 1140, 1074, 1005, 900, 828, 804, 764, 710, 610 cm^{-1}; EA (%) calcd for $C_7H_2N_{14}O_8$ (410.18): C 20.50, H 0.49, N 47.81; found: C 20.72, H 0.51, N 47.53; HRMS (FAB) calcd for $C_7H_1N_{14}O_8$, $[M-H]^+$ 409.0102, found 409.0103.

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Chapter II: 4,5-Dinitro-*N*,*N*'-dialkylimidazolium cations as candidates for high-energy materials

Introduction

1. Energetic ionic liquids (EILs)

In recent decades, numerous ionic liquids (ILs) having unique physical properties have been reported by combining cations and anions with diverse functional groups installed.[1] Because of their unique properties such as ionic conductivity, wide liquid temperature range, negligible vapor pressure, and wide solvency, ILs are used in a variety of chemical engineering applications such as electrochemistry,[2] organic synthesis,[3] materials chemistry,[4] catalysis,[5] and separation science.[6]

Among them, the research field on energetic ionic liquids (EILs) has been gradually expanded to the development of high-energy materials (HEMs).[7] This is due to the expectation that the properties of HEMs can be easily tailored by using the tunability of ILs including the selection of each ion containing various alkyl chains and functional groups (Figure 7). In addition, the inherent properties of ILs such as the reduced

sensitivity and the low volatility are expected to solve safety issues and environmental concerns that are increasingly being emphasized in the field of modern HEMs development.

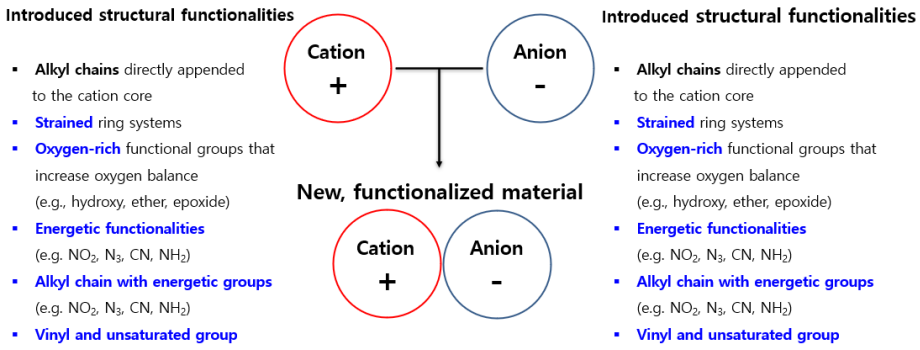


Figure 7. Independent design of components in multifunctional EILs.[7]

1.1. Characteristics of EILs[8]

The advent of EILs has completely changed the terms greeness and safety, which represent the properties of ILs. This is because EILs are used as flammable fuels or dangerously explosive HEMs. While traditional ILs have been used in green applications, EILs make use of their flammability and vigorous reactivity. EILs can take full advantage of the unique properties of ILs, such as (1) EILs generally have very low volatility like ILs, (2) EILs are easy to handle and transport due to their reduced sensitivity, (3) The main properties of ILs, such as low melting

temperature, high thermal stability, and low viscosity, can have advantages over traditional high energy materials, (4) EILs in liquid form can avoid polymorphism that occurs in solid high energy materials.

1.2. Physical and chemical properties of EILs[8]

The physical and chemical properties of EILs are different for each EILs, thus determining their application as new HEMs. Similar to the characteristics of ILs, the properties of EILs can also be tuned as desired through the appropriate combination of cation and anion. The functional groups substituted in each of the cation and anion affect the physicochemical properties of EILs. Since energetic functional groups are avoided in traditional ILs, the effect of their introduction on the properties of EILs is more complex. However, similar to typical ILs, predicted energetic performance can be pursued by independently designing and functionalizing ions of each EILs. The introduction of different energetic functional groups will affect the physicochemical properties of EILs such as thermal stability, explosive performance, and sensitivity, etc.

Characterization of new EILs requires (1) identification of a new molecular structure, (2) confirmation of purity, and (3) calculation of physicochemical properties through individual tests. First, analysis

methods such as NMR analysis of as many constituent atoms as possible, mass spectrometry, FT-IR, and single-crystal XRD are used to confirm the molecular structure. In particular, elemental analysis is an essential analysis method that can simultaneously identify the molecular structure of EILs and their purity. After the investigation of the molecular structure and purity of EILs is completed, it is necessary to investigate the physicochemical properties to confirm their practical use. As important properties that determine the field of application of EILs as HEMs, measurement and calculation of the following properties are required; (1) Measurement of thermal properties, (2) calculation of explosive performances reflecting the measured density and heat of formation, and (3) measurement of sensitivities important for both handling and operation.

1.2.1. Thermal Properties[8]

The melting temperature and decomposition temperature are representitive thermal properties of EILs. Melting temperature (T_m) is a thermal property that generally distinguishes EILs from energetic salts. Traditionally, a reference point of 100 °C, lower values are classified as EILs, and higher values are classified as energetic salts. The melting temperature of EILs can range from room temperature to more than

100 °C by the combination of each cation and anion. EILs that are liquid at room temperature are referred to as room temperature EILs (RT-EILs). EILs including cations or anions in which many energetic functional groups are introduced have melting temperatures that are considerably higher than room temperature. It is known that the reason for their high melting temperature is that the introduced energetic functional groups induce strong hydrogen bonds, which leads to dense packing of the crystal lattice. These high melting temperatures can be tailored to a lower level through combination with an appropriate counter ion. In many previous studies, azoles, heterocycles containing a large number of nitrogens, were selected as the cation of EILs. This is because the structure of azoles has low symmetry, which makes the packing of the crystal lattice less dense.

Decomposition temperature is a representative indicator of the thermal stability of EILs. Unlike traditional ILs, in which stability-enhancing functional groups are introduced, EILs contain energetic functional groups in their cation or anion, so they generally tend to have lower thermal stability than that of ILs. In certain cases, the energetic functional groups introduced into EILs may have a rather high decomposition temperature by inducing strong hydrogen bonding. Nevertheless, their decomposition temperature tends to be generally lower than that of energetic salts with high symmetry.

1.2.2. Density[8]

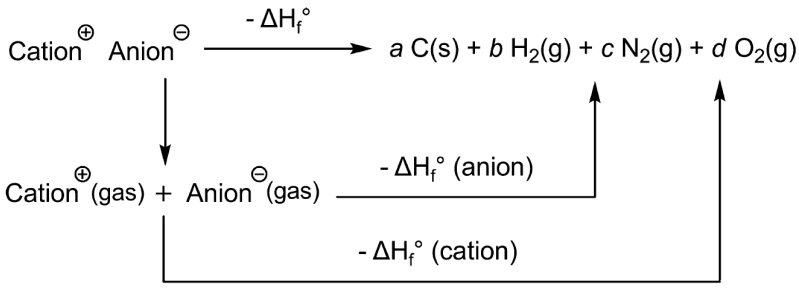
In HEMs, density is known to be an important index directly related to their explosive performance. This is because the higher the density of HEMs, the higher the number of moles can be filled into the limited volume. In addition, it can be seen that the density of HEMs is proportional to the detonation velocity in the equation for calculating the detonation velocity. The densities of EILs are each affected by the structure of their component ions. The densities of EILs are each affected by the structure of their constituent ions, which depends on how tightly each constituent ions can bond. In order to obtain a high density, it is necessary to carefully examine the shapes and sizes of each component ions in EILs and the interactions between them. In general, the densities of hypergolic EILs for use as propellant fuels range from 0.9 g cm^{-3} to 1.3 g cm^{-3}, and the density of EILs for use as explosives exceeds 1.5 g cm^{-3}. These differences in densities are caused by differences in molecular structures designed differently depending on the purpose of use of each EILs. In the design of hypergolic EILs, unsaturated sunstituents with fuel-rich properties such as allyl or propargyl are introduced in their cations or anions. These unsaturated substituents are not only low density by themselves, but are largely responsible for the low densities of EILs because they do not induce additional ion-ion

interactions. On the other hand, in the design of EILs for use as explosives, dense energetic functional groups such as $-NO_2$ or $-N_3$ are introduced into the component ions. These energetic functional groups contribute to the increase in the densities of EILs, causing strong hydrogen bond interactions between molecules.

1.2.3. Heat of Formation[8]

Heat of formation (ΔH_f) is one of the essential parameters for predicting the explosive properties of energetic materials. In order to improve the prediction accuracy of the detonation velocity and detonation pressure representing the performance of energetic materials, the actually measured ΔH_f value is required. Several methods are known, such as molecular orbital theory, group additive method, and ab initio calculations for calculating the ΔH_f value of energetic materials. Recently, high-level ab initio calculations have been applied in many studies due to their highest prediction accuracy. In this calculation method, geometrical optimization and frequency analysis for the structure of the EILs to be calculated are performed preferentially. In addition, calculations for single energy points of EILs are also required. Using the results of the empirical approach and the results of MP2 and DFT (B3LYP) calculations, the entropies and the lattice enthalpies of

EILs are calculated. The structures of the calculated EILs have a minimum of local energy at the surface of potential energy, excluding imaginary frequencies. According to Born−Haber energy cycle (Hess's law of constant summation), heats of formation of EILs can be calculated using the lattice energy and gas-phase heat of formation (Scheme 6).



Scheme 6. Born−Haber Cycle for the Formation of EILs[8]

Based on Scheme 6, ΔH_f can be represented by eq 1.2.2.1:[9]

$$\Delta H_f^\circ \text{(EIL, 298 K)} = \Sigma\Delta H_f^\circ \text{(cation, 298 K)} + \Sigma\Delta H_f^\circ \text{(anion, 298 K)} - \Delta H_L \qquad \text{(eq.1.2.2.1)}$$

where ΔH_L is the lattice energy of EILs. And, when EILs are 1:1 salts of cation and anion, considering the nonlinear characteristics of each ions, ΔH_L can be calculated via eq 1.2.2.2 established by Jenkins et al.:[10]

$$\Delta H_L = U_{POT} + [p(nM/2 - 2) + q(nX/2 - 2)]RT \quad \text{(eq.1.2.2.2)}$$

where nM and nX are determined by the properties of the ions M_p^+ and X_q^-, respectively. For example, monoatomic ions have a value of 3, linear polyatomic have a value of 5, and nonlinear polyatomic have a value of 6. Based on this, the equation for the lattice potential energy (U_{POT}) is derived as eq 1.2.2.3:

$$U_{POT}(\text{kJ mol}^{-1}) = \gamma(\rho_m / M_m)^{1/3} + \delta \quad \text{(eq.1.2.2.3)}$$

where ρ_m is density (g cm^{-3}) and M_m (g) is the molar mass of EILs. And γ (kJ mol^{-1}) and δ (kJ mol^{-1}) are the coefficients derived from the paper of Jenkins et al. [11]

2. Imidazole based EILs

EILs containing imidazolium cations have been widely studied because the imidazole ring is known to have high chemical energy and stable structure with aromaticity.[12] In addition, the structural dissymmetry of *N*,*N'*-dialkylimidazolium cations can lead to the decrease of melting points of the imidazolium-based EILs.[13] Introduction of explosophoric functional groups such as nitro groups onto the imidazolium ring is also

essential to improve their explosive performances. However, their structural modifications were limited to changing the alkyl groups on the imidazolium ring without nitro group because the nucleophilicity of the imidazole ring decreases as the number of the strongly electron-withdrawing nitro group increases.[14] A few reported studies on the synthesis of mononitro-substituted *N*,*N'*-dialkylimidazolium cations are shown in Figure 8.[15] In general, the quaternization of an imidazole ring with no nitro group can be done by a simple alkylation reaction with readily available alkylating agents such as alkyl halides. On the other hand, stronger alkylating reagents than alkyl halides were required for the quaternization of nitroimidazoles. In mononitro-imidazoles, their quaternizations were possible by using methyl triflate, a more electrophilic alkylating reagent. Dinitro-*N*,*N'*-dialkylimidazolium cations could not be obtained even using methyl fluorosulfonate due to the weaker nucleophilicity of dinitro-imidazoles.

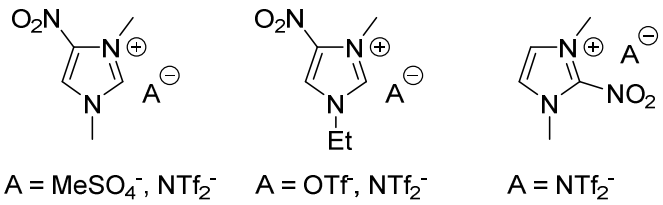


Figure 8. Reported nitro-substituted imidazolium cations.

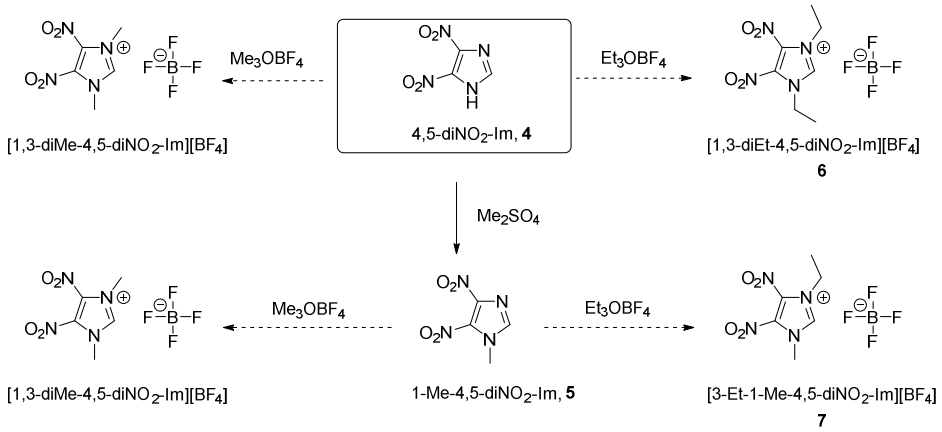
Results and Discussion

1. Synthetic strategy[16]

In order to achieve the challenging quaternization of dinitro-imidazoles, it is necessary to use a more electrophilic alkylating reagent. For this reason, we focused on Meerwien reagents ($R_3O^+BF_4^-$) having strong electrophilic properties.[17]

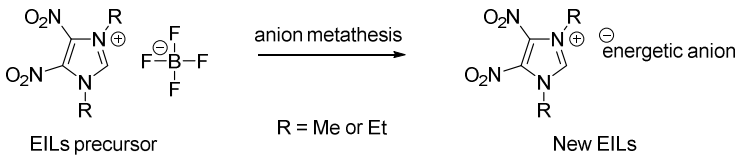
Meerwein's reagents is a very strong nucleophilic alkylating reagents, as well as commercially available reagents. They also have advantages in chemical process, because the by-products of the alkylation reaction using $R_3O^+BF_4^-$ are only dialkyl ether (R_2O) and BF_4^-. R_2O can be easily removed because of its volatility, and BF_4^- might be the proper anion of the resulting ionic liquids in certain cases.[18]

The main study was conducted on two dinitro-imidazoles, 4,5-dinitroimidazole (4,5-diNO2-Im) **4** and its *N*-methylated derivative 1-methyl-4,5-dinitro-imidazole (1-Me -4,5-diNO2-Im) **5**. To synthesize new *N*,*N'*-dialkyl-dinitro-imidazolium, two dinitroimidazoles were quaternized with Meerwein's reagents, triethyloxonium tetrafluoroborate (Et_3OBF_4) and trimethyloxonium tetrafluoroborate (Me_3OBF_4), respectively (Scheme 7).



Scheme 7. Synthetic strategy for the new *N*,*N'*-dialkyl-dinitro-imidazolium cations.

Then, the newly obtained dinitro-imidazolium tetrafluoroborates were converted into new EILs via metathesis reaction with energetic anion (Scheme 8).



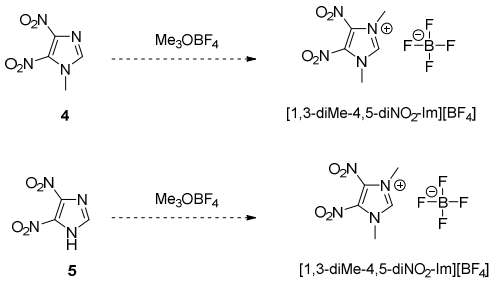
Scheme 8. Synthetic strategy for the new EILs via anion metathesis.

2. Synthesis and characterization[16]

2.1. Quaternization of dinitro-imidazoles

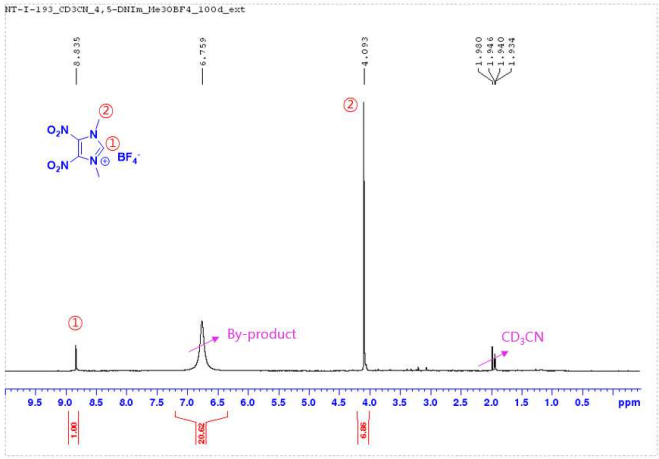
The quaternization experiments using Meerwein's reagents were attempted on 4,5-dinitroimidazole (4,5-diNO_2-Im) **4** and its *N*-methylated derivative 1-methyl-4,5-dinitro-imidazole (1-Me-4,5-diNO2-Im) **5**, respectively. As a first trial, a methylation reaction was attempted using trimethyloxonium tetrafluoroborate ($Me_3O^+BF_4^-$).

As a result of the experiments using $Me_3O^+BF_4$, even in experiments conducted under the same reaction condition, consistent results could not be obtained. (Scheme 9).

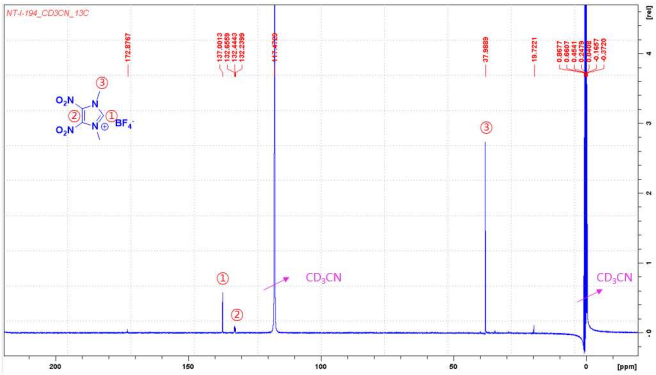


Scheme 9. Synthetic results of quaternization using Me_3OBF_4.

However, there were also promising results. Although it has not been reproduced, this reaction is thought to require further study because a crude product which is estimated to be the target material was obtained (Figure 9).



(A)

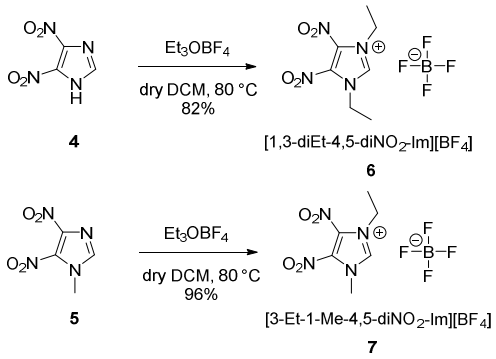


(B)

Figure 9. ^{1}H (A) / ^{13}C (B) NMR spectra of crude product obtained as a result of quaternization of compounds **4** and **5** using Me_3OBF_4 (Peak assigns in each spectrum are based on estimation, additional analysis is required.).

On the other hand, it was confirmed that desired EILs compounds **6**, **7** were produced in the ethylation reaction using triethyloxonium

tetrafluoroborate ($Et_3O^+BF_4^-$) (Scheme 10). The solvent used in the reaction was distilled because highly hygroscopic Meerwein's reagent reacts with a trace amount of water to produce tetrafluoroboric acid (HBF_4).[19] Distilled dichloromethane (DCM) was used as suitable reaction solvent because of the solubility of the starting material.

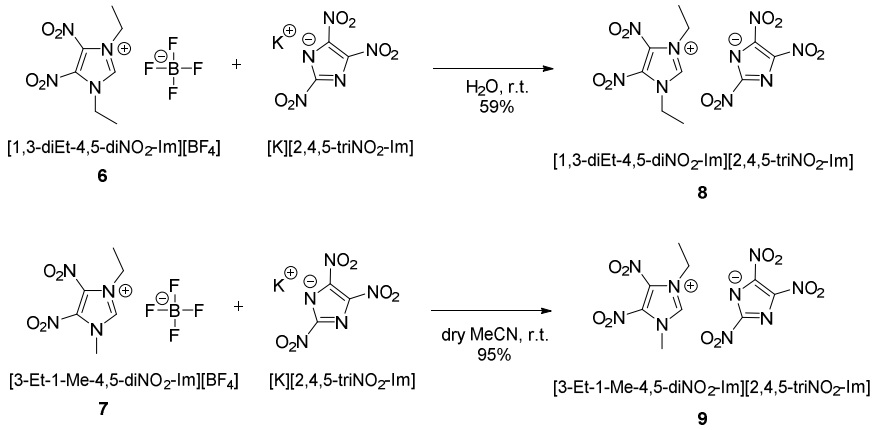


Scheme 10. Quaternization reactions of using Et_3OBF_4.

At room temperature, the reaction did not proceed at all, however, when the reaction temperature was gradually increased in the pressure tube, the target compounds **6** and **7** were obtained, and the optimum reaction temperature was 80 °C. Since the product precipitated as a fine crystalline solid when the reaction mixture cooled to room temperature under vigorous stirring, they could be obtained purely by simple filtering without complicated purification process (**6**, 82%; **7**, 96%). The structures of **6**, **7** were characterized by ^1H, ^{13}C, and ^{19}F NMR and elemental analysis, respectively.

2.2. Anion metathesis for new EILs

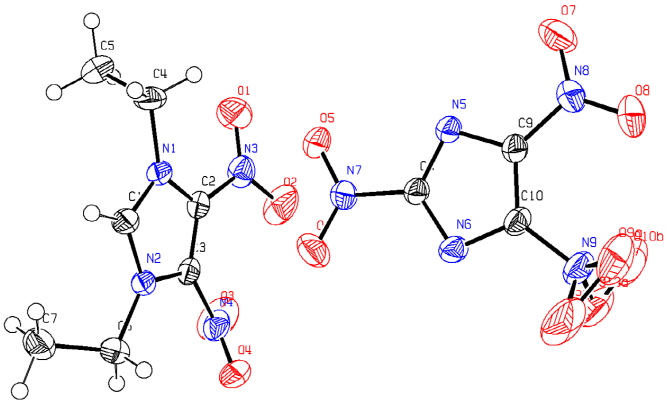
In order to enhance the explosive properties of compounds **6** and **7**, anion metathesis that change tetrafluoroborate anion (BF_4^-) into more energetic anions were attempted (Scheme 11). Polynitroimidazolides having two or more nitro groups were selected as the target energetic anion, and the experiments were carried out using potassium polynitroimidazolides (potassium 2,4-dinitroimidazolide,[15b] potassium 4,5-dinitroimidazolide,[15b] and potassium 2,4,5-tinitroimidazolide[20] in various solvents (alcohols, acetonitrile, and distilled water).



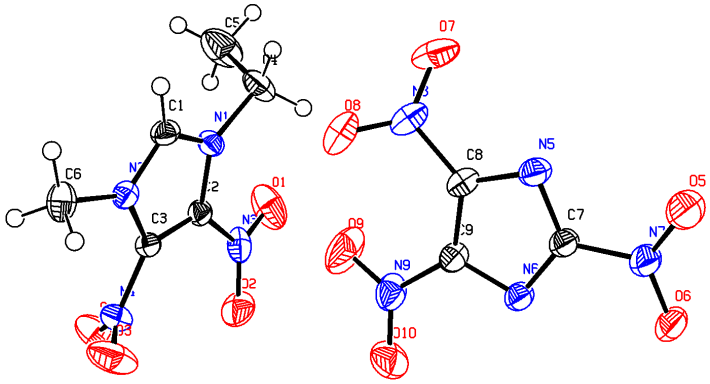
Scheme 11. Anion metathesis of compounds **6** and **7**.

