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# Structural and thermal behavior of imidazolium N,N'-dinitrourea

## Long Liu<sup>a,b</sup>, Zengxi Li<sup>a,\*</sup>, Chunshan Li<sup>b,\*</sup>, Suojiang Zhang<sup>b</sup>

<sup>a</sup> Graduate University of the Chinese Academy of Sciences, Beijing 100049, People's Republic of China <sup>b</sup> Beijing Key Laboratory of Ionic Liquids Clean Process, State Key Laboratory of Multiphase Complex Systems, Institute of Process Engineering, Chinese Academy of Sciences, Beijing 100190, People's Republic of China

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## ABSTRACT

The structural and thermal behavior of energetic salts based on N,N'-dinitrourea (DNU) should be fully investigated for their further applications. In the present paper, the crystal structure and vibrational spectrum of imidazolium N,N'-dinitrourea ([IMI][DNU]) were investigated in detail. A slight twist or torsion was found in the cation and anion because of their interactions. These interactions also formed a stabilized hydrogen bond network. The vibrations of the functional groups were mainly exhibited in an infrared (IR) spectrum, and the skeletal stretching vibrations mainly appeared in a Raman spectrum. The non-isothermal kinetics of the title compound and its mixture with polyethylene glycol 10000 (PEG10000) were investigated with the methods of Kissinger and Ozawa. In situ IR analysis, mass spectral fragmentation, and bond dissociation enthalpy calculations showed that the initial decomposition step of [IMI][DNU] was the breakage of the N—N bond in the anion. The in situ IR of gaseous phase products and mass spectral fragmentation indicated that the main final products of [IMI][DNU] decomposition were N<sub>2</sub>O and imidazole.

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## 1. Introduction

Energetic salts are of considerable interest due to their advantages over neutral molecules. These salts often possess lower vapor pressures and higher thermal stabilities than similar nonionic analogues [1–6]. The synthesis and characterization of new energetic ionic salts, including nitrogen rich salts [2,7-11], high density energetic salts [12], coordination complexes [13-15], and high oxygen balance salts [5,16,17], have been successfully carried out in the past decade. To study the application of energetic salts as propellants, explosives, or pyrotechnics, the thermal behavior of some energetic salts have also been systematically studied [18]. For example, non-isothermal kinetic studies of the coordination complexes  $[Co(DAT)_6](ClO_4)_2$  and  $[Cd(DAT)_6](ClO_4)_2$  have shown that they can be used as a primary explosive [13,15]. The thermal decomposition behaviors of 1,2,3-triazole nitrate and hydrazine, 3-nitro-1,2,4-triazole-5-one were investigated by thermal analyses and quantum chemical calculations [19,20].

Energetic salts based on the N,N'-dinitrourea (DNU) anion have been synthesized because of the high density (1.98 g/cm<sup>3</sup>) of DNU [12,21–24]. The structural and thermal behaviors of its potassium and ammonium salts have been studied, and several tautomeric forms with high thermal stabilities are found [21,23]. Energetic salts based on nitrogen heterocycles, which often possess high

\* Corresponding authors. *E-mail addresses*: zxli@home.ipe.ac.cn (Z. Li), csli@home.ipe.ac.cn (C. Li). density as well as high heat of formation, have been synthesized. The crystal structure and physical properties of triazolium, including the heat of formation and detonation parameters, have also been calculated in literature [12]. However, the investigation of imidiazolium salts, another typical nitrogen heterocycle energetic salt, has not been reported.

The present work aimed to synthesize imidazolium DNU ([IMI][DNU]) and its precursor according to existing methods [21,22], as well as to investigate further its structural and thermal behaviors. The structural properties were extensively studied by single X-ray crystal diffraction, infrared (IR), and Raman spectrum analysis. The non-isothermal kinetics of the title compound and its mixture with polyethylene glycol (PEG) 10000 (PEG10000) were investigated with the methods of Kissinger [25] and Ozawa [26]. The compatibility of [IMI][DNU] with PEG10000 was analyzed according to the peak temperature of differential thermal analysis (DTA). The possible decomposition mechanisms and initial decomposition step were predicted by combining in situ IR analyses and mass spectral fragmentation with bond dissociation enthalpy (BDE) calculations. The obtained results are beneficial in the design of thermally stable energetic salts.

## 2. Experimental section

*Caution*: DNU and its imidazolium salt, which are powerful and sensitive explosives, were handled with extreme care using the best safety practices. The preparation involved small amounts and strict reaction temperature control.



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#### 2.1. General methods for characterization

<sup>1</sup>H NMR spectra were recorded on Bruker AV-600 at 600 MHz. The spectra were measured in  $[D_6]$  dimethyl sulfoxide (DMSO). The chemical shifts were given in ppm relative to tetramethylsilane. IR spectra were recorded on a Thermo Nicolet 6700 spectrometer as KBr pellets at room temperature. Microanalyses were performed using a Vario EL element analyzer. ESI/MS analyses were carried out using an FT-ICR mass spectrometer.