As a result of such trials, the target compounds 3 and 4 were obtained from the experiments using potassium 2,4,5-tinitroimidazolide

([K][2,4,5-triNO2-Im]). These results are considered to be due to the high acidity of 2,4,5-trinitro-1*H*-imidazole.[21] Compounds 3 and 4 were each obtained in moderate to good yield under appropriate solvent conditions (**8**, distilled water, 59%; **9**, acetonitrile, 95%). These also have a very simple purification process, because purification is completed simply by filtering the precipitated products. The structures of **8**, **9** were characterized by ^{1}H, ^{13}C NMR and elemental analysis, respectively. Molecular structures of 3 and 4 were also confirmed by single-crystal X-ray diffraction analysis (Figure 10). In compound **8**, although minor disorders were observed due to thermal vibration of the nitro group in the anion, the structure of the cation was clearly confirmed.



(A)



(B)

Figure 10. Single-crystal X-ray structure of compound **8** (A) and **9** (B).

3. Thermal investigation[16]

The DSC and TGA analysis results to investigate the thermal properties of the synthesized ionic salts **6** to **9** are presented in Table 7. In general, it has been reported that melting temperature (T_m) of EILs increases as the number of substituents in the imidazole cation increases. In particular, when an electron withdrawing group such as nitro group is introduced than an electron donating group such as methyl group, T_m tends to rise significantly.[14]

T_m of compounds **6** and **7** (**6**, 107 °C; **7**, 103 °C) clearly demonstrated above trend, and slightly exceeding the general requirements of EILs (< 100 °C). After anion metathesis, T_m of both compounds **8** and **9** increased (**8**, 147 °C; **9**, 108 °C) and the increase of **8** was remarkably high. This result is considered to be due to the increase in cation symmetry as the same ethyl groups were introduced into *N* and *N'* position of imidazole. Decomposition temperatures (T_d) were measured by TGA and determined as the onset to 5 wt% mass loss temperature. Factors affecting T_d of EILs are known to be quite complex. Representative factors include interactions between anion-cations, differences in the structure of each ion component, the presence of hydrogen bonds, and differences in introduced energetic substituents.[22] The new EILs generally showed lower T_d than the widely used explosives TNT (**6**,

188 °C; **7**, 192 °C; **8**, 182 °C; **9**, 144 °C). It is considered to be due to the absence of hydrogen bonds and the introduction of multiple energetic nitro groups.[8]

Table 7. Thermal properties of newly obtained compounds.

Compounds	T_m[a] (°C)	T_d[b] (°C)
6	107	188
7	103	192
8	147	182
9	108	144
TNT[22]	81	295

[a]Melting temperature (DCS, 10 °Cmin^{-1}, onset).
[b]Decomposition temperature (TGA, 10 °Cmin^{-1}, -5 wt% mass, onset).

4. Explosive properties investigation[16]

The explosive properties of compounds **8** and **9** were investigated by actual measurements and computational calculations (Table 8). Data of density (ρ) and heat of formation (ΔH_f) were both obtained based on measured values.

In general, HEMs require a high density to allow more explosive materials to be loaded per unit volume, and a high heat of formation to emit high energy during an explosion.[23] Compared with TNT (2,4,6-trinitrotoluene) as representative HEM, the density of compound **8** is

somewhat lower, while its heat of formation showed more positive value (**8**, ρ = 1.51 g cm^{-3}; ΔH_f = -27.3 kJ mol^{-1}). Compound **9** showed more positive results because both density and heat of production were much better than TNT (**9**, ρ = 1.68 g cm^{-3}; ΔH_f = 280.8 kJ mol^{-1}).

Table 8. Explosive properties of compounds **8** and **9** compared to TNT.

Compounds	ρ^a (g cm^{-3})	ΔH_f^b (kJ mol^{-1})	P^c (GPa)	v_d^d (m s^{-1})	IS^e (J)	FS^f (J)
8	1.51	-27.3	18	6815	18	>353
9	1.68	280.8	25	7738	75	>353
TNT[24]	1.65	-67.0	20	6881	15	>353

[a]Pycnometric density (25 °C).
[b]Heat of formation (calculated from measured heat of combustion).
[c]Detonation pressure (calculated by Explo5 computation).
[d]Detonation velocity (calculated by Explo5 computation).
[e]Impact sensitivity (measured according to the modified STANAG 4489 instruction using a BAM Fallhammer).
[f]Friction sensitivity (measured according to the modified STANAG 4487 instruction using a BAM friction tester).

Based on these measured data, the explosive performances were calculated using the explosive performance prediction software Explo5.[25] The calculated explosive performances showed the same trend as the measured values. The explosive performance of compound **8** was calculated to be close to that of TNT, which is thought to be because its improvement due to the high heat of formation offset the decrease due to the low density (v_d = 6815 m s^{-1}, P = 18 Gpa). Compound **9** was confirmed to have an explosive performance exceeding TNT due to its

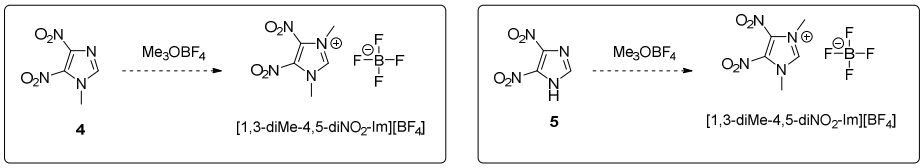
high density and heat of formation (v_d = 6881 m s^{-1}, P = 25 Gpa). In addition, measured sensitivities of **9** are considerably higher than those of TNT, so it is expected to be applicable as a candidate for a new insensitive HEMs (IS = 75 J, FS >353 J).

5. Future plans to obtain EILs with superior physical properties

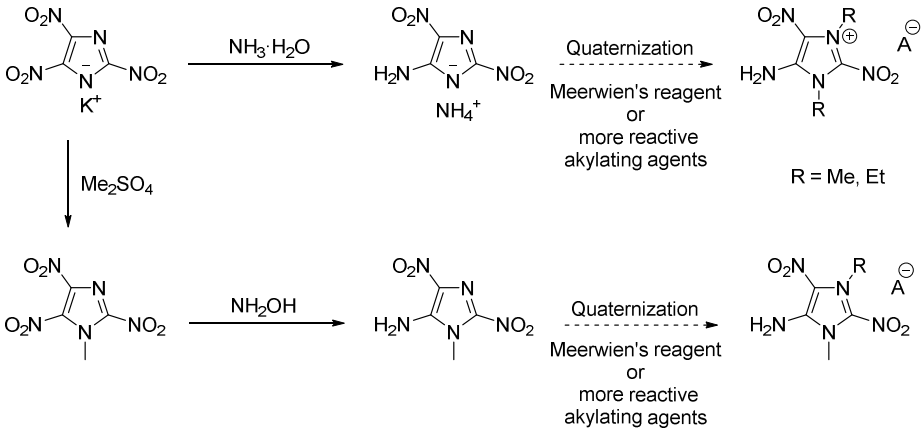
As a result of the current investigation, compounds **8** and **9** showed relatively good insensitivity, but it can be seen that further improvement is required in their explosive performance and thermal stability. In order to improve the characteristics of EILs, it is necessary to consider both cation and anion due to its tunability.

First, there is a strategy to adjust the properties of EILs by improving its cation. The improvement of the explosive performance can be achieved by increasing the nitrogen content of the cation (or reducing its carbon content). To do this, it is necessary to reduce the carbon content by shortening the alkyl chain of the cation, or to increase the nitrogen content by introducing an energetic functional group having nitrogen into it. The most probable route is to quaternize compounds **4** and **5** using Me_3OBF_4, which has confirmed some possibilities in previous studies (Scheme 12, A). Changing the alkyl chain of EILs from ethyl to methyl will not only reduce its carbon content, but also improve its symmetry. If this is achieved, it can be expected that both the explosive performance and the thermal stability are improved.

Next, a path for introducing a new energetic group may be considered.



(A)



(B)

Scheme 12. Promising routes for obtaining cations with superior physical properties.

In order to improve the explosive performance, the introduction of a nitro group into the cation may be most effective, but this introduces an additional electron withdrawing group into the cation, so there is a concern about a decrease in thermal stability and difficulty in quaternization due to a decrease in nucleophilicity Therefore, it may be a better alternative route to increase the nitrogen content of the cations as well as introduce an amine group that has a stabilizing effect on the cations. Routes for synthesizing 5-amino-2,4-dinitroimidazole

derivatives from potassium 2,4,5-trinitroimidazol-1-ide have already been reported.[26,27] If the quaternization of these compounds is successful, it is expected that new EILs with improved explosive performance and thermal stability will be obtained (Scheme 12, B).

Second, it is possible to control the physical properties of EILs via the metathesis with anions having various functional groups. Since so many energetic anions have already been reported, various anion metathesis attempts will be possible. For successful anion metathesis, the acidity of the anions should be carefully considered.

Conclusion

Our group succeeded in the first synthesis of two new EILs composed of 4,5-dinitro-*N*,*N'*-dialkyl imidazolium cations. The quaternizations of 4,5-dinitroimidazoles **4**, **5** were achieved using Meerwein's reagent. Newly obtained EILs **6** and **7** are expected to be used as precursors for new HEMs via metathesis reaction with energetic anions. In fact, the anion metathesis of BF_4^- to 2,4,5-trinitroimidazol-1-ide was able to obtain new insensitive HEMs candidates **8** and **9**. Compound **9** could be a candidate for new insensitive HEMs because it has better explosive properties and insensitivity than those of TNT.

Experimental Details[16]

Caution

We did not experience any dangerous problems while doing this work, however, the synthesized materials are potentially HEMs. Therefore, be sure to follow appropriate safety procedures. In addition, to prevent unexpected accidents, experiments on a minimum scale are recommended, and avoid excessive scale-up experiments. When reproducing experiments or handling these materials, be sure to use appropriate safety equipment and laboratory tools.

General Methods

All analytical grade chemical reagents were purchased from commercial sources and all reagents were used as received without further purification, except for the reaction solvent, dichloromethane (DCM). DCM was used after distillation to remove residual moisture. Nuclear magnetic resonance (NMR) spectra (Bruker Avance III 400 FT-NMR, ^{1}H at 400 MHz, ^{13}C at 100 MHz and ^{19}F at 376 MHz) were obtained in CD_3CN using solvent as internal standard (^{1}H and ^{13}C) or

$CFCl_3$ as external standard (^{19}F). Single-crystal X-ray diffraction analysis was performed by Bruker D8 Venture and a PHOTON II 14 detector in the Western Seoul Center of Korea Basic Science Institute. Melting temperatures were measured by differential scanning calorimetry (DSC, Mettler Toledo DSC 3, at a scan rate of 10 °Cmin^{-1}, onset). Decomposition temperatures were measured by thermogravimetric analysis (TGA, SDTA851e, Mettler Toledo, at a scan rate of 10 °Cmin^{-1}, -5 wt% mass, onset). Impact sensitivity tests were performed according to the modified STANAG 4489 instruction using a BAM fall-hammer instrument (OZM research, Czech Republic). The friction sensitivity tests were performed according to the modified STANAG 4487 instruction using a BAM friction tester (OZM research, Czech Republic).

1,3-Diethyl-4,5-dinitro-1*H*-imidazol-3-ium tetrafluoroborate (6): 4,5-dinitro-1*H*-imidazole **4**[26] (0.20 g, 1.23 mmol) and Et_3OBF_4 (0.72 g, 3.79 mmol) into the pressure tube and closed it with a rubber septum. Distilled DCM (6 mL) was added dropwise using a glass syringe under nitrogen atmosphere. Seal the pressure tube using a screw cap, then the reaction mixture was heated for 2 h at 80 °C in an oil bath. The reaction mixture was cooled to room temperature. After opening the screw cap of the pressure tube, it was closed with a rubber septum. Diethyl ether (10 mL) was added dropwise to the reaction mixture under a nitrogen atmosphere, and then stirred vigorously to precipitate a white solid. The precipitated solid was filtered using a Büchner funnel and washed with diethyl ether to obtain a white solid (0.31 g, 82%). T_m 107 °C (DSC); T_d 103 °C (TGA); ^{1}H NMR (CD_3CN) δ 8.96 (s, 1H), 4.52 (q, 4H, *J* = 7.2 Hz), 1.57 (t, 6H, *J* = 7.2 Hz); ^{13}C NMR (CD_3CN) δ 136.2, 133.1, 48.8, 14.2; ^{19}F NMR (CD_3CN) δ [-151.79, - 151.84] (4F); EA (%) calcd for $C_7H_{11}BF_4N_4O_4$ (301.99): C 27.84, H 3.67, N 18.55, found: C 27.71, H 3.69, N 18.76.

3-Ethyl-1-methyl-4,5-dinitro-1*H*-imidazol-3-ium tetrafluoroborate (7): 1-methyl-4,5-dinitro-1*H*-imidazole **5**[27] (0.20 g, 1.16 mmol) and Et_3OBF_4 (0.44 g, 2.32 mmol) into the pressure tube and closed it with a rubber septum. Distilled DCM (6 mL) was added dropwise using a glass syringe under nitrogen atmosphere. Seal the pressure tube using a screw cap, then the reaction mixture was heated for 2 h at 80 °C in an oil bath. The reaction mixture was cooled to room temperature under vigorous stirring, a pale yellow solid precipitated. The precipitated solid was filtered using a Büchner funnel and washed with DCM to obtain a pale-yellow solid (0.32 g, 96%). T_m 103 °C (DSC); T_d 192 °C (TGA); ^{1}H NMR (CD_3CN) δ 8.85 (s, 1H), 4.50 (q, 2H, *J* = 7.2 Hz), 4.09 (s, 3H), 1.56 (t, 3H, *J* = 7.2 Hz); ^{13}C NMR (CD_3CN) δ 137.1, 133.2, 48.9, 39.0, 14.3; ^{19}F NMR (CD_3CN) δ [-153.69, - 153.74] (4F); EA (%) calcd for $C_6H_9BF_4N_4O_4$ (287.97): C 25.03, H 3.15, N 19.46, found: C 25.27, H 3.18, N 19.53.

3-Diethyl-4,5-dinitro-1*H*-imidazol-3-ium 2,4,5-trinitro imidazol-1-ide (8): Compound **6** (0.30 g, 0.99 mmol) was dissolved in distilled water (10 mL). Potassium 2,4,5-trinitroimidazol-1-ide[20] (0.16 g, 0.66 mmol) was added to the reaction mixture in one portion and it was stirred vigorously for 5 minutes at room temperature. A white solid precipitated from the reaction mixture within about 1 minute. The precipitated solid was filtered using a Büchner funnel and washed with cold water to obtain a white solid (0.24 g, 59%). T_m 147 °C (DSC); T_d 182 °C (TGA); ^{1}H NMR (CD_3CN) δ 9.14 (s, 1H), 4.55 (q, 4H, *J* = 7.2 Hz), 1.57 (t, 6H, *J* = 7.2 Hz); ^{13}C NMR (CD_3CN) δ 147.6, 139.1, 136.6, 133.2, 49.0, 14.4; EA (%) calcd for $C_{10}H_{11}N_9O_{10}$ (417.25): C 28.79, H 2.66, N 30.21, found: C 28.64, H 2.73, N 30.34; Impact sensitivity 18 J; Friction sensitivity >353 J.

3-Ethyl-1-methyl-4,5-dinitro-1*H*-imidazol-3-ium 2,4,5-trinitroimidazol-1-ide (9): Compound **7** (0.20 g, 0.69 mmol) was dissolved in acetonitrile (6 mL). Potassium 2,4,5-trinitroimidazol-1-ide[20] (0.17 g, 0.70 mmol) was added to the reaction mixture in one portion and it was stirred for 30 minutes at room temperature. The solvent was removed under reduced pressure to obtain crude product mixture. The reaction mixture was dissolved in 3 mL of acetonitrile then cooled at -20 °C for 1 h, a white by-product (potassium tetrafluoroborate, KBF_4) solid was precipitated. The by-product and the dissolved target material were separated using a syringe filter, and the separated target material was concentrated under reduced pressure. DCM (20 mL) was added to the concentrated yellow gel and stirred. The precipitated solid was filtered using a Büchner funnel and washed with DCM to obtain a white solid (0.27 g, 95%). T_m 108 °C (DSC); T_d 144 °C (TGA); ^{1}H NMR (CD_3CN) δ 8.97 (s, 1H), 4.52 (q, 2H, *J* = 7.2 Hz), 4.11 (s, 3H), 1.56 (t, 3H, *J* = 7.2 Hz); ^{13}C NMR (CD_3CN) δ 147.7, 139.2, 137.4 133.2, 49.0, 39.1, 14.5; EA (%) calcd for $C_9H_9N_9O_{10}$ (403.22): C 26.81, H 2.25, N 31.26, found: C 27.00, H 2.30, N 31.32; Impact sensitivity 75 J; Friction sensitivity >353 J.

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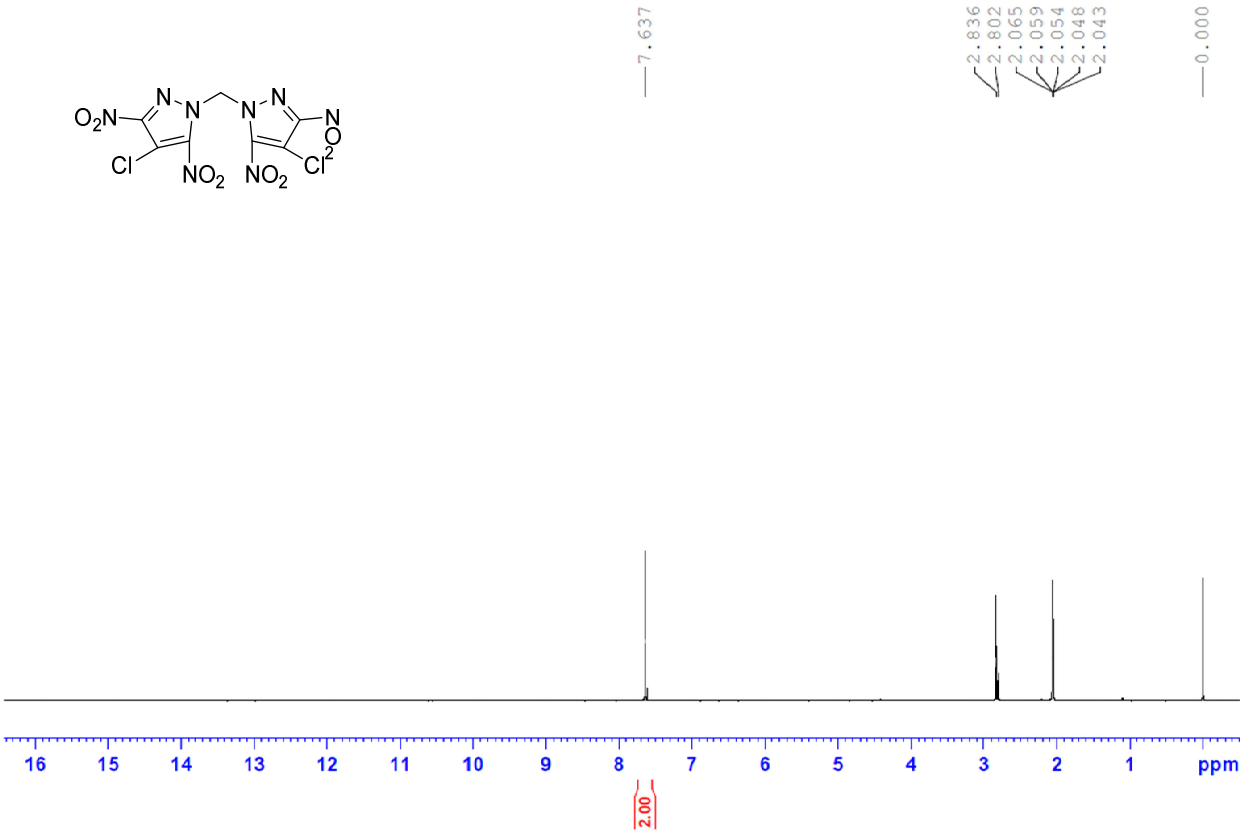
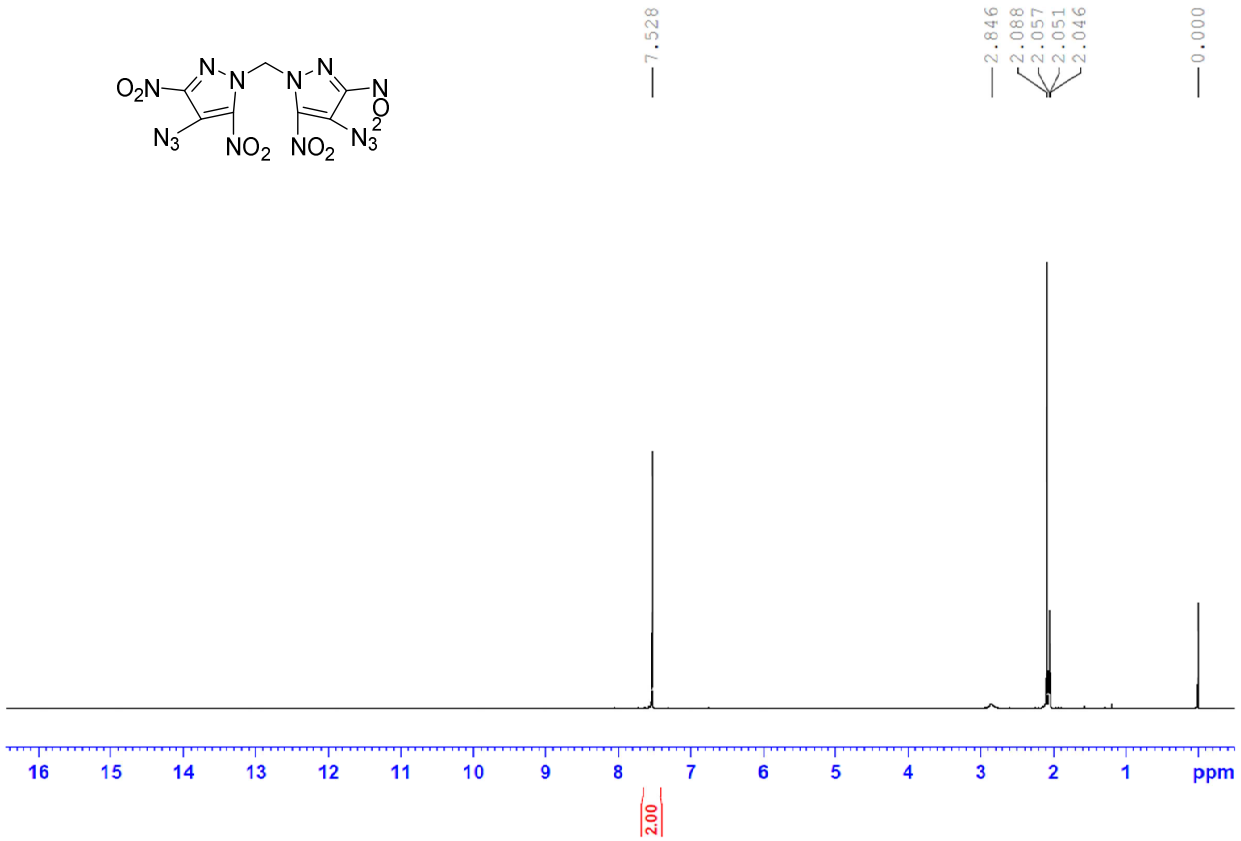
APPENDICES

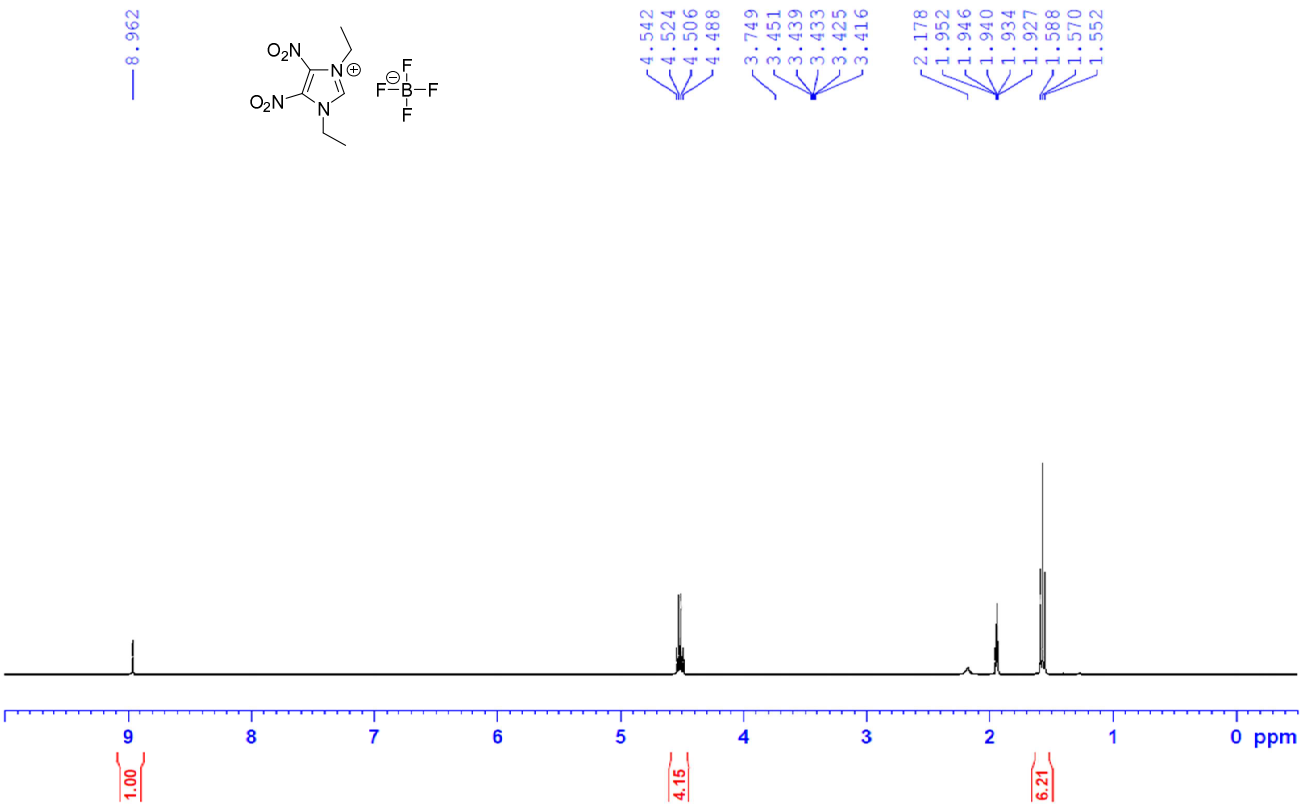
List of ^{1}H NMR Spectra of Selected Compounds



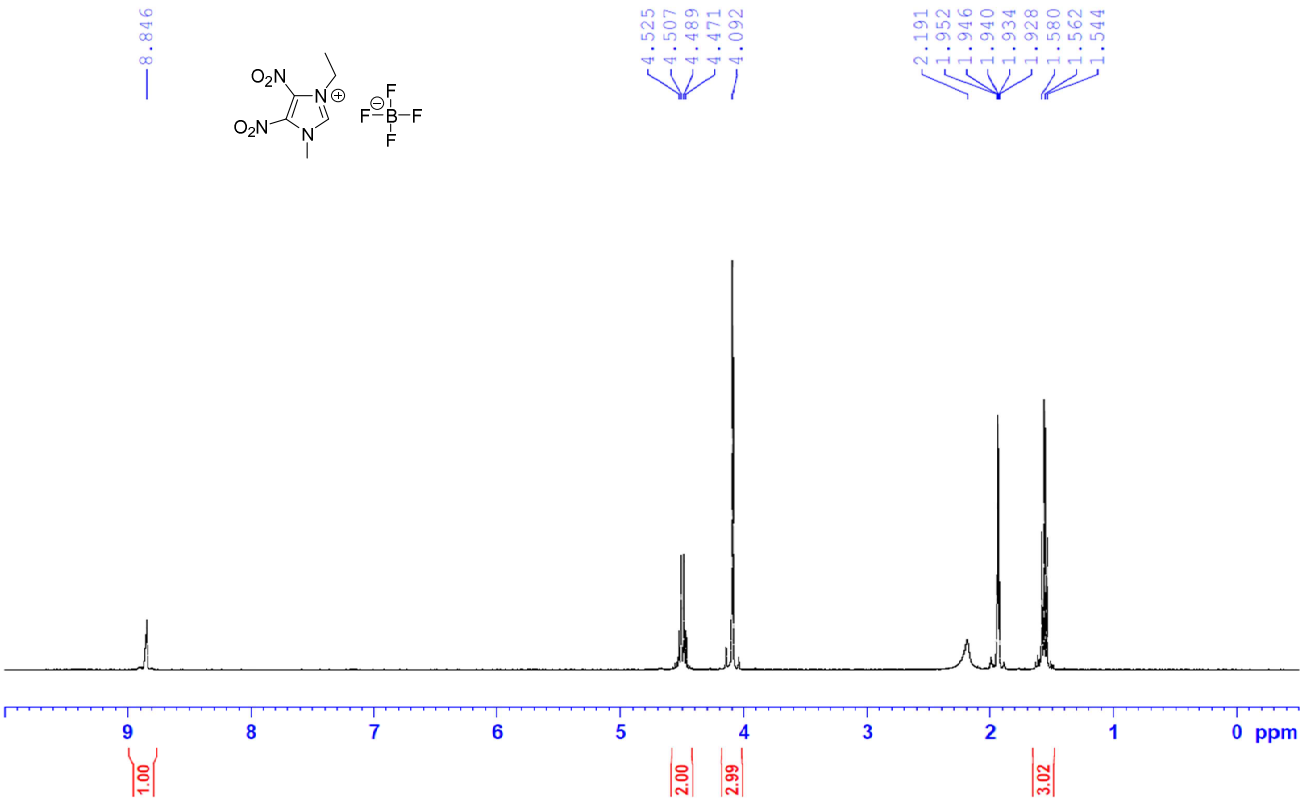
400MHz ^{1}H NMR Spectrum (Acetone-d_6) of compound **2**.



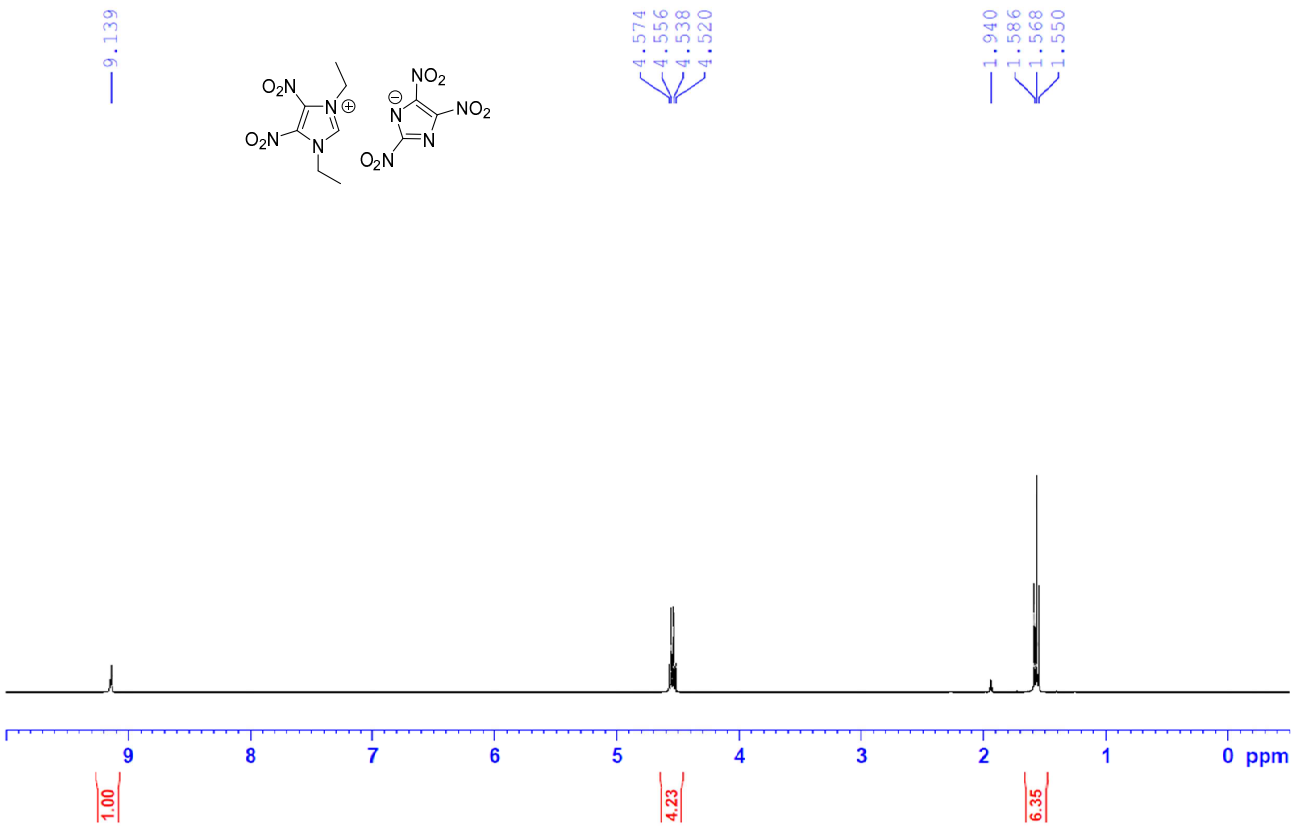
400MHz ^{1}H NMR Spectrum (Acetone-d_6) of compound **3**.



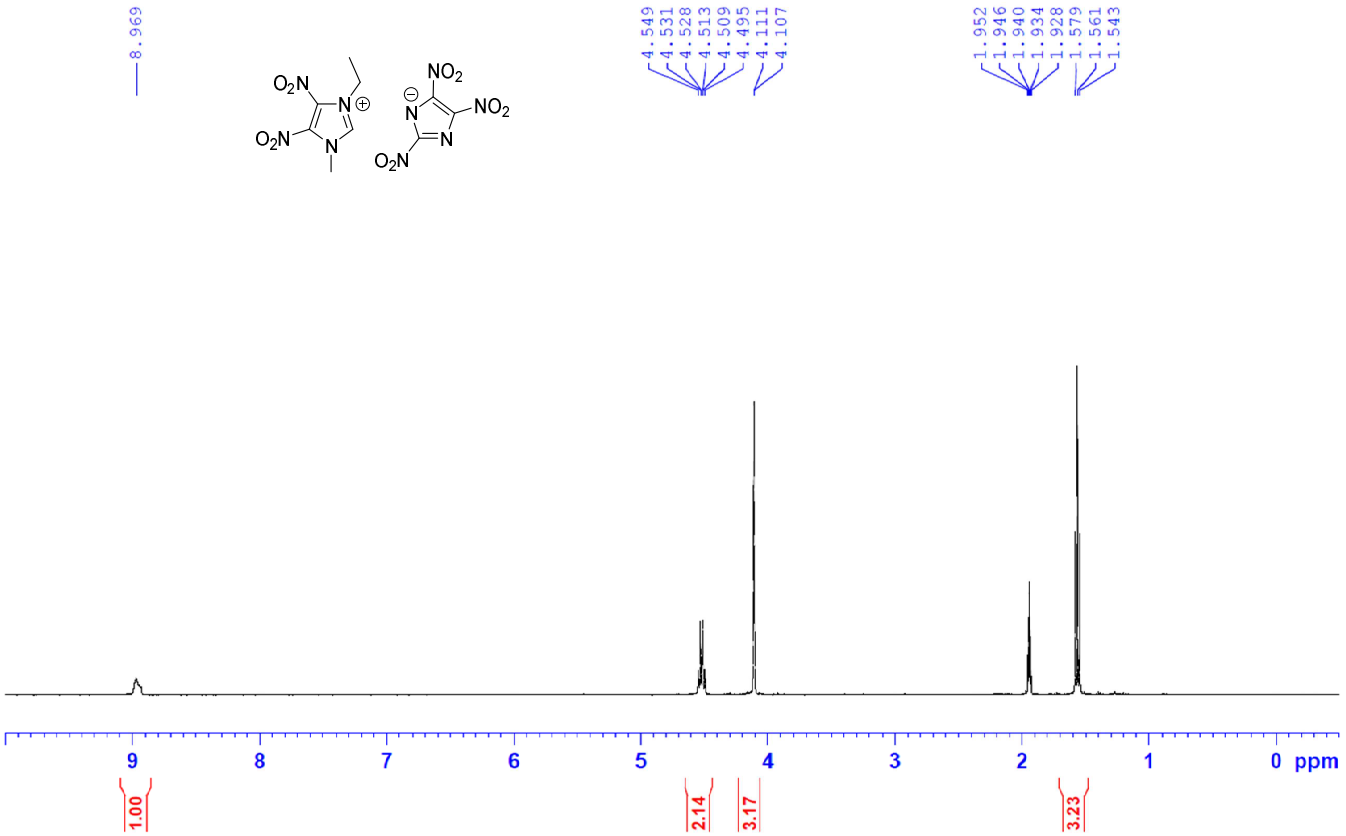
400MHz ^{1}H NMR Spectrum (CD_3CN) of compound **6**.



400MHz ^{1}H NMR Spectrum (CD_3CN) of compound **7**.

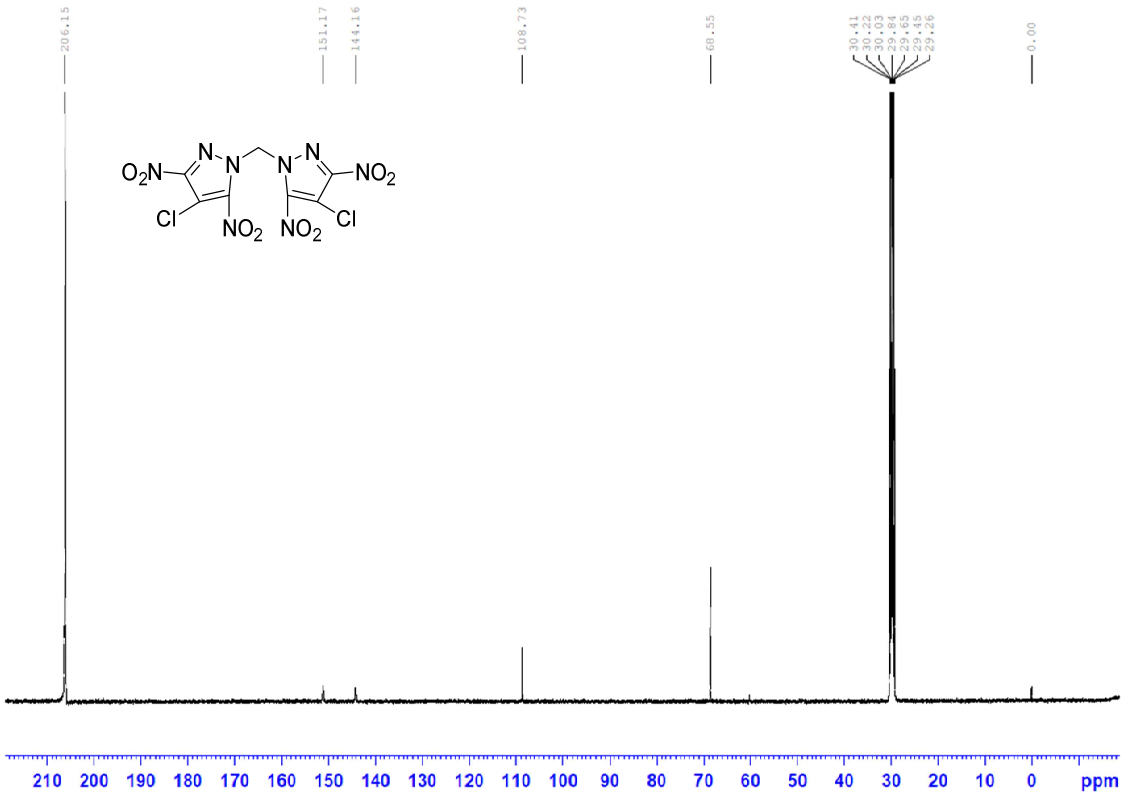


400MHz ^{1}H NMR Spectrum (CD_3CN) of compound **8**.

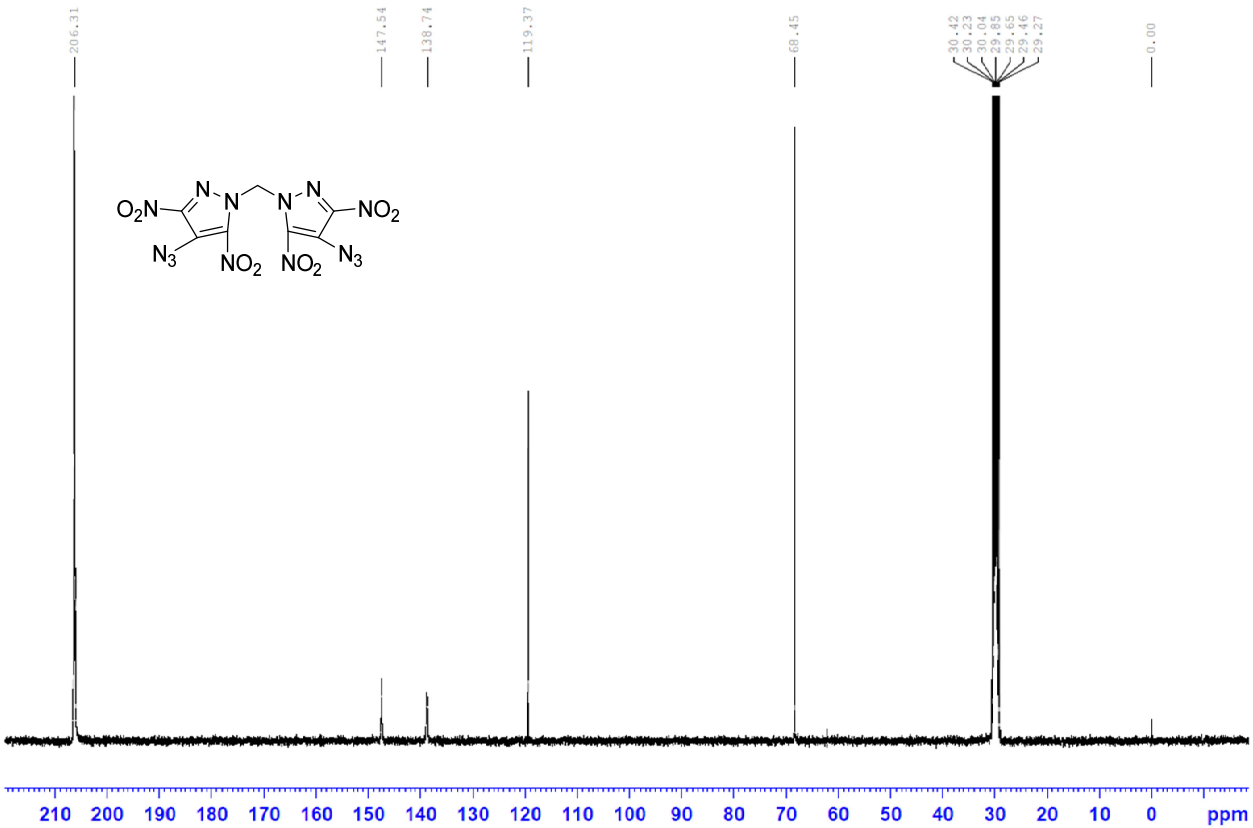


400MHz ^{1}H NMR Spectrum (CD_3CN) of compound **9**.

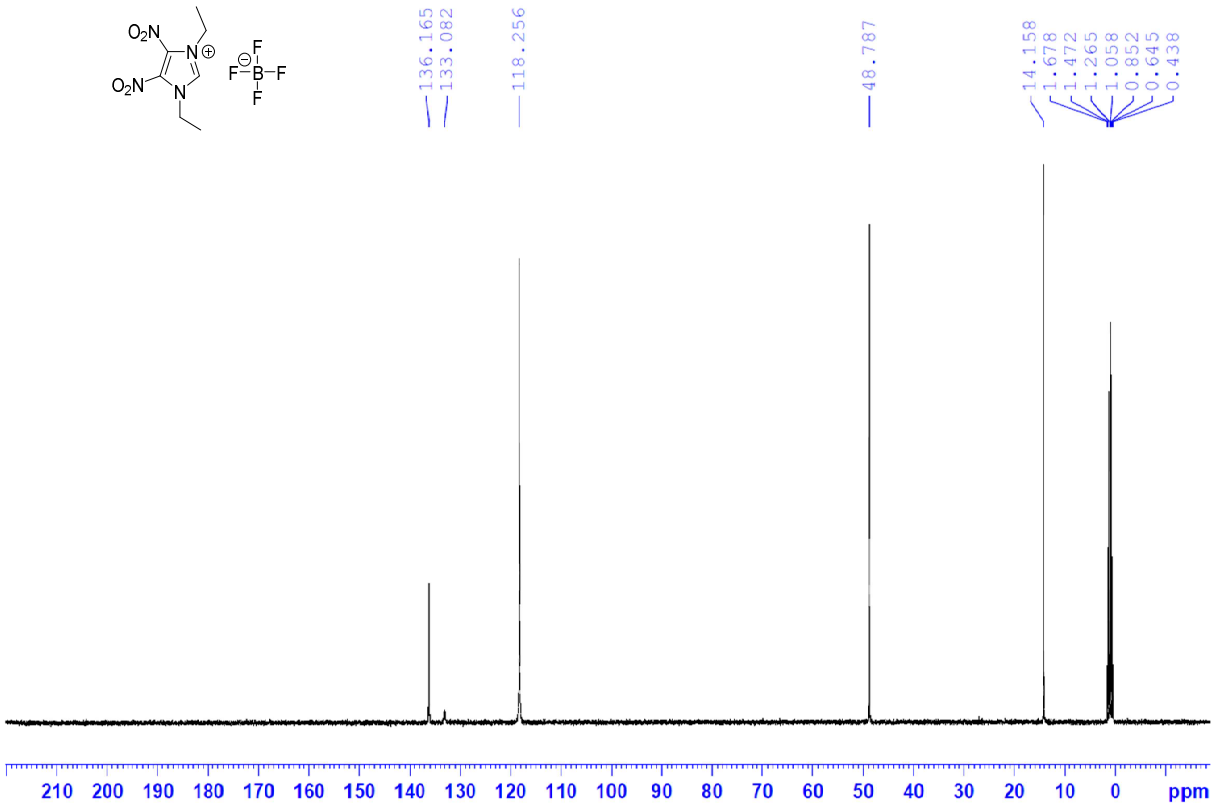
List of ^{13}C NMR Spectra of Selected Compounds



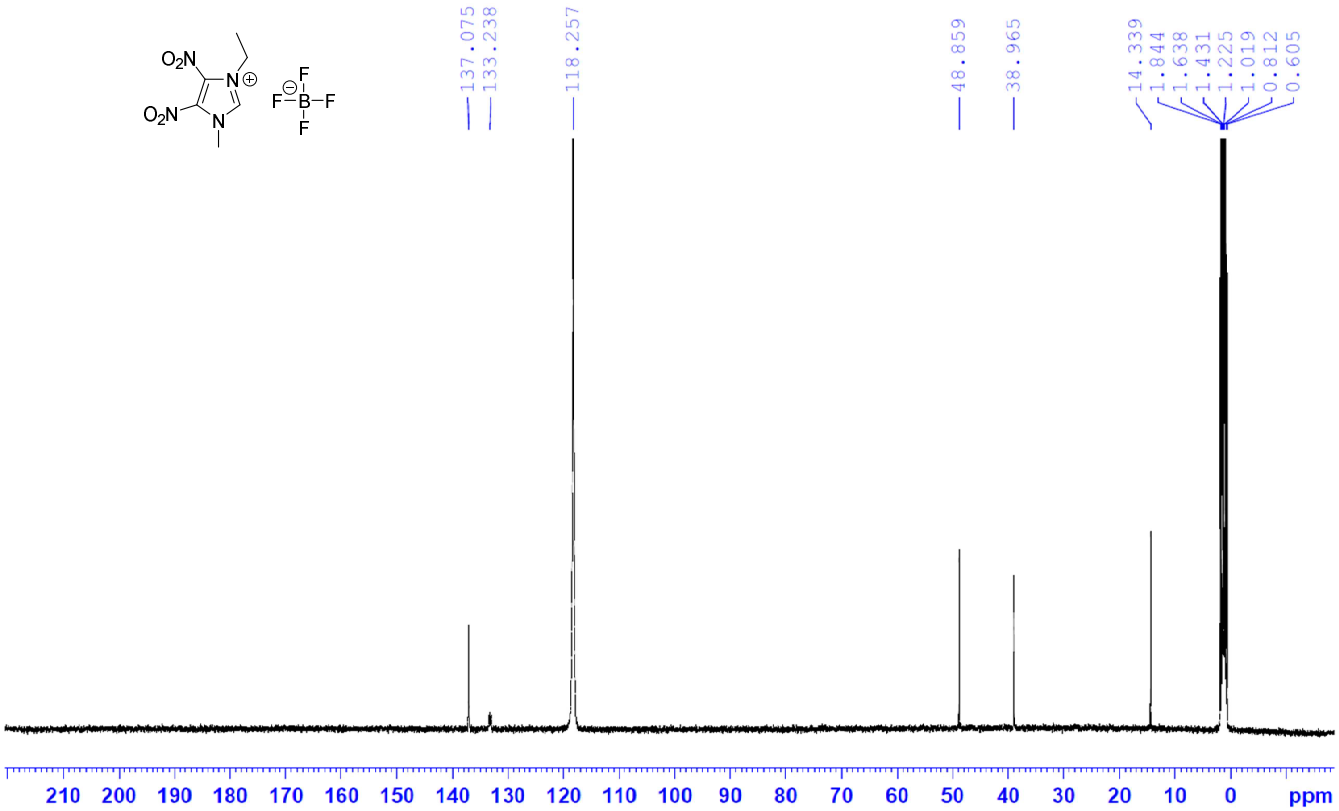
100MHz ^{1}H NMR Spectrum (Aceton-*d6*) of compound **2**.