## 2.1.1. Synthesis of DNU

DNU was synthesized according to literature [22]. Urea (3 g, 0.05 mol) was added to a mixture of 98% sulfuric acid (6 mL) and 100% nitric acid (8 mL) at 0–5 °C. The mixture was then stirred for about 30 min at 0 °C, and DNU as a white solid was precipitated in 60% yield. <sup>1</sup>H NMR (600 MHz, [D<sub>6</sub>]DMSO):  $\delta$  = 11.2 (s, 2H); elemental analysis calcd. (%) for CN<sub>4</sub>O<sub>5</sub>H<sub>2</sub>: C 8.00%, H 1.34%, N 37.34%; found: C 8.18%, H 1.53%, N 37.04%; MS *m/z*: DNU<sup>-</sup>, 148.9. UV: 223 nm. IR (KBr):  $\nu$  = 1762, 1705, 1610, 1310, and 1080 cm<sup>-1</sup>.

## 2.1.2. Synthesis of [IMI][DNU]

Imidazole (0.68 g, 10 mmol) was added to a solution of DNU (1.8 g, 12 mmol) dissolved in acetonitrile (20 mL), and stirred at room temperature for 12 h. A white product was obtained after filtration, and was washed with CH<sub>3</sub>CN as well as diethyl ether as in literature [12], yield 76%. <sup>1</sup>H NMR 600 MHz, [D<sub>6</sub>]DMSO:  $\delta$  = 13.85 (s, 1H), 9.06 (s, 1H), 7.63 (s, 2H); elemental analysis calcd. (%) for C<sub>4</sub>H<sub>6</sub>N<sub>6</sub>O<sub>5</sub>: C 22.03%, H 2.77%, N 38.53%; found: C 22.24%, H 2.88%, N 37.69%; IR (KBr):  $\nu$  = 3161, 2878, 1710, 1592, 1293, 1172, 1069, 1003, and 769 cm<sup>-1</sup>.

## 2.2. In situ pyrolytic FT-IR spectroscopy

The experiments were carried out in a grease-free sodium borosilicate glass cell. The cells were cylindrical, with a length of 13.5 cm and internal diameter of 2.3 cm. ZnSn windows were fixed with Crystal sealant. IR spectra were recorded using a Nicolet 6700 IR spectrometer. The light source was a glow bar from which the interferometer analyzed the spectral region from 650 cm<sup>-1</sup> to 4000 cm<sup>-1</sup>. The cell was heated using a thermolyne heating tape, which was controlled by an analogue temperature controller. The condensed and gas phase products from the thermal decomposition of DNU were collected every 5 °C at a heating rate of 5 °C/min in a vacuum.

## 2.3. Compatibility of [IMI][DNU] with PEG10000

[IMI][DNU] was composed of PEG10000 at a mass ratio of 1:1. The decomposition processes of [IMI][DNU] and [IMI][DNU] + -PEG10000 were determined by a SHIMADZU DTG-60H system at the heating rates of 2, 5, 10, 15, and 20 °C/min. The kinetic parameters were calculated according to the Kissinger and Ozawa methods.

## 2.4. Computational procedures

Density functional theory (DFT) calculations are used to study the thermal decomposition of energetic compounds, such as HMX, RDX, TNT, and HNTO [19,27–31]. The Becke three-parameter hybrid density functional approximation with the Lee–Yang–Parr correlation functional approximation (B3LYP) [32] is adequate for calculating the thermal decomposition mechanism of similarsized systems [33,34]. In the present study, all calculations were performed with the Gaussian 09 program package [35]. The optimization and frequency determinations of the isolated DNU structure were carried out using the 6-311G (d, p)/B3LYP basis set at the DFT level. The frequency values were scaled down by a factor 0.9668 [36].

## 2.5. X-ray analyses

X-ray single-crystal data were collected on a Bruker CCD X-ray diffractometer equipped with an area detector using graphite monochromated Mo K $\alpha$  radiation ( $\lambda$  = 0.7103 Å). The structures were solved and refined using the SHELXTL software package [37]. Absorption corrections were made using SADABS [38]. The structures were refined by full-matrix least squares on  $F^2$ . All non-hydrogen atoms were anisotropically refined. The hydrogen atoms of N—H were found from difference Fourier maps and isotropically refined without restraint. The hydrogen atoms were placed in a calculated position with C—H = 0.95 Å. CCDC-829453 contained the supplementary crystallographic data for the present paper. These data can be obtained free of charge from The Cambridge Crystallographic DataCentre via http://www.ccdc.cam.a-c.uk/data\_request/cif.

## 3. Results and discussion

## 3.1. Crystal structure

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Suitable [IMI][DNU] crystals for X-ray diffraction were obtained by slow recrystallization from ethyl acetate at room temperature. The structures and crystallographic data are shown in Table 1 and Fig. 1a, respectively.