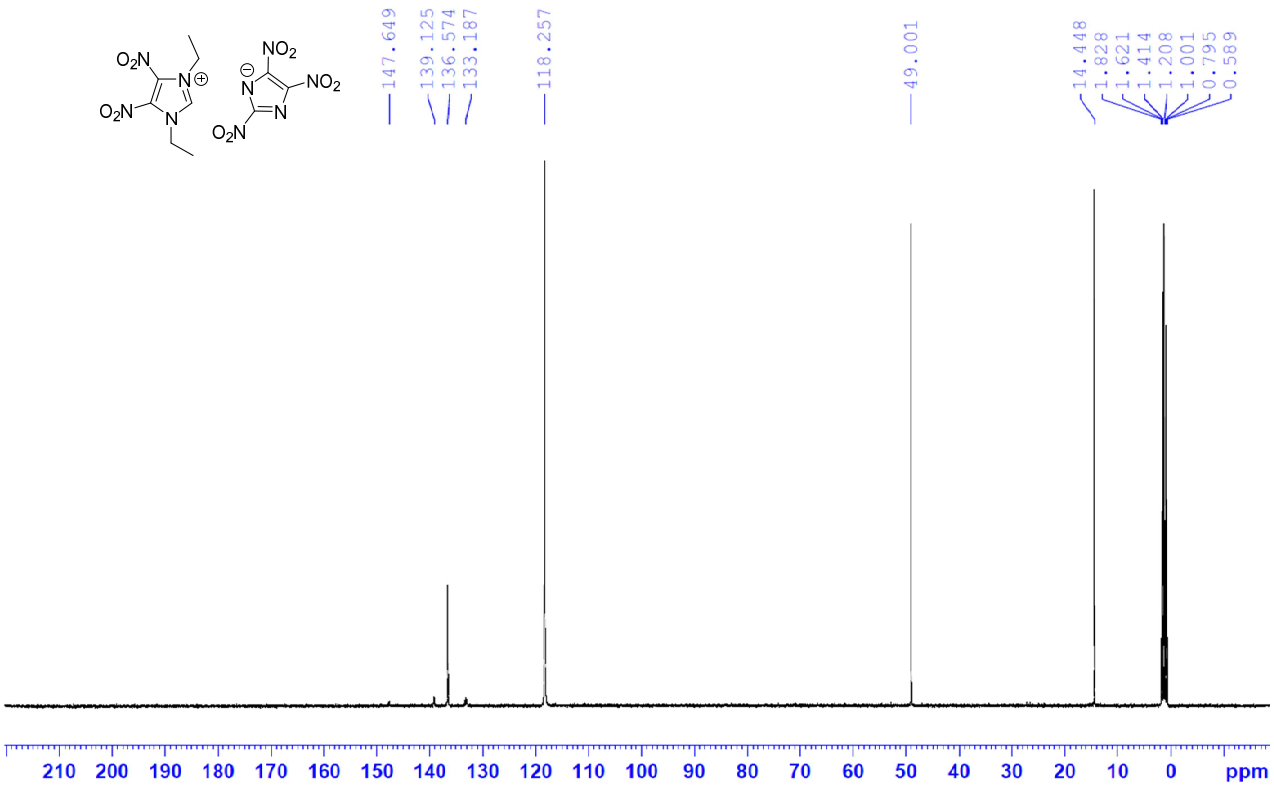
100MHz ^{1}H NMR Spectrum (Aceton-*d6*) of compound **3**.



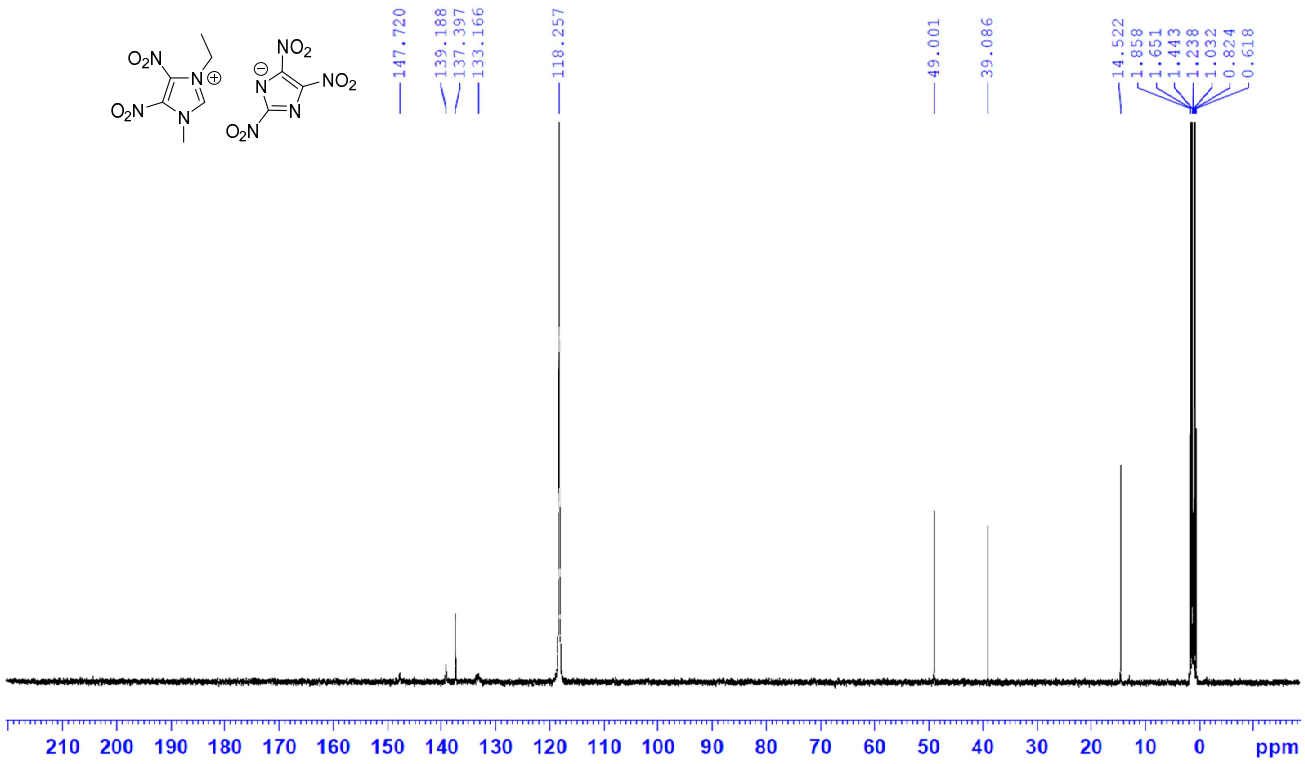
100MHz ^{1}H NMR Spectrum (CD_3CN) of compound **6**.



100MHz ^{1}H NMR Spectrum (CD_3CN) of compound **7**.

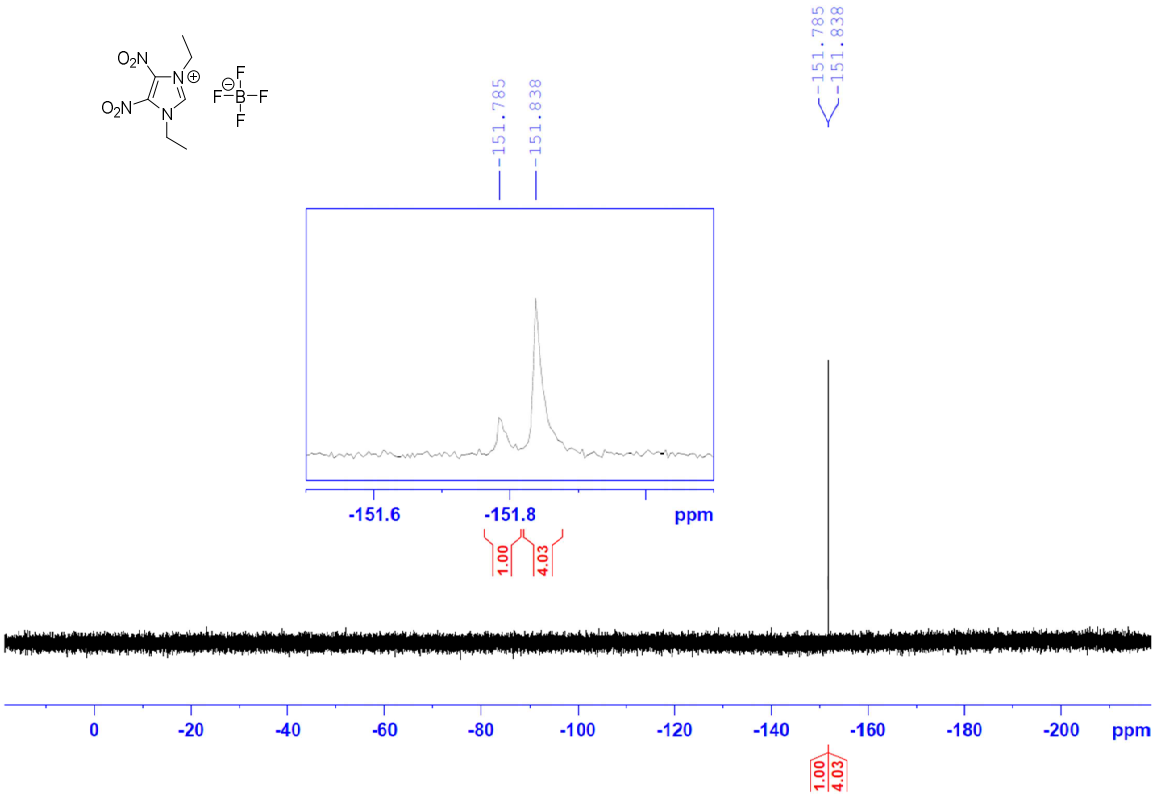


100MHz ^{1}H NMR Spectrum (CD_3CN) of compound **8**.

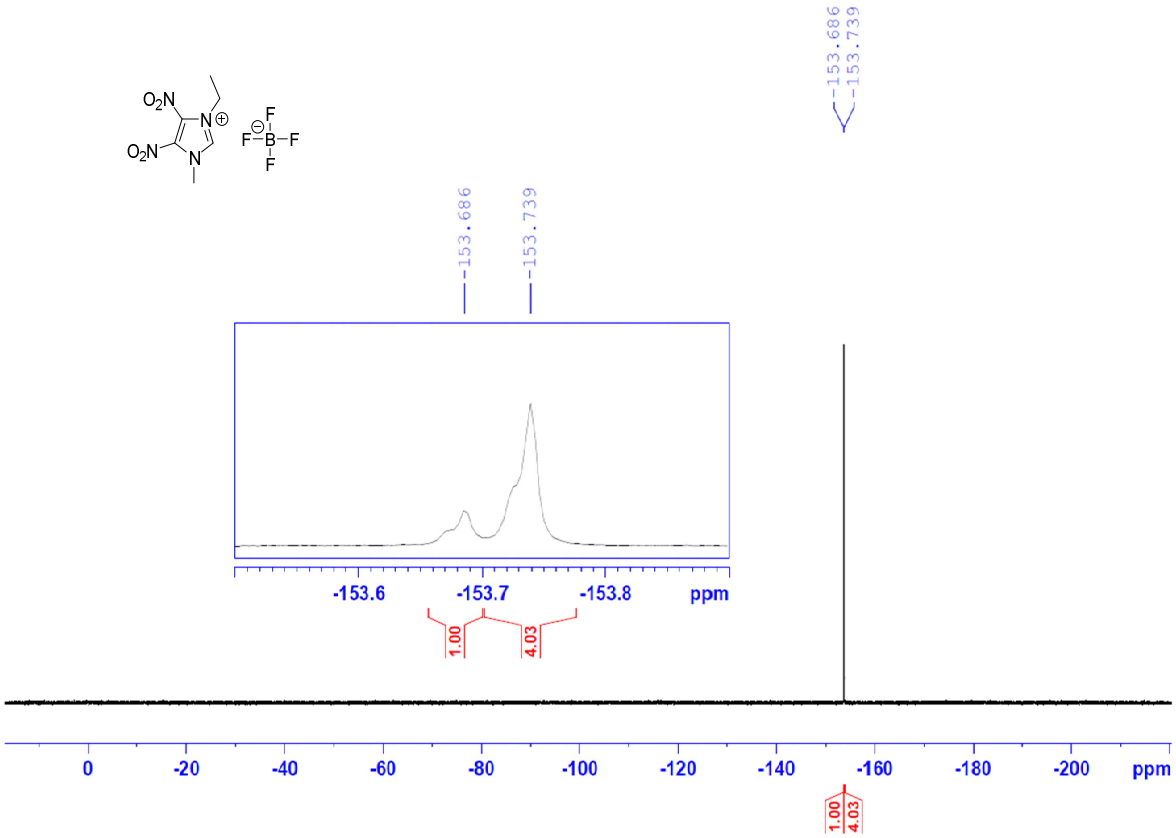


100MHz ^{1}H NMR Spectrum (CD_3CN) of compound **9.**

List of ^{19}F NMR Spectra of Selected Compounds

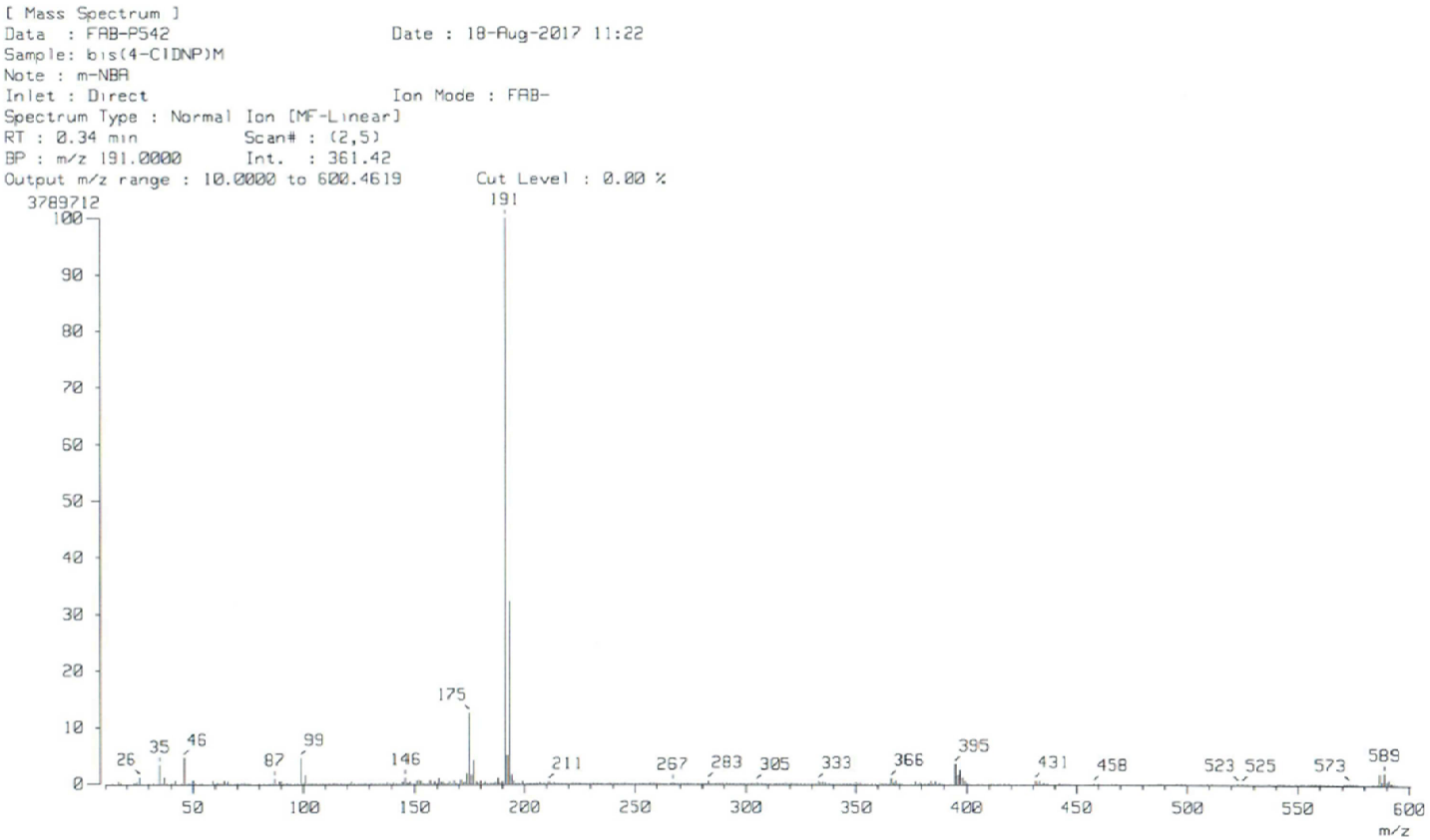


376MHz ^{19}F NMR Spectrum (CD_3CN) of compound **6**.

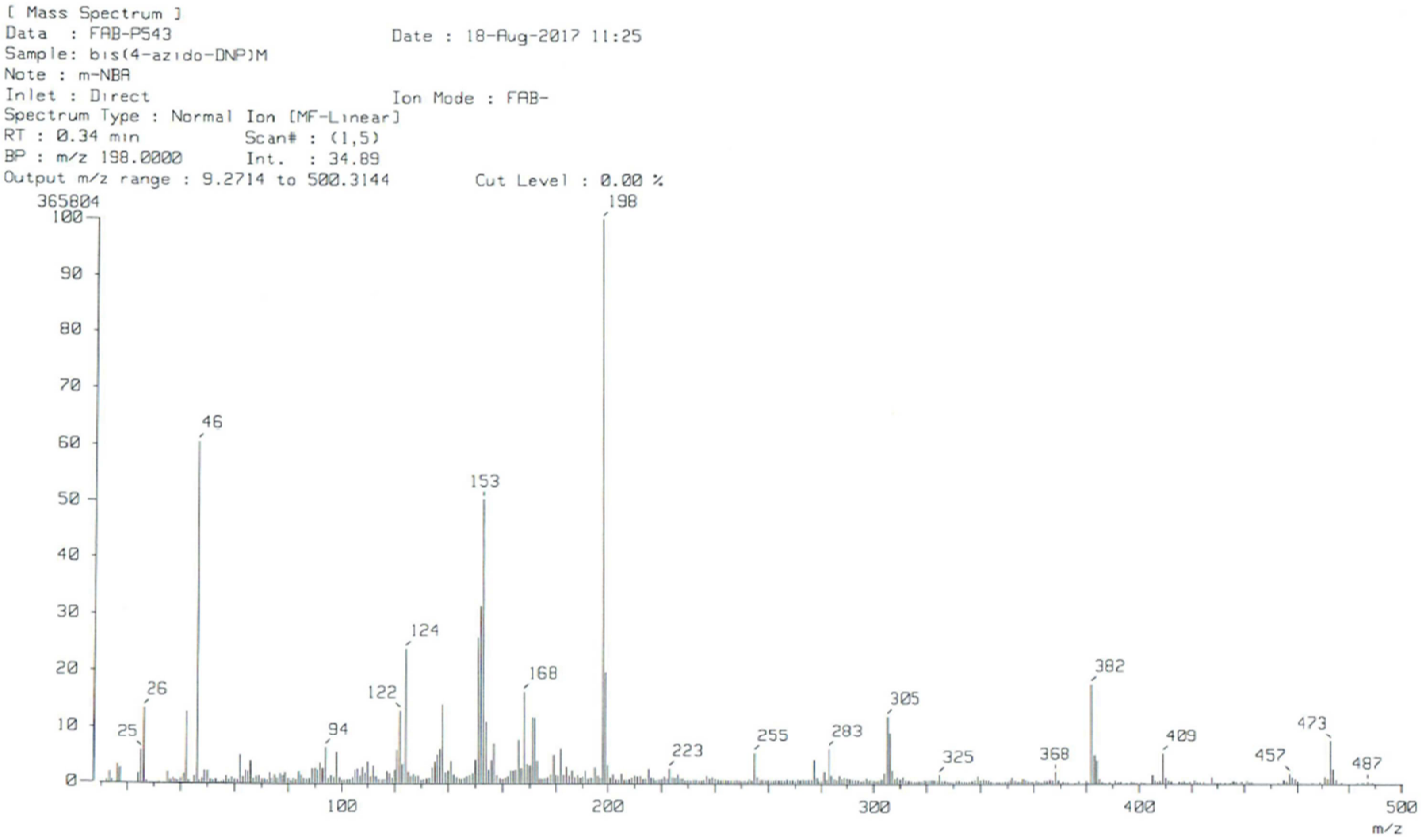


376MHz ^{19}F NMR Spectrum (CD_3CN) of compound **7**.

List of high-resolution mass data

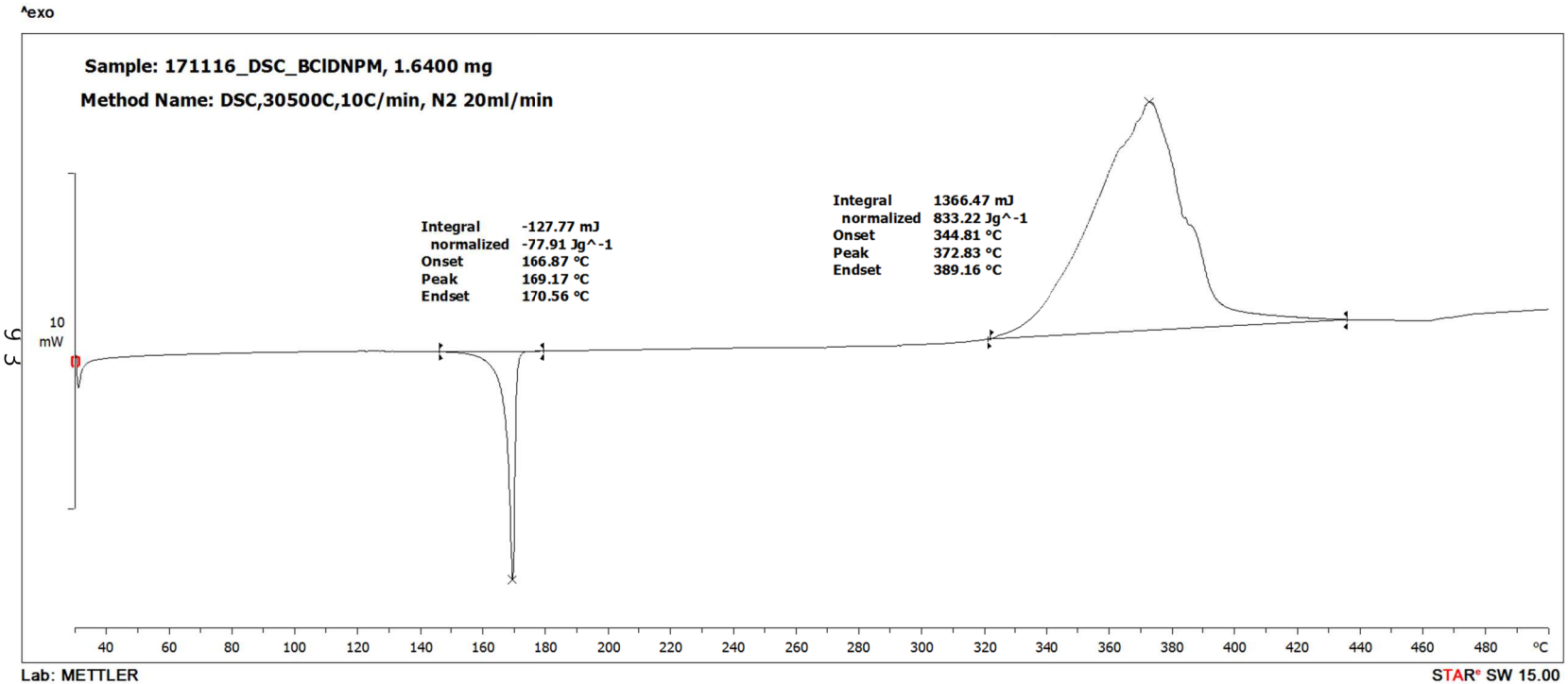


High resolution mass data of compound **2**.

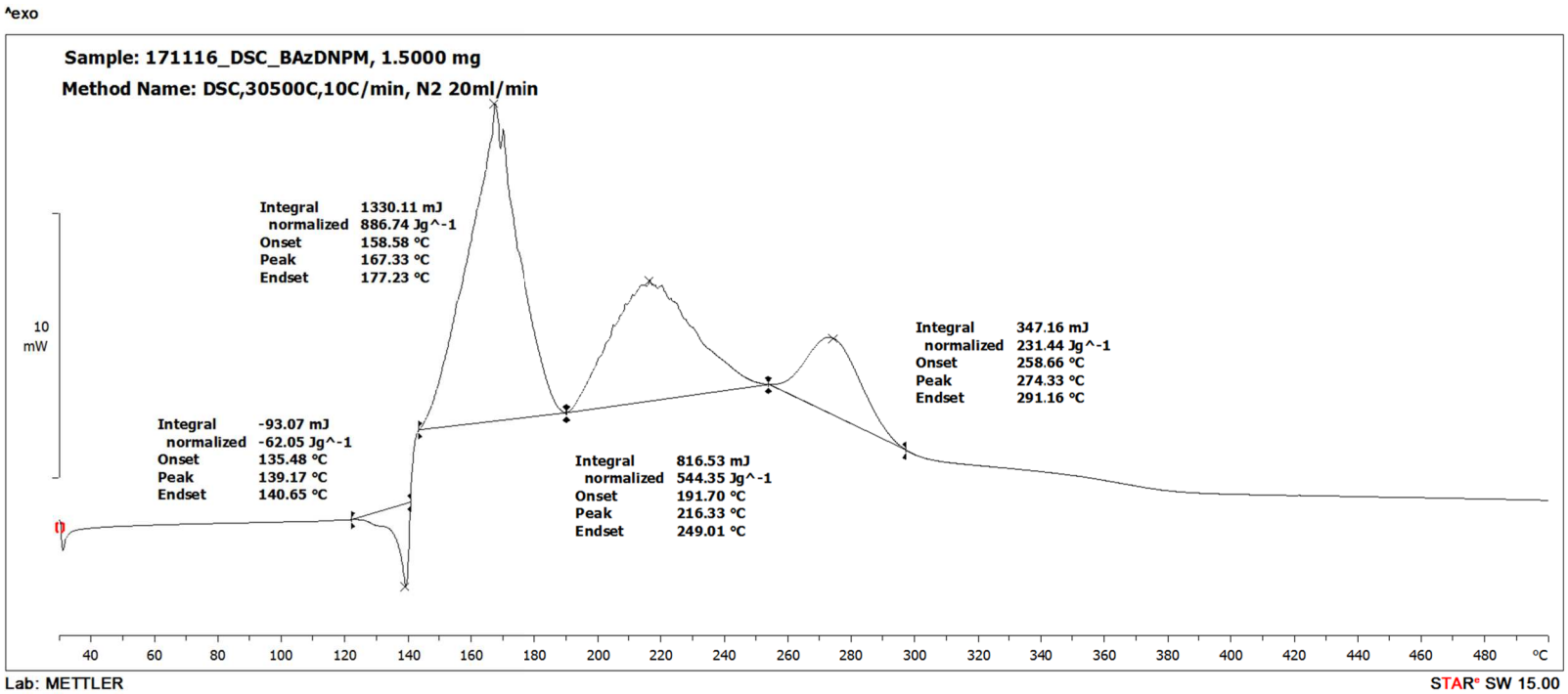


High resolution mass data of compound **3**.

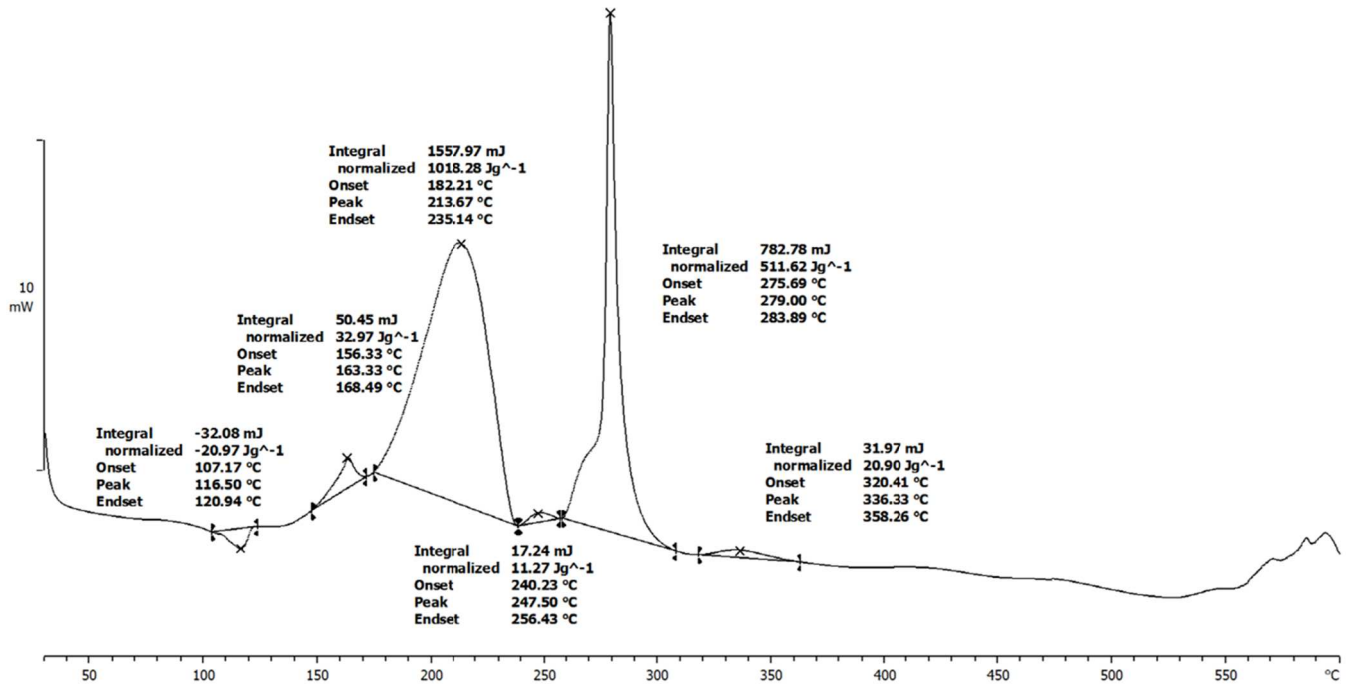
List of themal analysis data



Differential scanning calorimetry data of compound **2.**



Differential scanning calorimetry data of compound **3.**



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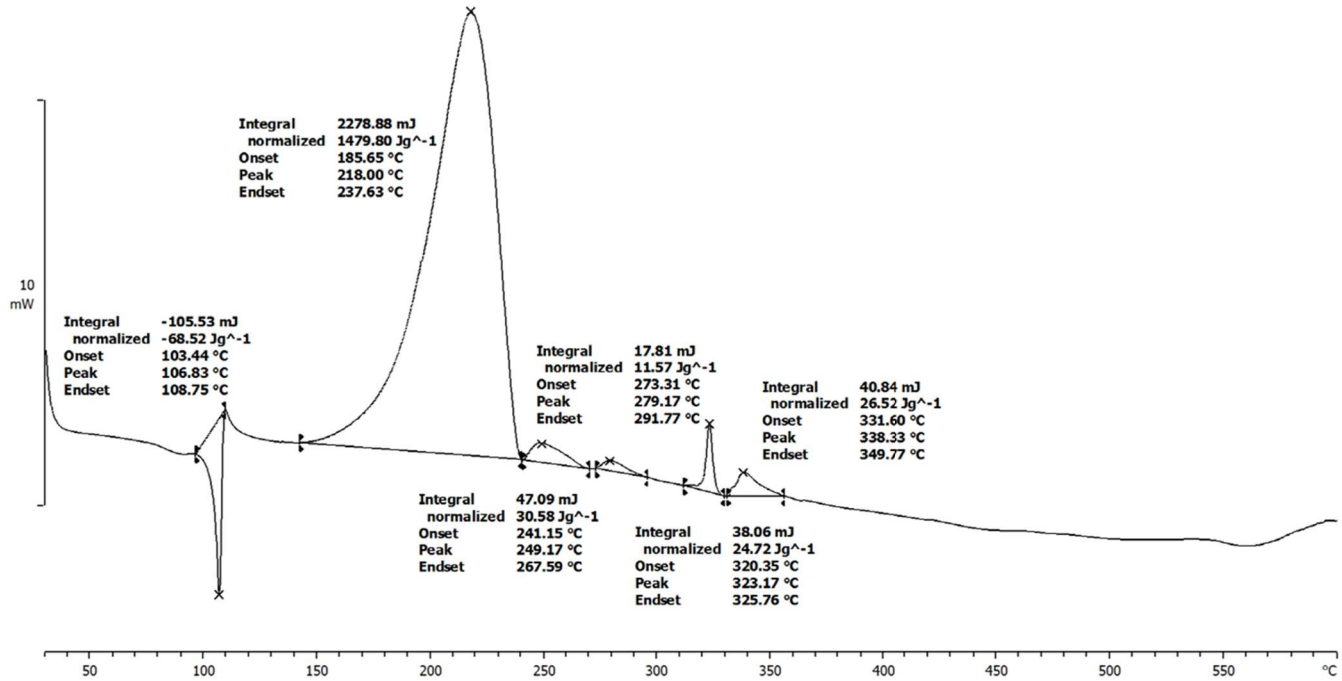
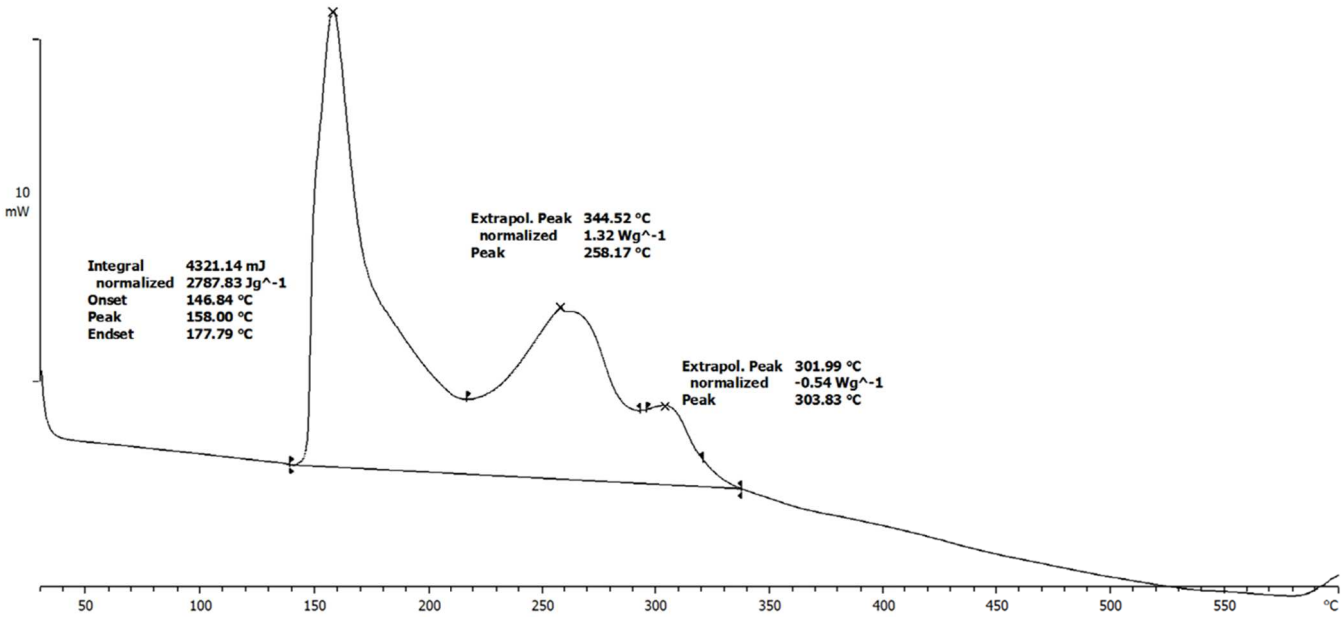
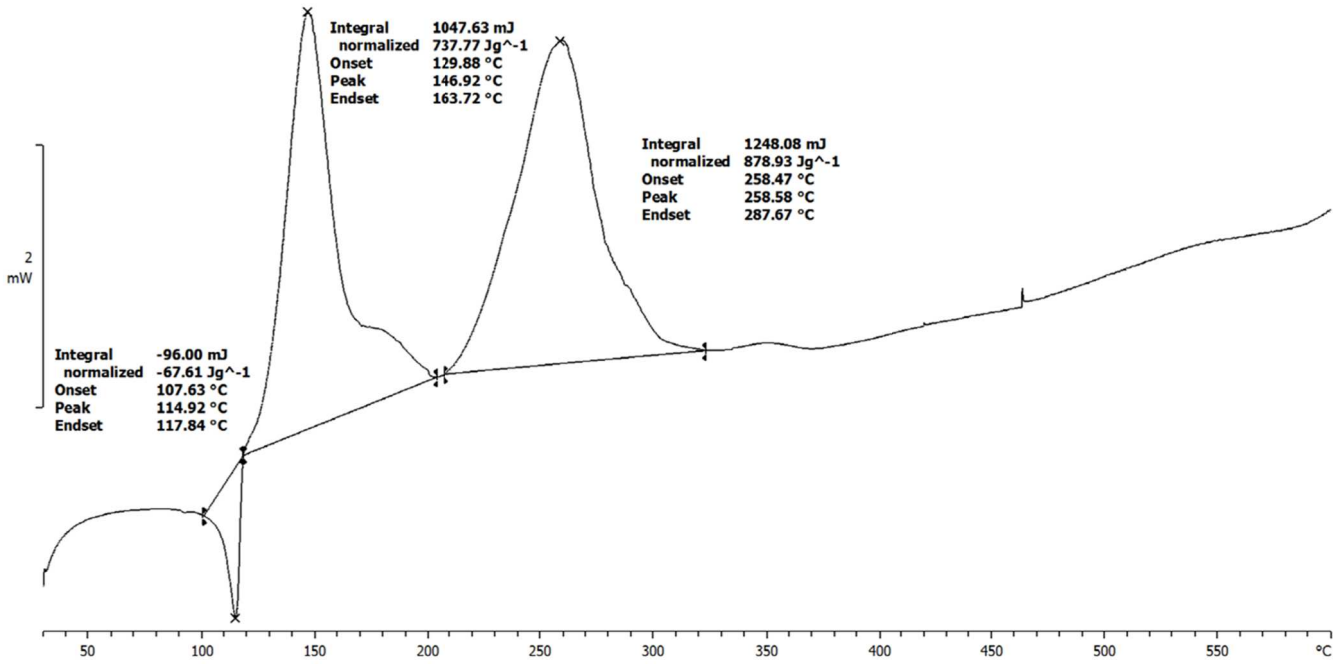


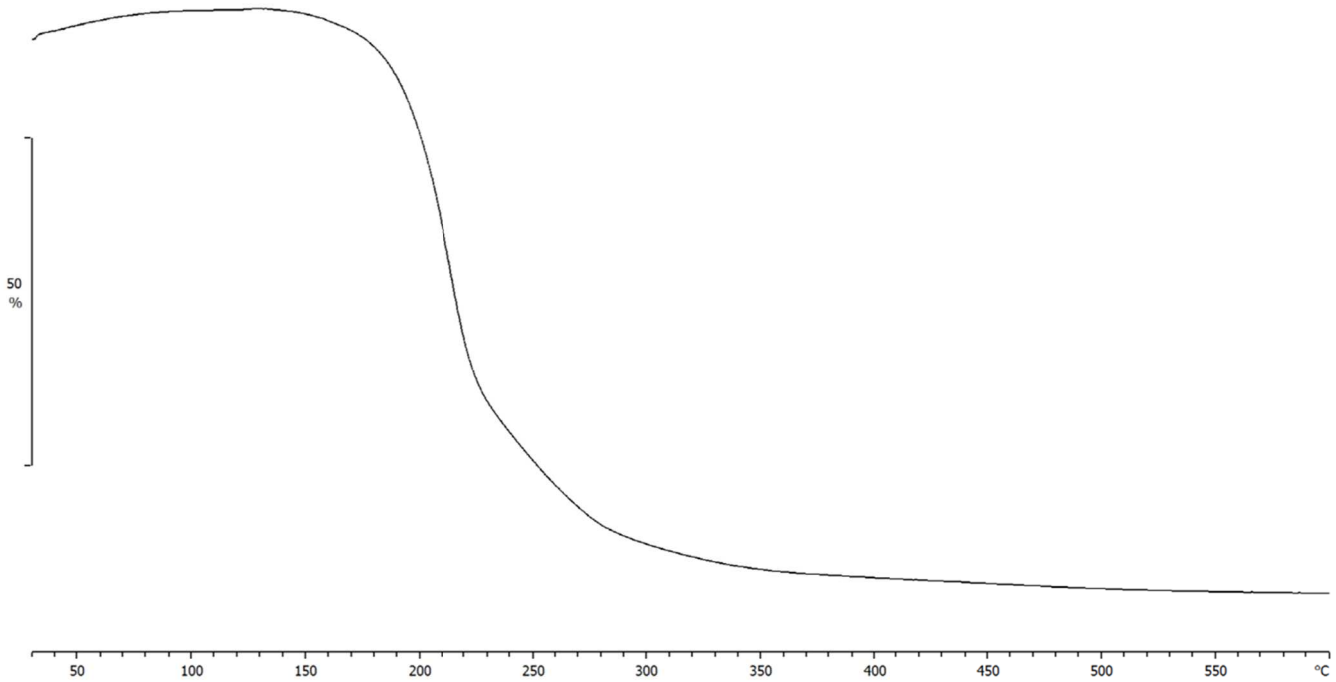
Differential scanning calorimetry data of compound **7.**



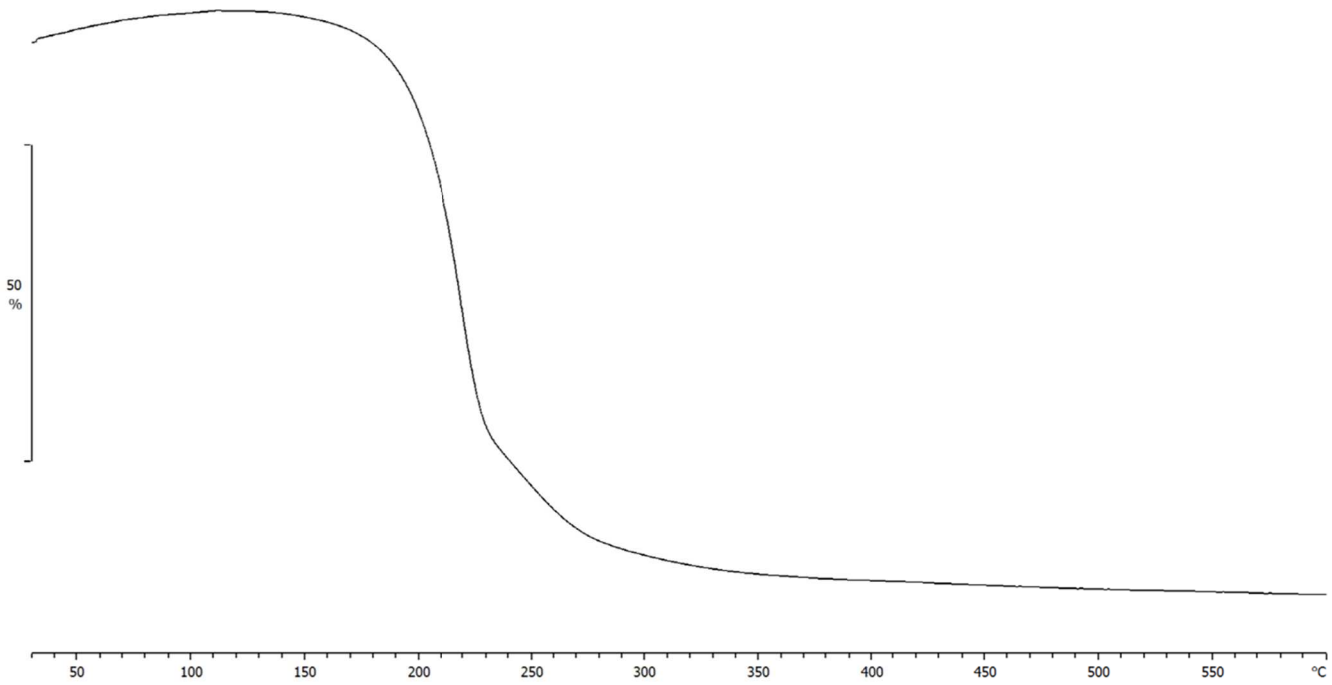
Differential scanning calorimetry data of compound **8.**



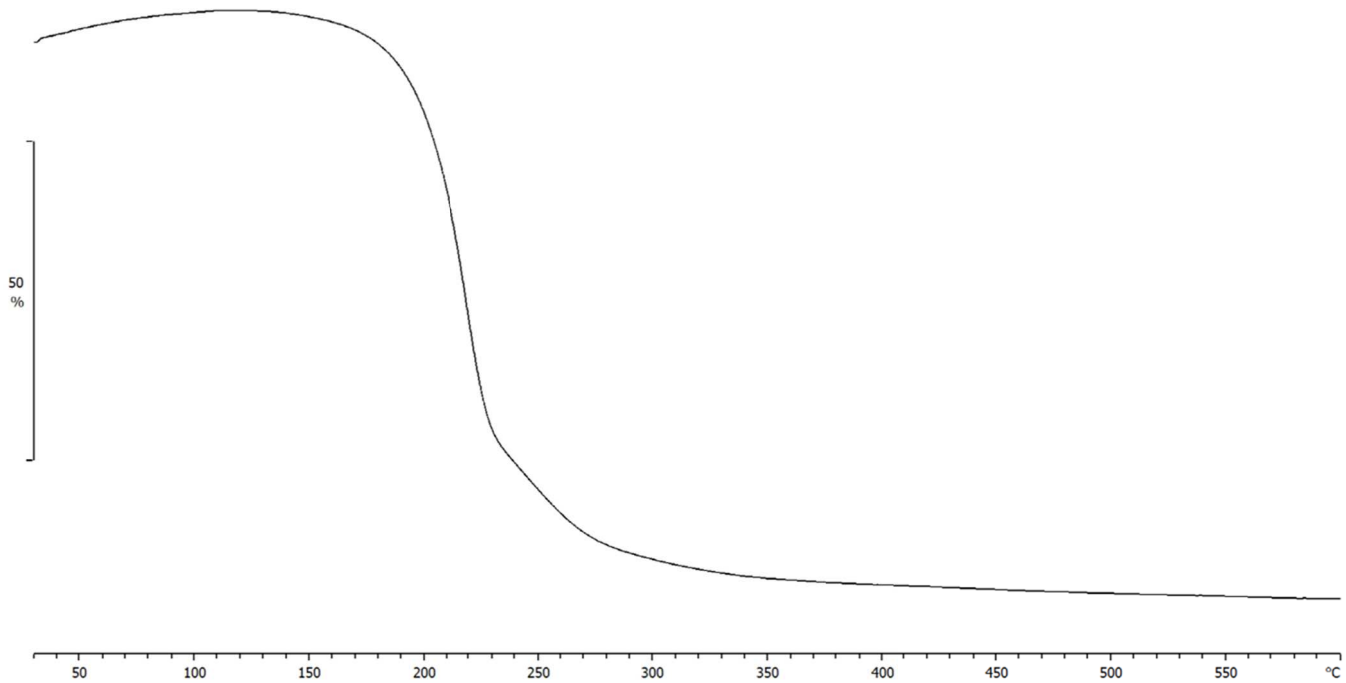
Differential scanning calorimetry data of compound **9.**



Thermogravimetric analysis data of compound **6.**



Thermogravimetric analysis data of compound **7.**



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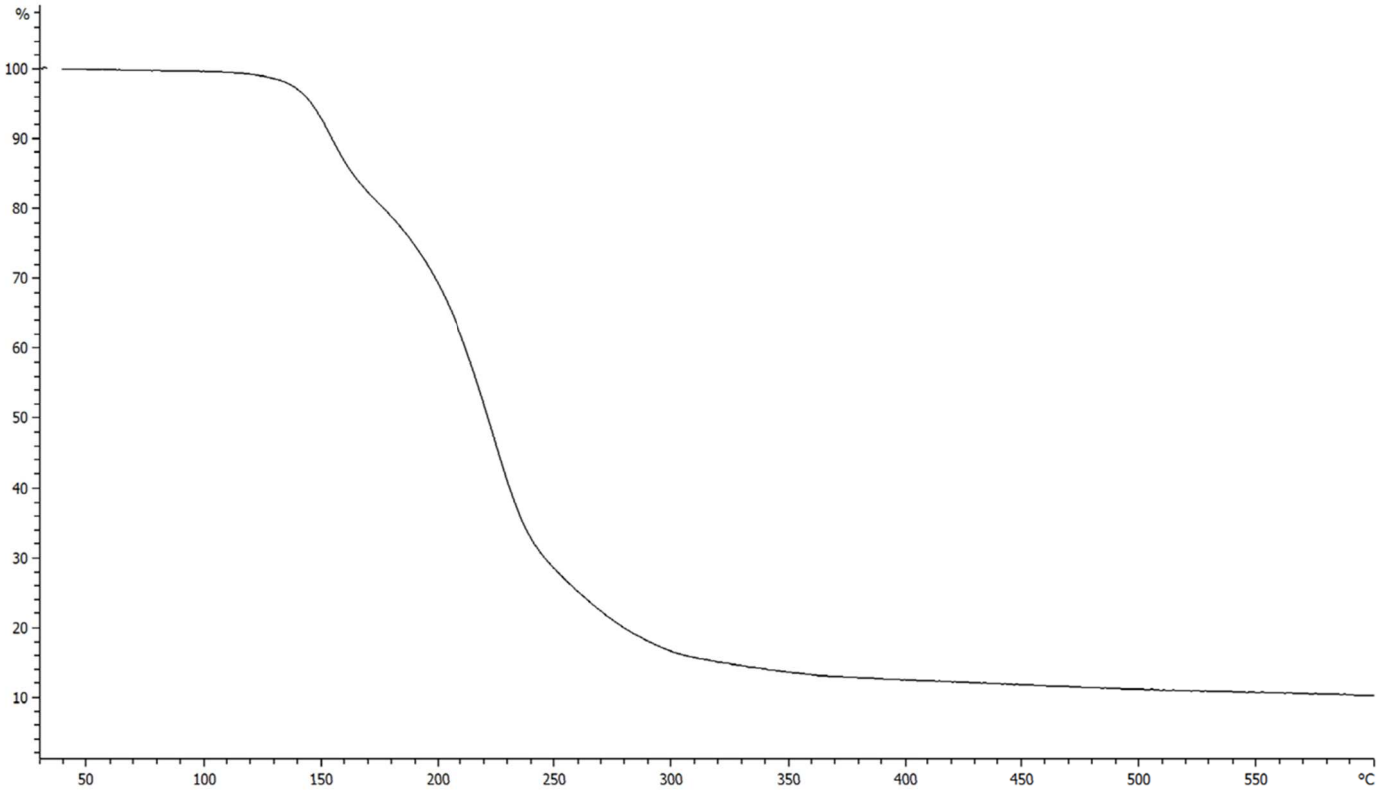

Thermogravimetric analysis data of compound **9.**

List of single-crystal XRD data of selected compounds

1. Bis(4-chloro-3,5-dinitro-1*H*-pyrazol-1-yl)methane 2

CCDC Deposition No. 586861

Crystal data and structure refinement for compound **2**.

Empirical formula	C7H2Cl2N8O8
Formula weight	397.07
Temperature/K	293.9(2)
Crystal system	monoclinic
Space group	P21/c
a/Å	13.5434(2)
b/Å	7.13240(10)
c/Å	15.3766(3)
α/°	90
β/°	106.771(2)
γ/°	90
Volume/Å3	1422.15(4)
Z	4
ρcalcg/cm3	1.854
μ/mm-1	4.761
F(000)	792
Crystal size/mm3	0.242 × 0.139 × 0.104
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	6.816 to 147.29
Index ranges	-16 ≤ h ≤ 14, -8 ≤ k ≤ 5, -15 ≤ l ≤ 18
Reflections collected	5540
Independent reflections	2802 [Rint = 0.0136, Rsigma = 0.0171]
Data/restraints/parameters	2802/6/245
Goodness-of-fit on F2	1.04
Final R indexes [I>=2σ (I)]	R1 = 0.0335, wR2 = 0.0874
Final R indexes [all data]	R1 = 0.0365, wR2 = 0.0897
Largest diff. peak/hole / e	Å-3 0.50/-0.47

Fractional atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for compound **2**.

Atom	x	y	z	U(eq)
Cl1	4959.1(4)	10720.2(8)	8441.0(4)	64.52(18)
O1	5841(6)	4676(8)	9107(18)	104(5)
O2	6185(10)	7491(19)	9604(11)	86(3)
O3	2827.0(16)	11294(3)	7233.3(16)	87.8(6)
O4	1630.0(12)	9212(3)	6973.2(11)	67.9(5)
N1	3006.8(11)	6589(2)	7941.6(9)	37.2(3)
N2	3834.6(12)	5651(2)	8435.8(10)	42.9(4)
N3	5596.3(14)	6309(3)	9171.7(15)	64.0(5)
N4	2513.2(14)	9724(3)	7306.3(11)	51.1(4)
C1	4576.2(14)	6904(3)	8640.7(12)	41.7(4)
C2	4266.0(14)	8689(3)	8290.5(12)	40.0(4)
C3	3246.0(14)	8409(3)	7830.5(11)	38.5(4)
C4	2039.4(14)	5585(3)	7698.6(11)	43.5(4)
Cl1'	413.2(4)	2248.4(7)	4544.5(3)	51.52(15)
O1'	2928.1(14)	6650(3)	4781.5(11)	71.6(5)
O2'	1980.0(15)	4535(3)	3957(1)	80.8(6)
O3'	-392.8(12)	2050(3)	6164.4(11)	63.5(4)
O4'	443.1(13)	3134(3)	7474(1)	68.7(5)
N1'	1775.1(10)	5006(2)	6733.7(9)	33.0(3)
N2'	2309.1(11)	5696(2)	6206.1(9)	36.9(3)
N3'	2309.2(13)	5398(3)	4664.7(10)	46.7(4)
N4'	316.2(11)	2927(2)	6668.4(10)	40.6(3)
C1'	1910.1(12)	4876(3)	5406.6(10)	34.8(3)
C2'	1112.5(12)	3634(2)	5398.2(11)	34.2(3)
C3'	1038.5(12)	3786(2)	6270.8(11)	32.5(3)
O1A	5610(20)	4680(20)	9472(11)	75(5)
O2A	6230(20)	7490(50)	9300(30)	85(5)

Anisotropic displacement parameters ($Å^2 \times 10^3$) for compound **2**.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Cl1	63.3(3)	49.6(3)	73.2(4)	11.2(2)	7.9(3)	-17.5(2)
O1	60(2)	51.1(18)	172(11)	15(3)	-15(4)	14.2(16)
O2	60(3)	76(2)	94(5)	10(4)	-25(3)	-13.0(19)
O3	84.5(12)	53.8(11)	112.5(16)	32.6(11)	8.4(11)	15.8(10)
O4	52.6(8)	74.7(11)	61.9(9)	-10.0(8)	-6.4(7)	19.1(8)
N1	39.3(7)	41.4(8)	28.4(6)	-3.2(6)	5.8(5)	0.5(6)
N2	46.0(8)	39.5(8)	38.2(8)	1.4(6)	4.0(6)	1.5(7)
N3	48.2(10)	53.0(11)	75.0(13)	10.3(10)	-7.1(9)	0.8(9)
N4	55.3(10)	51.5(10)	42.7(8)	0.8(7)	8.2(7)	16.6(8)
C1	39.3(9)	41.0(9)	40.4(9)	1.2(7)	4.7(7)	0.6(7)
C2	44.6(9)	38.1(9)	37.2(8)	-0.4(7)	11.5(7)	0.5(7)
C3	44.1(9)	39.1(9)	32.0(8)	-1.2(7)	10.7(7)	5.4(7)
C4	42.1(9)	59.3(12)	30.4(8)	-8.8(8)	12.4(7)	-8.2(8)
Cl1'	61.2(3)	51.9(3)	36.7(2)	-10.94(19)	6.64(19)	-15.7(2)
O1'	86.6(11)	84.1(12)	51.8(8)	-4.3(8)	32.1(8)	-40.3(10)
O2'	100.1(13)	113.1(16)	34.8(7)	-18.6(8)	28.3(8)	-44.2(12)
O3'	53.0(8)	79.7(11)	58.0(9)	-6.8(8)	16.5(7)	-28.6(8)
O4'	66.4(9)	105.0(14)	40.8(7)	-2.9(8)	25.1(7)	-29.4(9)
N1'	32.0(6)	39.5(7)	27.6(6)	-1.3(6)	8.6(5)	-0.6(6)
N2'	36.1(7)	44.5(8)	31.1(7)	-1.4(6)	11.4(5)	-4.1(6)
N3'	50.4(9)	58.8(10)	31.7(7)	1.0(7)	13.3(6)	-7.2(8)
N4'	36.5(7)	45.4(8)	40.6(8)	4.7(7)	12.2(6)	-1.6(6)
C1'	37.3(8)	39.7(9)	27.6(7)	1.0(7)	9.8(6)	0.2(7)
C2'	36.5(8)	33.5(8)	30.2(7)	0.7(6)	5.5(6)	1.3(6)
C3'	31.3(7)	33.2(8)	31.9(7)	3.3(6)	7.5(6)	0.7(6)
O1A	70(8)	66(5)	70(8)	19(4)	-8(4)	17(5)
O2A	44(4)	79(5)	112(11)	18(10)	-12(8)	-17(4)

Bond lengths for compound **2**.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Cl1	C2	1.7056(19)	C2	C3	1.373(3)
O1	N3	1.223(8)	C4	N1'	1.481(2)
O2	N3	1.217(11)	Cl1'	C2'	1.6970(17)
O3	N4	1.215(3)	O1'	N3'	1.202(2)
O4	N4	1.214(2)	O2'	N3'	1.218(2)
N1	N2	1.338(2)	O3'	N4'	1.218(2)
N1	C3	1.360(2)	O4'	N4'	1.209(2)
N1	C4	1.445(2)	N1'	N2'	1.3276(19)
N2	C1	1.313(2)	N1'	C3'	1.360(2)
N3	C1	1.451(2)	N2'	C1'	1.327(2)
N3	O1A	1.250(17)	N3'	C1'	1.445(2)
N3	O2A	1.18(3)	N4'	C3'	1.432(2)
N4	C3	1.433(2)	C1'	C2'	1.394(2)
C1	C2	1.398(3)	C2'	C3'	1.378(2)

Bond angles for compound **2.**

Atom			Angle/°	Atom			Angle/°
N2	N1	C3	110.94(14)	C2	C3	N4	128.72(18)
N2	N1	C4	116.60(15)	N1	C4	N1'	109.66(13)
C3	N1	C4	132.20(16)	N2'	N1'	C4	119.46(14)
C1	N2	N1	104.69(15)	N2'	N1'	C3'	111.36(13)
O1	N3	C1	118.0(4)	C3'	N1'	C4	129.17(14)
O2	N3	O1	123.6(7)	C1'	N2'	N1'	104.75(13)
O2	N3	C1	118.2(6)	O1'	N3'	O2'	124.69(17)
O1A	N3	C1	113.1(13)	O1'	N3'	C1'	118.49(15)
O2A	N3	C1	114.6(16)	O2'	N3'	C1'	116.82(16)
O2A	N3	O1A	132(2)	O3'	N4'	C3'	117.26(15)
O3	N4	C3	116.85(18)	O4'	N4'	O3'	124.56(16)
O4	N4	O3	124.53(19)	O4'	N4'	C3'	118.18(15)
O4	N4	C3	118.62(19)	N2'	C1'	N3'	118.20(15)
N2	C1	N3	118.31(17)	N2'	C1'	C2'	113.32(14)
N2	C1	C2	113.77(16)	C2'	C1'	N3'	128.44(15)
C2	C1	N3	127.92(18)	C1'	C2'	Cl1'	129.44(13)
C1	C2	Cl1	128.94(14)	C3'	C2'	Cl1'	128.13(13)
C3	C2	Cl1	128.75(15)	C3'	C2'	C1'	102.42(14)
C3	C2	C1	102.24(16)	N1'	C3'	N4'	122.59(14)
N1	C3	N4	122.94(16)	N1'	C3'	C2'	108.13(14)
N1	C3	C2	108.34(16)	C2'	C3'	N4'	129.24(15)

2. Bis(4-azido-3,5-dinitro-1*H*-pyrazol-1-yl)methane 3

CCDC Deposition No. 586862

Crystal data and structure refinement for comound **3**.

Empirical formula	C7 H2 N14 O8
Formula weight	410.23
Temperature	223(2) K
Wavelength	0.71073 Å
Crystal system	Triclinic
Space group	P-1
Unit cell dimensions	a = 10.7821(8) Å, α= 65.506(2)°
	b = 12.3312(10) Å, β= 71.897(2)°
	c = 12.8309(9) Å, γ = 88.916(2)°
Volume	1463.61(19) $Å^3$
Z	4
Density (calculated)	1.862 Mg/m^3
Absorption coefficient	0.168 mm^{-1}
F(000)	824
Crystal size	0.256 x 0.150 x 0.102 mm^3
Theta range for data collection	1.850 to 26.033°.
Index ranges	-13<=h<=13, -15<=k<=15, -15<=l<=15
Reflections collected	39971
Independent reflections	5772 [R(int) = 0.0784]
Completeness to theta = 25.242°	100.00%
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7453 and 0.6993
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	5772 / 0 / 523
Goodness-of-fit on F^2	1.038
Final R indices [I>2sigma(I)]	R1 = 0.0525, wR2 = 0.1129
R indices (all data)	R1 = 0.1159, wR2 = 0.1472
Extinction coefficient	n/a
Largest diff. peak and hole	0.439 and -0.320 e.$Å^{-3}$

Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for compound **3**.

	x	y	z	U(eq)
C(1)	5229(3)	6061(4)	11147(3)	52(1)
N(1)	6570(3)	6535(3)	10335(3)	42(1)
N(2)	7319(3)	5746(3)	10061(3)	43(1)
C(2)	8439(3)	6405(3)	9260(3)	38(1)
C(3)	8444(3)	7638(3)	8964(3)	39(1)
C(4)	7214(3)	7675(3)	9688(3)	41(1)
N(3)	9474(3)	5797(3)	8811(3)	42(1)
O(1)	9305(2)	4696(2)	9255(2)	52(1)
O(2)	10475(3)	6418(2)	8019(2)	55(1)
N(4)	9425(3)	8642(2)	8241(3)	41(1)
N(5)	10123(3)	8723(3)	7256(3)	50(1)
N(6)	10837(4)	8966(3)	6305(4)	69(1)
N(7)	6641(4)	8693(4)	9829(3)	55(1)
O(3)	7263(3)	9681(3)	9223(3)	77(1)
O(4)	5542(3)	8498(3)	10572(3)	84(1)
N(8)	4323(3)	6546(3)	10467(2)	42(1)
N(9)	4635(3)	6587(3)	9362(2)	43(1)
C(5)	3713(4)	7138(3)	8937(3)	46(1)
C(6)	2779(3)	7474(3)	9743(4)	47(1)
C(7)	3201(3)	7055(3)	10735(3)	45(1)
N(10)	3793(4)	7320(3)	7730(3)	61(1)
O(5)	4567(4)	6792(3)	7248(3)	80(1)
O(6)	3090(3)	8006(4)	7262(3)	99(1)
N(11)	1690(4)	8088(4)	9481(4)	67(1)
N(12)	1297(4)	8626(4)	9862(6)	99(2)
N(13)	735(6)	9230(6)	10401(7)	158(3)
N(14)	2571(3)	7027(3)	11904(3)	63(1)
O(7)	3153(3)	6759(4)	12634(3)	93(1)
O(8)	1422(3)	7228(3)	12133(3)	90(1)

	x	y	z	U(eq)
C(8)	1064(3)	4802(3)	6550(3)	35(1)
N(15)	1517(2)	3930(2)	6062(2)	31(1)
N(16)	1560(2)	4202(2)	4933(2)	34(1)
C(9)	1972(3)	3267(3)	4735(3)	32(1)
C(10)	2213(3)	2353(3)	5727(3)	32(1)
C(11)	1909(3)	2825(3)	6565(3)	32(1)
N(17)	2049(3)	3281(3)	3591(3)	44(1)
O(9)	2120(3)	2326(3)	3519(2)	62(1)
O(10)	2005(3)	4241(2)	2768(2)	58(1)
N(18)	2585(3)	1199(3)	5982(3)	46(1)
N(19)	3255(3)	997(3)	5167(3)	43(1)
N(20)	3922(4)	665(3)	4509(4)	69(1)
N(21)	1989(3)	2312(3)	7763(3)	45(1)
O(11)	2600(3)	1461(3)	8021(3)	91(1)
O(12)	1427(3)	2723(2)	8477(2)	56(1)
N(22)	1808(2)	5977(2)	5738(2)	33(1)
N(23)	1158(3)	6833(2)	5185(2)	36(1)
C(12)	2040(3)	7789(3)	4489(3)	34(1)
C(13)	3312(3)	7583(3)	4535(3)	34(1)
C(14)	3105(3)	6394(3)	5369(3)	32(1)
N(24)	1575(3)	8885(3)	3835(3)	44(1)
O(13)	456(3)	8832(2)	3834(3)	69(1)
O(14)	2336(3)	9805(2)	3354(3)	61(1)
N(25)	4541(3)	8269(3)	3983(3)	50(1)
N(26)	4759(3)	9195(3)	3032(3)	45(1)
N(27)	5155(3)	10044(3)	2168(3)	65(1)
N(28)	4026(3)	5662(3)	5832(3)	36(1)
O(15)	3577(2)	4713(2)	6743(2)	47(1)
O(16)	5195(2)	6028(2)	5300(2)	49(1)

Bond lengths [Å] for compound **3**.

Bond	length (Å)	Bond	length (Å)
C(1)-N(1)	1.452(4)	C(8)-N(22)	1.449(4)
C(1)-N(8)	1.465(4)	C(8)-N(15)	1.461(4)
C(1)-H(1A)	0.98	C(8)-H(8A)	0.98
C(1)-H(1B)	0.98	C(8)-H(8B)	0.98
N(1)-N(2)	1.342(4)	N(15)-N(16)	1.331(3)
N(1)-C(4)	1.364(4)	N(15)-C(11)	1.368(4)
N(2)-C(2)	1.322(4)	N(16)-C(9)	1.320(4)
C(2)-C(3)	1.406(5)	C(9)-C(10)	1.401(4)
C(2)-N(3)	1.437(4)	C(9)-N(17)	1.438(4)
C(3)-C(4)	1.375(5)	C(10)-C(11)	1.377(4)
C(3)-N(4)	1.414(4)	C(10)-N(18)	1.402(4)
C(4)-N(7)	1.442(5)	C(11)-N(21)	1.430(4)
N(3)-O(2)	1.220(4)	N(17)-O(9)	1.218(4)
N(3)-O(1)	1.227(3)	N(17)-O(10)	1.229(4)
N(4)-N(5)	1.217(4)	N(18)-N(19)	1.191(4)
N(5)-N(6)	1.137(4)	N(19)-N(20)	1.138(4)
N(7)-O(3)	1.208(4)	N(21)-O(11)	1.212(4)
N(7)-O(4)	1.220(4)	N(21)-O(12)	1.221(4)
N(8)-N(9)	1.330(4)	N(22)-N(23)	1.331(3)
N(8)-C(7)	1.368(4)	N(22)-C(14)	1.363(4)
N(9)-C(5)	1.324(4)	N(23)-C(12)	1.317(4)
C(5)-C(6)	1.396(5)	C(12)-C(13)	1.405(4)
C(5)-N(10)	1.444(5)	C(12)-N(24)	1.441(4)
C(6)-C(7)	1.379(5)	C(13)-C(14)	1.381(4)
C(6)-N(11)	1.437(5)	C(13)-N(25)	1.391(4)
C(7)-N(14)	1.426(5)	C(14)-N(28)	1.429(4)
N(10)-O(6)	1.220(4)	N(24)-O(13)	1.209(3)
N(10)-O(5)	1.223(4)	N(24)-O(14)	1.217(3)
N(11)-N(12)	0.994(6)	N(25)-N(26)	1.236(4)
N(12)-N(13)	1.246(7)	N(26)-N(27)	1.125(4)
N(14)-O(7)	1.217(4)	N(28)-O(16)	1.221(3)
N(14)-O(8)	1.226(4)	N(28)-O(15)	1.227(3)

Bond angles [°] for compound **3**.

Bond	Angle(°)	Bond	Angle(°)	Bond	Angle(°)
N(1)-C(1)-N(8)	109.0(3)	C(6)-C(5)-N(10)	128.6(3)	C(10)-C(11)-N(21)	128.4(3)
N(1)-C(1)-H(1A)	109.9	C(7)-C(6)-C(5)	102.1(3)	O(9)-N(17)-O(10)	124.7(3)
N(8)-C(1)-H(1A)	109.9	C(7)-C(6)-N(11)	134.0(4)	O(9)-N(17)-C(9)	117.1(3)
N(1)-C(1)-H(1B)	109.9	C(5)-C(6)-N(11)	123.9(4)	O(10)-N(17)-C(9)	118.2(3)
N(8)-C(1)-H(1B)	109.9	N(8)-C(7)-C(6)	108.3(3)	N(19)-N(18)-C(10)	118.9(3)
H(1A)-C(1)-H(1B)	108.3	N(8)-C(7)-N(14)	122.9(3)	N(20)-N(19)-N(18)	170.6(4)
N(2)-N(1)-C(4)	111.2(3)	C(6)-C(7)-N(14)	128.6(3)	O(11)-N(21)-O(12)	123.4(3)
N(2)-N(1)-C(1)	116.3(3)	O(6)-N(10)-O(5)	124.9(4)	O(11)-N(21)-C(11)	117.0(3)
C(4)-N(1)-C(1)	132.2(3)	O(6)-N(10)-C(5)	117.1(4)	O(12)-N(21)-C(11)	119.6(3)
C(2)-N(2)-N(1)	104.5(3)	O(5)-N(10)-C(5)	118.0(3)	N(23)-N(22)-C(14)	110.8(3)
N(2)-C(2)-C(3)	113.7(3)	N(12)-N(11)-C(6)	121.2(5)	N(23)-N(22)-C(8)	116.8(2)
N(2)-C(2)-N(3)	117.7(3)	N(11)-N(12)-N(13)	175.4(6)	C(14)-N(22)-C(8)	132.3(3)
C(3)-C(2)-N(3)	128.6(3)	O(7)-N(14)-O(8)	123.3(4)	C(12)-N(23)-N(22)	105.3(2)
C(4)-C(3)-C(2)	102.2(3)	O(7)-N(14)-C(7)	120.0(3)	N(23)-C(12)-C(13)	113.5(3)
C(4)-C(3)-N(4)	124.1(3)	O(8)-N(14)-C(7)	116.6(4)	N(23)-C(12)-N(24)	116.9(3)
C(2)-C(3)-N(4)	133.3(3)	N(22)-C(8)-N(15)	110.5(2)	C(13)-C(12)-N(24)	129.5(3)
N(1)-C(4)-C(3)	108.5(3)	N(22)-C(8)-H(8A)	109.6	C(14)-C(13)-N(25)	122.7(3)
N(1)-C(4)-N(7)	122.5(3)	N(15)-C(8)-H(8A)	109.6	C(14)-C(13)-C(12)	101.8(3)
C(3)-C(4)-N(7)	129.0(4)	N(22)-C(8)-H(8B)	109.6	N(25)-C(13)-C(12)	135.5(3)
O(2)-N(3)-O(1)	124.4(3)	N(15)-C(8)-H(8B)	109.6	N(22)-C(14)-C(13)	108.6(3)
O(2)-N(3)-C(2)	117.3(3)	H(8A)-C(8)-H(8B)	108.1	N(22)-C(14)-N(28)	122.4(3)
O(1)-N(3)-C(2)	118.4(3)	N(16)-N(15)-C(11)	110.7(2)	C(13)-C(14)-N(28)	129.0(3)
N(5)-N(4)-C(3)	117.4(3)	N(16)-N(15)-C(8)	117.6(2)	O(13)-N(24)-O(14)	124.9(3)
N(6)-N(5)-N(4)	169.8(4)	C(11)-N(15)-C(8)	131.7(3)	O(13)-N(24)-C(12)	118.2(3)
O(3)-N(7)-O(4)	123.6(4)	C(9)-N(16)-N(15)	105.1(2)	O(14)-N(24)-C(12)	116.8(3)
O(3)-N(7)-C(4)	119.1(4)	N(16)-C(9)-C(10)	113.6(3)	N(26)-N(25)-C(13)	119.9(3)
O(4)-N(7)-C(4)	117.2(4)	N(16)-C(9)-N(17)	117.6(3)	N(27)-N(26)-N(25)	169.1(4)
N(9)-N(8)-C(7)	111.1(3)	C(10)-C(9)-N(17)	128.7(3)	O(16)-N(28)-O(15)	124.9(3)
N(9)-N(8)-C(1)	117.9(3)	C(11)-C(10)-C(9)	101.9(3)	O(16)-N(28)-C(14)	117.8(3)
C(7)-N(8)-C(1)	130.9(3)	C(11)-C(10)-N(18)	122.9(3)	O(15)-N(28)-C(14)	117.3(3)
C(5)-N(9)-N(8)	104.7(3)	C(9)-C(10)-N(18)	135.0(3)		
N(9)-C(5)-C(6)	113.8(3)	N(15)-C(11)-C(10)	108.6(3)		

Anisotropic displacement parameters ($Å^2$x 10^3) for compound **3**.

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C(1)	41(2)	74(3)	34(2)	-19(2)	-12(2)	9(2)
N(1)	39(2)	54(2)	37(2)	-22(2)	-15(1)	9(2)
N(2)	43(2)	50(2)	39(2)	-19(2)	-16(2)	7(2)
C(2)	41(2)	42(2)	36(2)	-19(2)	-17(2)	7(2)
C(3)	45(2)	51(2)	34(2)	-24(2)	-21(2)	8(2)
C(4)	45(2)	51(2)	40(2)	-27(2)	-20(2)	14(2)
N(3)	47(2)	42(2)	41(2)	-19(2)	-21(2)	9(2)
O(1)	60(2)	39(2)	57(2)	-20(1)	-20(1)	7(1)
O(2)	49(2)	47(2)	51(2)	-17(1)	1(1)	4(1)
N(4)	44(2)	37(2)	38(2)	-18(1)	-8(2)	3(1)
N(5)	47(2)	34(2)	62(2)	-15(2)	-18(2)	6(2)
N(6)	68(3)	53(2)	65(3)	-21(2)	-2(2)	0(2)
N(7)	55(2)	76(3)	56(2)	-44(2)	-25(2)	21(2)
O(3)	94(2)	59(2)	71(2)	-31(2)	-14(2)	16(2)
O(4)	54(2)	100(3)	121(3)	-80(2)	-16(2)	15(2)
N(8)	37(2)	56(2)	35(2)	-22(2)	-10(1)	6(1)
N(9)	43(2)	51(2)	33(2)	-18(1)	-11(1)	4(2)
C(5)	44(2)	46(2)	43(2)	-14(2)	-17(2)	-5(2)
C(6)	35(2)	40(2)	62(3)	-18(2)	-16(2)	-2(2)
C(7)	33(2)	55(2)	48(2)	-27(2)	-5(2)	1(2)
N(10)	72(3)	61(2)	46(2)	-12(2)	-28(2)	-9(2)
O(5)	131(3)	67(2)	48(2)	-30(2)	-30(2)	8(2)
O(6)	85(2)	134(3)	75(2)	-22(2)	-53(2)	17(2)
N(11)	49(2)	67(3)	90(3)	-32(2)	-30(2)	6(2)
N(12)	39(2)	44(3)	194(6)	-34(3)	-40(3)	11(2)
N(13)	90(4)	113(5)	275(9)	-97(5)	-48(5)	16(4)
N(14)	48(2)	84(3)	60(2)	-43(2)	-4(2)	1(2)
O(7)	76(2)	153(3)	67(2)	-73(2)	-14(2)	14(2)
O(8)	52(2)	117(3)	92(3)	-58(2)	4(2)	12(2)

Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for compound **3**.

	x	y	z	U(eq)
H(1A)	5038	6290	11821	62
H(1B)	5117	5182	11484	62
H(8A)	128	4851	6655	42
H(8B)	1168	4538	7348	42

Torsion angles [°] for compound **3**.

Bond	Angle(°)	Bond	Angle(°)
(8)-C(1)-N(1)-N(2)	-111.1(3)	N(22)-C(8)-N(15)-N(16)	-53.1(3)
N(8)-C(1)-N(1)-C(4)	62.1(5)	N(22)-C(8)-N(15)-C(11)	128.0(3)
C(4)-N(1)-N(2)-C(2)	1.3(3)	C(11)-N(15)-N(16)-C(9)	0.3(3)
C(1)-N(1)-N(2)-C(2)	175.8(3)	C(8)-N(15)-N(16)-C(9)	-178.8(3)
N(1)-N(2)-C(2)-C(3)	-1.6(4)	N(15)-N(16)-C(9)-C(10)	0.0(3)
N(1)-N(2)-C(2)-N(3)	178.3(3)	N(15)-N(16)-C(9)-N(17)	176.8(3)
N(2)-C(2)-C(3)-C(4)	1.3(4)	N(16)-C(9)-C(10)-C(11)	-0.2(4)
N(3)-C(2)-C(3)-C(4)	-178.6(3)	N(17)-C(9)-C(10)-C(11)	-176.6(3)
N(2)-C(2)-C(3)-N(4)	174.7(3)	N(16)-C(9)-C(10)-N(18)	176.2(3)
N(3)-C(2)-C(3)-N(4)	-5.2(6)	N(17)-C(9)-C(10)-N(18)	-0.1(6)
N(2)-N(1)-C(4)-C(3)	-0.5(4)	N(16)-N(15)-C(11)-C(10)	-0.4(3)
C(1)-N(1)-C(4)-C(3)	-173.9(3)	C(8)-N(15)-C(11)-C(10)	178.5(3)
N(2)-N(1)-C(4)-N(7)	-178.7(3)	N(16)-N(15)-C(11)-N(21)	178.5(3)
C(1)-N(1)-C(4)-N(7)	7.9(5)	C(8)-N(15)-C(11)-N(21)	-2.5(5)
C(2)-C(3)-C(4)-N(1)	-0.5(3)	C(9)-C(10)-C(11)-N(15)	0.4(3)
N(4)-C(3)-C(4)-N(1)	-174.7(3)	N(18)-C(10)-C(11)-N(15)	-176.6(3)
C(2)-C(3)-C(4)-N(7)	177.6(3)	C(9)-C(10)-C(11)-N(21)	-178.5(3)
N(4)-C(3)-C(4)-N(7)	3.4(5)	N(18)-C(10)-C(11)-N(21)	4.5(5)
N(2)-C(2)-N(3)-O(2)	175.7(3)	N(16)-C(9)-N(17)-O(9)	-163.0(3)
C(3)-C(2)-N(3)-O(2)	-4.4(5)	C(10)-C(9)-N(17)-O(9)	13.3(5)
N(2)-C(2)-N(3)-O(1)	-5.2(4)	N(16)-C(9)-N(17)-O(10)	15.3(4)
C(3)-C(2)-N(3)-O(1)	174.7(3)	C(10)-C(9)-N(17)-O(10)	-168.5(3)
C(4)-C(3)-N(4)-N(5)	-143.2(3)	C(11)-C(10)-N(18)-N(19)	-153.9(3)
C(2)-C(3)-N(4)-N(5)	44.6(5)	C(9)-C(10)-N(18)-N(19)	30.2(5)
C(3)-N(4)-N(5)-N(6)	170(2)	N(15)-C(11)-N(21)-O(11)	-164.9(3)

N(1)-C(4)-N(7)-O(3)	-179.7(3)	C(10)-C(11)-N(21)-O(11)	13.8(5)
C(3)-C(4)-N(7)-O(3)	2.6(5)	N(15)-C(11)-N(21)-O(12)	16.7(5)
N(1)-C(4)-N(7)-O(4)	0.9(5)	C(10)-C(11)-N(21)-O(12)	-164.6(3)
C(3)-C(4)-N(7)-O(4)	-176.9(3)	N(15)-C(8)-N(22)-N(23)	112.9(3)
N(1)-C(1)-N(8)-N(9)	43.0(4)	N(15)-C(8)-N(22)-C(14)	-64.0(4)
N(1)-C(1)-N(8)-C(7)	-132.3(4)	C(14)-N(22)-N(23)-C(12)	-1.1(3)
C(7)-N(8)-N(9)-C(5)	0.8(4)	C(8)-N(22)-N(23)-C(12)	-178.6(3)
C(1)-N(8)-N(9)-C(5)	-175.4(3)	N(22)-N(23)-C(12)-C(13)	1.7(4)
N(8)-N(9)-C(5)-C(6)	0.1(4)	N(22)-N(23)-C(12)-N(24)	-176.2(3)
N(8)-N(9)-C(5)-N(10)	179.8(3)	N(23)-C(12)-C(13)-C(14)	-1.6(4)
N(9)-C(5)-C(6)-C(7)	-0.9(4)	N(24)-C(12)-C(13)-C(14)	176.0(3)
N(10)-C(5)-C(6)-C(7)	179.4(3)	N(23)-C(12)-C(13)-N(25)	179.3(3)
N(9)-C(5)-C(6)-N(11)	179.8(3)	N(24)-C(12)-C(13)-N(25)	-3.1(6)
N(10)-C(5)-C(6)-N(11)	0.1(6)	N(23)-N(22)-C(14)-C(13)	0.1(3)
N(9)-N(8)-C(7)-C(6)	-1.5(4)	C(8)-N(22)-C(14)-C(13)	177.1(3)
C(1)-N(8)-C(7)-C(6)	174.1(3)	N(23)-N(22)-C(14)-N(28)	179.3(3)
N(9)-N(8)-C(7)-N(14)	173.6(3)	C(8)-N(22)-C(14)-N(28)	-3.7(5)
C(1)-N(8)-C(7)-N(14)	-10.8(6)	N(25)-C(13)-C(14)-N(22)	-179.9(3)
C(5)-C(6)-C(7)-N(8)	1.4(4)	C(12)-C(13)-C(14)-N(22)	0.9(3)
N(11)-C(6)-C(7)-N(8)	-179.4(4)	N(25)-C(13)-C(14)-N(28)	0.9(5)
C(5)-C(6)-C(7)-N(14)	-173.3(4)	C(12)-C(13)-C(14)-N(28)	-178.3(3)
N(11)-C(6)-C(7)-N(14)	5.9(7)	N(23)-C(12)-N(24)-O(13)	-9.5(5)
N(9)-C(5)-N(10)-O(6)	-167.5(4)	C(13)-C(12)-N(24)-O(13)	173.0(3)
C(6)-C(5)-N(10)-O(6)	12.2(6)	N(23)-C(12)-N(24)-O(14)	168.3(3)
N(9)-C(5)-N(10)-O(5)	11.7(5)	C(13)-C(12)-N(24)-O(14)	-9.2(5)
C(6)-C(5)-N(10)-O(5)	-168.6(4)	C(14)-C(13)-N(25)-N(26)	160.6(3)
C(7)-C(6)-N(11)-N(12)	29.0(8)	C(12)-C(13)-N(25)-N(26)	-20.5(6)
C(5)-C(6)-N(11)-N(12)	-152.0(5)	C(13)-N(25)-N(26)-N(27)	-174.6(18)
N(8)-C(7)-N(14)-O(7)	14.9(6)	N(22)-C(14)-N(28)-O(16)	166.9(3)
C(6)-C(7)-N(14)-O(7)	-171.1(4)	C(13)-C(14)-N(28)-O(16)	-14.1(5)
N(8)-C(7)-N(14)-O(8)	-161.8(4)	N(22)-C(14)-N(28)-O(15)	-13.6(4)
C(6)-C(7)-N(14)-O(8)	12.1(6)	C(13)-C(14)-N(28)-O(15)	165.4(3)

3. 3-Diethyl-4,5-dinitro-1*H*-imidazol-3-ium 2,4,5-trinitro imidazol-1-ide 8

CCDC Deposition No. 2038551

Crystal data and structure refinement for compound **8**.

Empirical formula	C20 H22 N18 O20	
Formula weight	834.55	
Temperature	193(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1/c$	
Unit cell dimensions	a = 11.8406(13) Å	a= 90°.
	b = 8.2153(9) Å	b= 97.324(6)°.
	c = 17.547(3) Å	g = 90°.
Volume	1693.0(4) Å3	
Z	2	
Density (calculated)	1.637 Mg/m3	
Absorption coefficient	0.147 mm-1	
F(000)	856	
Crystal size	0.217 x 0.209 x 0.200 mm3	
Theta range for data collection	2.340 to 28.524°.	
Index ranges	-12<=h<=15, -10<=k<=10, -23<=l<=22	
Reflections collected	24091	
Independent reflections	4257 [R(int) = 0.0233]	
Completeness to theta = 25.242°	99.10%	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7457 and 0.6545	
Refinement method	Full-matrix least-squares on F2	
Data / restraints / parameters	4257 / 0 / 283	
Goodness-of-fit on F2	1.053	
Final R indices [I>2sigma(I)]	R1 = 0.0451, wR2 = 0.1158	
R indices (all data)	R1 = 0.0509, wR2 = 0.1200	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.396 and -0.355 e.Å-3	

Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3) for compound **8**.

	x	y	z	U(eq)
C(1)	3004(1)	3857(2)	3108(1)	29(1)
N(1)	3257(1)	2350(1)	2918(1)	26(1)
C(2)	3483(1)	1483(2)	3586(1)	27(1)
C(3)	3371(1)	2516(2)	4175(1)	26(1)
N(2)	3076(1)	4004(1)	3869(1)	28(1)
C(4)	3258(1)	1854(2)	2100(1)	36(1)
C(5)	2124(2)	1121(2)	1779(1)	47(1)
C(6)	2846(1)	5552(2)	4276(1)	40(1)
C(7)	1965(2)	6566(2)	3800(1)	46(1)
N(3)	3838(1)	-184(2)	3619(1)	38(1)
O(1)	3697(1)	-977(2)	3027(1)	51(1)
O(2)	4264(2)	-678(2)	4244(1)	66(1)
N(4)	3519(1)	2265(2)	5000(1)	37(1)
O(3)	3103(1)	1060(2)	5241(1)	68(1)
O(4)	4040(1)	3322(2)	5385(1)	48(1)
C(8)	7600(1)	1822(2)	3730(1)	27(1)
N(5)	8114(1)	918(1)	3251(1)	28(1)
C(9)	9208(1)	1078(2)	3560(1)	29(1)
C(10)	9268(1)	2052(2)	4205(1)	30(1)
N(6)	8231(1)	2547(2)	4321(1)	32(1)
N(7)	6381(1)	2027(2)	3602(1)	33(1)
O(5)	5844(1)	1182(2)	3102(1)	41(1)
O(6)	5944(1)	3021(2)	3990(1)	58(1)
N(8)	10100(1)	256(2)	3229(1)	39(1)
O(7)	9846(1)	-668(2)	2693(1)	61(1)
O(8)	11077(1)	508(2)	3519(1)	65(1)
N(9)	10248(1)	2529(2)	4743(1)	42(1)
O(9A)	11012(2)	3246(3)	4499(1)	63(1)
O(10A)	10302(2)	1988(3)	5401(1)	59(1)
O(9B)	10211(5)	4123(7)	4929(4)	89(3)
O(10B)	10951(6)	1780(9)	4944(5)	100(3)

Bond lengths [Å] for compound **8**.

Bond	Bond length [Å]	Bond	Bond length [Å]
C(1)-N(1)	1.3269(18)	N(3)-O(2)	1.2165(19)
C(1)-N(2)	1.3334(16)	N(3)-O(1)	1.2192(18)
C(1)-H(1)	0.95	N(4)-O(3)	1.2062(19)
N(1)-C(2)	1.3689(17)	N(4)-O(4)	1.2180(19)
N(1)-C(4)	1.4923(17)	C(8)-N(5)	1.3259(17)
C(2)-C(3)	1.3566(19)	C(8)-N(6)	1.3387(17)
C(2)-N(3)	1.4320(18)	C(8)-N(7)	1.4420(17)
C(3)-N(2)	1.3624(18)	N(5)-C(9)	1.3456(17)
C(3)-N(4)	1.4521(17)	C(9)-C(10)	1.3815(19)
N(2)-C(6)	1.4996(18)	C(9)-N(8)	1.4358(18)
C(4)-C(5)	1.513(2)	C(10)-N(6)	1.3336(18)
C(4)-H(4A)	0.99	C(10)-N(9)	1.4530(18)
C(4)-H(4B)	0.99	N(7)-O(6)	1.2191(17)
C(5)-H(5A)	0.98	N(7)-O(5)	1.2305(16)
C(5)-H(5B)	0.98	N(8)-O(7)	1.2162(19)
C(5)-H(5C)	0.98	N(8)-O(8)	1.2213(18)
C(6)-C(7)	1.502(2)	N(9)-O(10B)	1.059(6)
C(6)-H(6A)	0.99	N(9)-O(9A)	1.204(2)
C(6)-H(6B)	0.99	N(9)-O(10A)	1.231(2)
C(7)-H(7A)	0.98	N(9)-O(9B)	1.351(6)
C(7)-H(7B)	0.98	O(9B)-O(9B)#1	1.556(12)
C(7)-H(7C)	0.98		

Bond angles [°] for compound **8**.

Bond	Bond angle [°]	Bond	Bond angle [°]
N(1)-C(1)-N(2)	110.43(12)	H(7A)-C(7)-H(7B)	109.5
N(1)-C(1)-H(1)	124.8	C(6)-C(7)-H(7C)	109.5
N(2)-C(1)-H(1)	124.8	H(7A)-C(7)-H(7C)	109.5
C(1)-N(1)-C(2)	107.20(11)	H(7B)-C(7)-H(7C)	109.5
C(1)-N(1)-C(4)	121.63(12)	O(2)-N(3)-O(1)	125.87(14)
C(2)-N(1)-C(4)	131.16(12)	O(2)-N(3)-C(2)	116.17(14)
C(3)-C(2)-N(1)	107.42(12)	O(1)-N(3)-C(2)	117.97(13)
C(3)-C(2)-N(3)	128.67(13)	O(3)-N(4)-O(4)	126.29(14)
N(1)-C(2)-N(3)	123.80(12)	O(3)-N(4)-C(3)	117.59(14)
C(2)-C(3)-N(2)	107.88(11)	O(4)-N(4)-C(3)	116.10(13)
C(2)-C(3)-N(4)	131.27(13)	N(5)-C(8)-N(6)	118.99(12)
N(2)-C(3)-N(4)	120.85(12)	N(5)-C(8)-N(7)	119.88(11)
C(1)-N(2)-C(3)	107.05(11)	N(6)-C(8)-N(7)	121.12(12)
C(1)-N(2)-C(6)	124.14(12)	C(8)-N(5)-C(9)	100.74(11)
C(3)-N(2)-C(6)	128.80(11)	N(5)-C(9)-C(10)	109.44(12)
N(1)-C(4)-C(5)	110.92(12)	N(5)-C(9)-N(8)	120.75(12)
N(1)-C(4)-H(4A)	109.5	C(10)-C(9)-N(8)	129.77(12)
C(5)-C(4)-H(4A)	109.5	N(6)-C(10)-C(9)	110.46(12)
N(1)-C(4)-H(4B)	109.5	N(6)-C(10)-N(9)	119.55(13)
C(5)-C(4)-H(4B)	109.5	C(9)-C(10)-N(9)	129.96(13)
H(4A)-C(4)-H(4B)	108	C(10)-N(6)-C(8)	100.36(11)
C(4)-C(5)-H(5A)	109.5	O(6)-N(7)-O(5)	123.92(13)
C(4)-C(5)-H(5B)	109.5	O(6)-N(7)-C(8)	118.65(12)
H(5A)-C(5)-H(5B)	109.5	O(5)-N(7)-C(8)	117.43(12)
C(4)-C(5)-H(5C)	109.5	O(7)-N(8)-O(8)	123.70(14)
H(5A)-C(5)-H(5C)	109.5	O(7)-N(8)-C(9)	118.94(13)
H(5B)-C(5)-H(5C)	109.5	O(8)-N(8)-C(9)	117.34(13)
N(2)-C(6)-C(7)	111.18(12)	O(9A)-N(9)-O(10A)	124.03(17)
N(2)-C(6)-H(6A)	109.4	O(10B)-N(9)-O(9B)	122.1(4)
C(7)-C(6)-H(6A)	109.4	O(10B)-N(9)-C(10)	126.1(4)
N(2)-C(6)-H(6B)	109.4	O(9A)-N(9)-C(10)	118.32(16)
C(7)-C(6)-H(6B)	109.4	O(10A)-N(9)-C(10)	116.98(14)
H(6A)-C(6)-H(6B)	108	O(9B)-N(9)-C(10)	111.7(3)
C(6)-C(7)-H(7A)	109.5	N(9)-O(9B)-O(9B)#1	163.1(7)
C(6)-C(7)-H(7B)	109.5		

Anisotropic displacement parameters ($Å^2$x 10^3) for compound **8**.

	U11	U22	U33	U23	U13	U12
C(1)	34(1)	32(1)	22(1)	2(1)	3(1)	5(1)
N(1)	27(1)	31(1)	21(1)	1(1)	2(1)	2(1)
C(2)	22(1)	29(1)	28(1)	4(1)	0(1)	0(1)
C(3)	20(1)	36(1)	23(1)	5(1)	2(1)	0(1)
N(2)	27(1)	34(1)	22(1)	1(1)	2(1)	5(1)
C(4)	45(1)	41(1)	22(1)	-4(1)	6(1)	2(1)
C(5)	48(1)	58(1)	33(1)	-12(1)	-7(1)	2(1)
C(6)	46(1)	41(1)	32(1)	-9(1)	1(1)	12(1)
C(7)	56(1)	42(1)	39(1)	0(1)	6(1)	18(1)
N(3)	38(1)	28(1)	46(1)	3(1)	-3(1)	2(1)
O(1)	63(1)	35(1)	56(1)	-8(1)	4(1)	4(1)
O(2)	86(1)	41(1)	62(1)	13(1)	-25(1)	13(1)
N(4)	33(1)	54(1)	25(1)	10(1)	2(1)	4(1)
O(3)	72(1)	87(1)	43(1)	32(1)	4(1)	-24(1)
O(4)	57(1)	58(1)	26(1)	-5(1)	-8(1)	14(1)
C(8)	22(1)	31(1)	27(1)	-2(1)	2(1)	-3(1)
N(5)	23(1)	35(1)	27(1)	-3(1)	2(1)	-2(1)
C(9)	23(1)	34(1)	30(1)	-1(1)	3(1)	-2(1)
C(10)	24(1)	37(1)	26(1)	-1(1)	0(1)	-6(1)
N(6)	27(1)	39(1)	30(1)	-8(1)	4(1)	-7(1)
N(7)	24(1)	38(1)	37(1)	-5(1)	4(1)	-2(1)
O(5)	25(1)	54(1)	41(1)	-10(1)	-3(1)	-4(1)
O(6)	30(1)	68(1)	78(1)	-35(1)	10(1)	3(1)
N(8)	29(1)	46(1)	44(1)	-5(1)	9(1)	2(1)
O(7)	47(1)	70(1)	70(1)	-34(1)	19(1)	0(1)
O(8)	24(1)	95(1)	76(1)	-19(1)	6(1)	4(1)
N(9)	29(1)	58(1)	38(1)	-7(1)	-2(1)	-12(1)
O(9A)	37(1)	78(2)	70(1)	11(1)	-4(1)	-29(1)
O(10A)	47(1)	92(2)	32(1)	5(1)	-10(1)	-15(1)
O(9B)	71(4)	66(4)	118(5)	-37(3)	-36(4)	-16(3)
O(10B)	62(4)	108(6)	114(6)	-45(5)	-50(4)	30(4)

Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^{2}x 10^3) for compound **8**.

	x	y	z	U(eq)
H(1)	2800	4711	2752	35
H(4A)	3870	1047	2064	43
H(4B)	3414	2816	1790	43
H(5A)	1976	155	2079	71
H(5B)	2142	810	1242	71
H(5C)	1518	1922	1809	71
H(6A)	3561	6183	4383	48
H(6B)	2578	5289	4773	48
H(7A)	2245	6872	3318	68
H(7B)	1813	7550	4086	68
H(7C)	1260	5936	3687	68

Torsion angles [°] for compound **8**.

Bond	Angle(°)	Bond	Angle(°)
N(2)-C(1)-N(1)-C(2)	1.07(15)	N(7)-C(8)-N(5)-C(9)	178.68(12)
N(2)-C(1)-N(1)-C(4)	-179.20(12)	C(8)-N(5)-C(9)-C(10)	0.59(15)
C(1)-N(1)-C(2)-C(3)	-0.74(14)	C(8)-N(5)-C(9)-N(8)	178.82(13)
C(4)-N(1)-C(2)-C(3)	179.57(13)	N(5)-C(9)-C(10)-N(6)	-0.56(17)
C(1)-N(1)-C(2)-N(3)	-177.22(12)	N(8)-C(9)-C(10)-N(6)	-178.58(14)
C(4)-N(1)-C(2)-N(3)	3.1(2)	N(5)-C(9)-C(10)-N(9)	177.66(14)
N(1)-C(2)-C(3)-N(2)	0.15(14)	N(8)-C(9)-C(10)-N(9)	-0.4(3)
N(3)-C(2)-C(3)-N(2)	176.40(13)	C(9)-C(10)-N(6)-C(8)	0.24(16)
N(1)-C(2)-C(3)-N(4)	-179.30(13)	N(9)-C(10)-N(6)-C(8)	-178.19(13)
N(3)-C(2)-C(3)-N(4)	-3.0(2)	N(5)-C(8)-N(6)-C(10)	0.16(17)
N(1)-C(1)-N(2)-C(3)	-0.98(15)	N(7)-C(8)-N(6)-C(10)	-178.99(13)
N(1)-C(1)-N(2)-C(6)	179.84(13)	N(5)-C(8)-N(7)-O(6)	-170.90(15)
C(2)-C(3)-N(2)-C(1)	0.49(15)	N(6)-C(8)-N(7)-O(6)	8.2(2)
N(4)-C(3)-N(2)-C(1)	-179.99(12)	N(5)-C(8)-N(7)-O(5)	8.9(2)
C(2)-C(3)-N(2)-C(6)	179.62(13)	N(6)-C(8)-N(7)-O(5)	-171.95(13)
N(4)-C(3)-N(2)-C(6)	-0.9(2)	N(5)-C(9)-N(8)-O(7)	-4.5(2)
C(1)-N(1)-C(4)-C(5)	-94.26(17)	C(10)-C(9)-N(8)-O(7)	173.34(16)
C(2)-N(1)-C(4)-C(5)	85.39(18)	N(5)-C(9)-N(8)-O(8)	177.03(15)
C(1)-N(2)-C(6)-C(7)	31.2(2)	C(10)-C(9)-N(8)-O(8)	-5.1(2)
C(3)-N(2)-C(6)-C(7)	-147.76(15)	N(6)-C(10)-N(9)-O(10B)	139.7(7)
C(3)-C(2)-N(3)-O(2)	-12.6(2)	C(9)-C(10)-N(9)-O(10B)	-38.4(8)
N(1)-C(2)-N(3)-O(2)	163.06(15)	N(6)-C(10)-N(9)-O(9A)	-123.3(2)
C(3)-C(2)-N(3)-O(1)	167.70(14)	C(9)-C(10)-N(9)-O(9A)	58.7(3)
N(1)-C(2)-N(3)-O(1)	-16.6(2)	N(6)-C(10)-N(9)-O(10A)	65.7(2)
C(2)-C(3)-N(4)-O(3)	-45.3(2)	C(9)-C(10)-N(9)-O(10A)	-112.3(2)
N(2)-C(3)-N(4)-O(3)	135.32(16)	N(6)-C(10)-N(9)-O(9B)	-44.8(4)
C(2)-C(3)-N(4)-O(4)	136.05(16)	C(9)-C(10)-N(9)-O(9B)	137.1(4)
N(2)-C(3)-N(4)-O(4)	-43.34(18)	O(10B)-N(9)-O(9B)-O(9B)#1	-160(3)
N(6)-C(8)-N(5)-C(9)	-0.49(17)	C(10)-N(9)-O(9B)-O(9B)#1	24(3)

4. 3-Ethyl-1-methyl-4,5-dinitro-1*H*-imidazol-3-ium 2,4,5-trinitroimidazol-1-ide 9

CCDC Deposition No. 2038553

Crystal data and structure refinement for compound **9**.

Empirical formula	C9 H9 N9 O10
Formula weight	403.25
Temperature	193(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	$P2_1/n$
Unit cell dimensions	a = 12.5903(18) Å, a= 90°.
	b = 9.5212(15) Å, b= 112.804(6)°.
	c = 14.513(3) Å, g = 90°
Volume	1603.8(5) Å3
Z	4
Density (calculated)	1.670 Mg/m3
Absorption coefficient	0.152 mm-1
F(000)	824
Crystal size	0.397 x 0.093 x 0.072 mm3
Theta range for data collection	2.626 to 28.285°.
Index ranges	-16<=h<=15, -12<=k<=12, -17<=l<=19
Reflections collected	21939
Independent reflections	3976 [R(int) = 0.0268]
Completeness to theta = 25.242°	99.60%
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7457 and 0.7077
Refinement method	Full-matrix least-squares on F2
Data / restraints / parameters	3976 / 0 / 255
Goodness-of-fit on F2	1.032
Final R indices [I>2sigma(I)]	R1 = 0.0414, wR2 = 0.1041
R indices (all data)	R1 = 0.0528, wR2 = 0.1118
Extinction coefficient	n/a
Largest diff. peak and hole	0.420 and -0.253 e.Å-3

Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3) of compound **9**.

	x	y	z	U(eq)
C(1)	3961(1)	-378(2)	6400(1)	27(1)
N(1)	4218(1)	414(1)	7210(1)	25(1)
C(2)	3211(1)	1022(1)	7164(1)	24(1)
C(3)	2364(1)	578(1)	6310(1)	23(1)
N(2)	2842(1)	-293(1)	5836(1)	24(1)
C(4)	5405(1)	509(2)	8000(1)	38(1)
C(5)	5560(2)	-550(3)	8817(2)	59(1)
C(6)	2261(2)	-1119(2)	4916(1)	36(1)
N(3)	3110(1)	2034(1)	7860(1)	34(1)
O(1)	3881(1)	2090(2)	8682(1)	56(1)
O(2)	2247(1)	2762(1)	7562(1)	46(1)
N(4)	1144(1)	899(1)	5921(1)	33(1)
O(3)	710(1)	1275(2)	5068(1)	60(1)
O(4)	655(1)	757(2)	6491(1)	54(1)
C(7)	6136(1)	6680(2)	6050(1)	28(1)
N(5)	6725(1)	5485(1)	6180(1)	30(1)
C(8)	5993(1)	4597(2)	6336(1)	28(1)
C(9)	5005(1)	5310(2)	6282(1)	28(1)
N(6)	5106(1)	6676(1)	6102(1)	28(1)
N(7)	6611(1)	7968(1)	5848(1)	38(1)
O(5)	7510(1)	7897(2)	5717(2)	73(1)
O(6)	6086(1)	9062(1)	5809(1)	44(1)
N(8)	6290(1)	3118(1)	6476(1)	35(1)
O(7)	7312(1)	2822(1)	6876(1)	54(1)
O(8)	5514(1)	2258(1)	6162(1)	50(1)
N(9)	4005(1)	4811(2)	6423(1)	41(1)
O(9)	4097(2)	3683(2)	6856(2)	74(1)
O(10)	3138(1)	5534(2)	6130(1)	51(1)

Bond lengths [Å] for compound **9**.

Bond	Bond length [Å]	Bond	Bond length [Å]
C(1)-N(1)	1.3278(19)	N(3)-O(1)	1.2130(19)
C(1)-N(2)	1.3306(18)	N(3)-O(2)	1.2187(19)
C(1)-H(1)	0.95	N(4)-O(3)	1.1980(19)
N(1)-C(2)	1.3713(17)	N(4)-O(4)	1.2145(18)
N(1)-C(4)	1.4929(19)	C(7)-N(6)	1.3279(18)
C(2)-C(3)	1.3523(19)	C(7)-N(5)	1.3309(18)
C(2)-N(3)	1.4362(18)	C(7)-N(7)	1.4432(19)
C(3)-N(2)	1.3575(17)	N(5)-C(8)	1.3336(19)
C(3)-N(4)	1.4483(18)	C(8)-C(9)	1.392(2)
N(2)-C(6)	1.4763(19)	C(8)-N(8)	1.4505(18)
C(4)-C(5)	1.510(3)	C(9)-N(6)	1.3415(19)
C(4)-H(4A)	0.99	C(9)-N(9)	1.4329(19)
C(4)-H(4B)	0.99	N(7)-O(5)	1.2202(18)
C(5)-H(5A)	0.98	N(7)-O(6)	1.2233(17)
C(5)-H(5B)	0.98	N(8)-O(8)	1.2191(19)
C(5)-H(5C)	0.98	N(8)-O(7)	1.2219(19)
C(6)-H(6A)	0.98	N(9)-O(10)	1.220(2)
C(6)-H(6B)	0.98	N(9)-O(9)	1.227(2)
C(6)-H(6C)	0.98		

Bond angles [°] for compound **9**.

Bond	Bond angle [°]	Bond	Bond angle [°]
N(1)-C(1)-N(2)	110.21(12)	N(2)-C(6)-H(6C)	109.5
N(1)-C(1)-H(1)	124.9	H(6A)-C(6)-H(6C)	109.5
N(2)-C(1)-H(1)	124.9	H(6B)-C(6)-H(6C)	109.5
C(1)-N(1)-C(2)	107.10(12)	O(1)-N(3)-O(2)	125.93(14)
C(1)-N(1)-C(4)	122.82(13)	O(1)-N(3)-C(2)	117.80(14)
C(2)-N(1)-C(4)	130.04(13)	O(2)-N(3)-C(2)	116.26(13)
C(3)-C(2)-N(1)	107.37(12)	O(3)-N(4)-O(4)	126.03(14)
C(3)-C(2)-N(3)	126.96(12)	O(3)-N(4)-C(3)	117.11(13)
N(1)-C(2)-N(3)	125.49(13)	O(4)-N(4)-C(3)	116.86(13)
C(2)-C(3)-N(2)	107.96(12)	N(6)-C(7)-N(5)	119.49(13)
C(2)-C(3)-N(4)	129.17(13)	N(6)-C(7)-N(7)	120.32(13)
N(2)-C(3)-N(4)	122.86(13)	N(5)-C(7)-N(7)	120.19(13)
C(1)-N(2)-C(3)	107.35(12)	C(7)-N(5)-C(8)	100.50(12)
C(1)-N(2)-C(6)	123.98(12)	N(5)-C(8)-C(9)	109.99(13)
C(3)-N(2)-C(6)	128.46(12)	N(5)-C(8)-N(8)	118.82(13)
N(1)-C(4)-C(5)	110.38(14)	C(9)-C(8)-N(8)	131.10(14)
N(1)-C(4)-H(4A)	109.6	N(6)-C(9)-C(8)	109.54(13)
C(5)-C(4)-H(4A)	109.6	N(6)-C(9)-N(9)	120.25(13)
N(1)-C(4)-H(4B)	109.6	C(8)-C(9)-N(9)	130.17(14)
C(5)-C(4)-H(4B)	109.6	C(7)-N(6)-C(9)	100.48(12)
H(4A)-C(4)-H(4B)	108.1	O(5)-N(7)-O(6)	123.85(14)
C(4)-C(5)-H(5A)	109.5	O(5)-N(7)-C(7)	117.87(13)
C(4)-C(5)-H(5B)	109.5	O(6)-N(7)-C(7)	118.28(13)
H(5A)-C(5)-H(5B)	109.5	O(8)-N(8)-O(7)	124.48(14)
C(4)-C(5)-H(5C)	109.5	O(8)-N(8)-C(8)	118.28(14)
H(5A)-C(5)-H(5C)	109.5	O(7)-N(8)-C(8)	117.19(14)
H(5B)-C(5)-H(5C)	109.5	O(10)-N(9)-O(9)	124.52(15)
N(2)-C(6)-H(6A)	109.5	O(10)-N(9)-C(9)	118.72(14)
N(2)-C(6)-H(6B)	109.5	O(9)-N(9)-C(9)	116.74(15)
H(6A)-C(6)-H(6B)	109.5		

Anisotropic displacement parameters ($Å^2$x 10^3) for compound **9**.

	U11	U22	U33	U23	U13	U12
C(1)	26(1)	24(1)	34(1)	3(1)	16(1)	4(1)
N(1)	20(1)	27(1)	30(1)	3(1)	10(1)	-1(1)
C(2)	23(1)	21(1)	29(1)	-1(1)	13(1)	-2(1)
C(3)	21(1)	21(1)	29(1)	2(1)	10(1)	1(1)
N(2)	26(1)	21(1)	26(1)	-1(1)	12(1)	-1(1)
C(4)	20(1)	52(1)	36(1)	8(1)	4(1)	-4(1)
C(5)	37(1)	82(2)	48(1)	28(1)	4(1)	-2(1)
C(6)	44(1)	33(1)	31(1)	-10(1)	16(1)	-10(1)
N(3)	36(1)	32(1)	39(1)	-12(1)	22(1)	-13(1)
O(1)	47(1)	80(1)	41(1)	-29(1)	16(1)	-21(1)
O(2)	50(1)	34(1)	66(1)	-12(1)	36(1)	2(1)
N(4)	23(1)	36(1)	38(1)	0(1)	9(1)	3(1)
O(3)	34(1)	88(1)	50(1)	30(1)	7(1)	13(1)
O(4)	28(1)	86(1)	52(1)	-5(1)	21(1)	1(1)
C(7)	29(1)	24(1)	35(1)	3(1)	16(1)	3(1)
N(5)	31(1)	27(1)	35(1)	3(1)	15(1)	6(1)
C(8)	36(1)	22(1)	27(1)	3(1)	14(1)	6(1)
C(9)	32(1)	24(1)	31(1)	1(1)	17(1)	1(1)
N(6)	30(1)	23(1)	35(1)	2(1)	17(1)	3(1)
N(7)	35(1)	29(1)	60(1)	8(1)	28(1)	4(1)
O(5)	58(1)	45(1)	145(2)	29(1)	72(1)	12(1)
O(6)	45(1)	23(1)	75(1)	6(1)	34(1)	4(1)
N(8)	52(1)	25(1)	30(1)	5(1)	18(1)	10(1)
O(7)	58(1)	42(1)	55(1)	10(1)	13(1)	26(1)
O(8)	71(1)	24(1)	55(1)	1(1)	27(1)	-2(1)
N(9)	45(1)	32(1)	58(1)	-2(1)	34(1)	-4(1)
O(9)	92(1)	37(1)	127(2)	20(1)	81(1)	1(1)
O(10)	36(1)	56(1)	69(1)	-5(1)	30(1)	-1(1)

Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for compound **9**.

	x	y	z	U(eq)
H(1)	4500	-928	6245	32
H(4A)	5538	1467	8288	46
H(4B)	5977	330	7701	46
H(5A)	4998	-366	9117	89
H(5B)	6341	-474	9331	89
H(5C)	5440	-1499	8533	89
H(6A)	2815	-1765	4819	54
H(6B)	1954	-483	4342	54
H(6C)	1627	-1658	4976	54

Torsion angles [°] for compound **9**.

Bond	Angle(°)	Bond	Angle(°)
N(2)-C(1)-N(1)-C(2)	0.53(16)	N(2)-C(3)-N(4)-O(4)	129.17(16)
N(2)-C(1)-N(1)-C(4)	178.57(12)	N(6)-C(7)-N(5)-C(8)	-0.05(19)
C(1)-N(1)-C(2)-C(3)	-0.29(15)	N(7)-C(7)-N(5)-C(8)	-179.63(14)
C(4)-N(1)-C(2)-C(3)	-178.13(13)	C(7)-N(5)-C(8)-C(9)	0.48(16)
C(1)-N(1)-C(2)-N(3)	-175.64(13)	C(7)-N(5)-C(8)-N(8)	177.54(13)
C(4)-N(1)-C(2)-N(3)	6.5(2)	N(5)-C(8)-C(9)-N(6)	-0.77(18)
N(1)-C(2)-C(3)-N(2)	-0.05(15)	N(8)-C(8)-C(9)-N(6)	-177.35(15)
N(3)-C(2)-C(3)-N(2)	175.22(13)	N(5)-C(8)-C(9)-N(9)	-178.17(15)
N(1)-C(2)-C(3)-N(4)	179.00(13)	N(8)-C(8)-C(9)-N(9)	5.3(3)
N(3)-C(2)-C(3)-N(4)	-5.7(2)	N(5)-C(7)-N(6)-C(9)	-0.39(18)
N(1)-C(1)-N(2)-C(3)	-0.56(16)	N(7)-C(7)-N(6)-C(9)	179.18(14)
N(1)-C(1)-N(2)-C(6)	-175.73(13)	C(8)-C(9)-N(6)-C(7)	0.66(16)
C(2)-C(3)-N(2)-C(1)	0.37(15)	N(9)-C(9)-N(6)-C(7)	178.35(14)
N(4)-C(3)-N(2)-C(1)	-178.75(13)	N(6)-C(7)-N(7)-O(5)	-173.46(18)
C(2)-C(3)-N(2)-C(6)	175.24(13)	N(5)-C(7)-N(7)-O(5)	6.1(3)
N(4)-C(3)-N(2)-C(6)	-3.9(2)	N(6)-C(7)-N(7)-O(6)	5.9(2)
C(1)-N(1)-C(4)-C(5)	-92.94(19)	N(5)-C(7)-N(7)-O(6)	-174.48(16)
C(2)-N(1)-C(4)-C(5)	84.6(2)	N(5)-C(8)-N(8)-O(8)	-146.07(15)
C(3)-C(2)-N(3)-O(1)	164.60(15)	C(9)-C(8)-N(8)-O(8)	30.3(2)
N(1)-C(2)-N(3)-O(1)	-20.9(2)	N(5)-C(8)-N(8)-O(7)	31.6(2)
C(3)-C(2)-N(3)-O(2)	-15.5(2)	C(9)-C(8)-N(8)-O(7)	-152.09(17)
N(1)-C(2)-N(3)-O(2)	158.99(14)	N(6)-C(9)-N(9)-O(10)	18.7(2)
C(2)-C(3)-N(4)-O(3)	130.42(18)	C(8)-C(9)-N(9)-O(10)	-164.14(16)
N(2)-C(3)-N(4)-O(3)	-50.7(2)	N(6)-C(9)-N(9)-O(9)	-159.79(17)
C(2)-C(3)-N(4)-O(4)	-49.8(2)	C(8)-C(9)-N(9)-O(9)	17.4(3)

ABSTRACT IN KOREAN

초록

아졸계 화합물에 다수의 니트로기가 치환될 경우, 폭발성능은 향상되지만, 증가된 전자끌기 유발효과로 인해 친핵성이 저하되어 알킬화 반응으로 새로운 구조의 고에너지 물질을 합성하는 시도들이 어려움을 겪어왔다. 본 논문에서는 반응조건의 조절과 높은 친전자성을 가진 알킬화 반응 시약의 사용을 통해 기존 합성이 어려운 것으로 보고된 새로운 고에너지 물질들을 합성한 결과를 제시한다.

첫째로, 2개의 강한 활성감소 치환기인 니트로기와 1개의 약한 활성감소 치환기인 염소기가 치환되어 기존 메틸렌 결합으로 커플링 반응이 어려운 것으로 보고된 4-chloro-3,5-dinitro-1*H*-pyrazole (ClDNP) **1**의 커플링 반응을 통해 새로운 고에너지 물질 합성을 시도하였다. 친전자성이 높은 디할로메텐인 디아이오도메테인을 과량으로 사용한 반응조건에서 ClDNP로부터 bis(4-chloro-3,5-dinitro-1H-pyrazol-1-yl)methane **2**을 79%의 수율로 얻을 수 있었다. 이러한 과량 반응조건은 친핵성이 저하된

니트로아졸계 물질의 커플링 반응에 적용할 수 있을 것으로 기대된다. 또한, 아지도화 반응을 통해 염소기를 고에너지기인 아지도기로 치환하여 새로운 1차 폭발물 후보로서 bis(4-azido-3,5-dinitro-1*H*-pyrazol-1-yl)methane **3**을 77% 수율로 얻을 수 있었다. 실측 및 계산을 통해 분석된 **3**의 물성은 군사적으로 널리 사용되는 1차 폭발물인 DDNP (2-diazo-4,6-dinitrophenol)보다 우수한 열적 안정성과 폭발성능을 가진 것으로 확인되었다.

둘째로, 2개의 강한 활성화 치환기인 니트로기 치환으로 *N,N'*-디알킬화 반응이 어려운 것으로 보고된 4,5-dinitro-1*H*-imidazole **4**와 1-methyl-4,5-dinitro-1*H*-imidazole **5**를 quaternization하여 새로운 에너지 이온성 액체(energetic ionic liquids, EILs)를 합성하였다. 강한 친핵성을 가진 것으로 보고된 Meerwein 시약을 사용하여 무수조건에서 반응하여 새로운 EILs인 1,3-diethyl-4,5-dinitro-1*H*-imidazol-3-ium tetrafluoroborate **6**과 3-ethyl-1-methyl-4,5-dinitro-1*H*-imidazol-3-ium tetrafluoroborate **7**를 각각 얻을 수 있었다. 이 반응조건은 활성감소 치환기로 인해 친핵성이 저하된 헤테로고리

화합물의 quaternization에 적용 가능할 것으로 기대된다. 또한, 폭발성능을 가진 potassium 2,4,5-trinitroimidazol-1-ide로 음이온 metathesis하여 새로운 고에너지 물질인 3-diethyl-4,5-dinitro-1*H*-imidazol-3-ium 2,4,5-trinitroimidazol-1-ide **8**와 3-ethyl-1-methyl-4,5-dinitro-1*H*-imidazol-3-ium 2,4,5-trinitroimidazol-1-ide **9**을 각각 얻을 수 있었다. 이 중에서, 화합물 **9**은 대표적인 고에너지 물질인 TNT에 비해 우수한 둔감성과 폭발성능을 동시에 갖춘 것으로 확인되었다.

주요어: 고에너지 물질, 폭발물, 1차 폭발물, 에너지 이온성 액체, 니트로아졸, 알킬화 반응, Meerwein 시약

학번: 2017-31412