The structure of [IMI][DNU] at 153 K crystallizes in the orthorhombic space group (P212121) with one molecule in the unit cell. The calculated density is 1.64 g/cm<sup>3</sup> (Table 1). There are also chiral configurations as DNU and triazolium dinitrourea. The bond length of N(3)—N(4) is also lowered to 1.316(2) Å because of the deprotonation of the DNU molecule [12]. However, the torsion angles of O(1)—N(3)—N(4)—C(4) = 1.9(3)° is smaller than that of O(7)—N(8)—N(9)—C(10) = 8.9(2)° for triazolium dinitrourea, and O(1)—N(1)—N(2)—C(1) = -11.2(2)° for DNU [12]. These values mean that the [IMI][DNU] anion is nearly coplanar because of the delocalization of the anionic charge and the hyper-conjugative effect that exists in nitramines [12,39]. A slightly twisted hydrogen atom H(1N) that connects to the nitrogen atoms out of the imidazole ring plane by 3° may be the consequence of competition among

Table 1			
Crystal data and	structure for	r title com	pound.

-		-
I	Formula	$C_4H_6N_6O_5$
I	Mol. wt.	218.15
1	Гетрегаture (К)	153
(	Crystal system	Orthorhombic
5	Space group	P212121
(	a (Å)	5.4173(12)
1	b (Å)	8.162(2)
(	c (Å)	19.978(5)
0	χ (°)	90
1	β (°)	90
1	y (°)	90
I	V (Å <sup>3</sup> )	883.3(4)
ź	Z	4
	$\rho_{calcd} (mg/m^3)$	1.64
1	$\mu ({\rm mm^{-1}})$	0.149
i	F (000)	448
(	Crystal size (mm <sup>3</sup> )	$0.24 \times 0.29 \times 0.36$
e	9 Range (°)	3.22-27.49
I	Limiting indices	$-7 \leqslant h \leqslant 5$
		$-10 \leqslant k \leqslant 10$
		$-24 \leqslant l \leqslant 25$
I	Data/restraints/param.	1208/0.025/6905
I	Final <i>R</i> indices $(I > 2\sigma(I))^{a}$	$R_1 = 0.0290, wR_2 = 0.0702$
I	Largest diff. peak and hole $(e^{A^{-3}})$	0.19 and -0.14



Fig. 1. Crystal structure of [IMI][DNU]. (a) ORTEP representation of the molecular structure. (b) Close contacts around each anion. (c) Close contacts around each cation. (d) The three-dimensional hydrogen-bonding network.

intramolecular hydrogen bonds. The detailed hydrogen bonds, torsion angles and bond length are listed in Supporting information.

The packing structure of the title compound built by hydrogen bonds is also depicted in Fig. 1. Fig. 1b shows that each DNU anion is connected to four cations via the terminal peripheral oxygen atoms through hydrogen bonds: N1–H(1 N)···O(1) = 3.051(2) Å, 122(2)°; N1–H(1N)···O(2) = 2.793(2) Å, 177(2)°; N(2)–H(2N)···O(1) = 2.818(2) Å, 151(2)°; N(2)–H(2N)···O(3) = 2.902(2) Å, 134(2)°; N(5)–H(5N)···O(2) = 2.804(2) Å, 170(2)°; C(2)–H(2) ···O(4) = 3.252(3) Å, 170°; C(3)–H(3)···O(4) = 3.006(2) Å, 121°. These hydrogen bonds also connect a cation to four anions, as shown in Fig. 1c. Another peripheral oxygen atom of an anion is connected to another anion by the hydrogen bond of N(5)–H(5N)···O(2). The above interactions enable the cations and anions to pack into complicated three-dimensional hydrogen bond networks (Fig. 1d).

## 3.2. Vibrational spectroscopy

The observed IR and Raman bands with their calculated wavenumbers and assignments are given in Table 2. The derivation of some wavenumbers may be attributed to the intermolecular hydrogen bonds, which were found in the crystal structure of the solid phase. The hydrogen bonds also formed a dominant broad band ranging from 2200 cm<sup>-1</sup> to 3600 cm<sup>-1</sup>, and weakened the vibrations of NH at 3480 and 3529 cm<sup>-1</sup> [40,41]. The absorption bands at 1592 and 1710 cm<sup>-1</sup> correspond to the stretching vibrations of N=O and C=O in the anion, respectively. The asymmetric stretching vibrations of the C4–N5–N6 and N6–N5–H bonds in the anion were observed at 1069 and 1293 cm<sup>-1</sup>. The C–N wagging mode in the anion was assigned to the medium strength band

Table 2
The wavenumbers (cm <sup>-1</sup> ) of IR and Raman spectra and the calculated results for title
compound

Correction	Assignment	IR spectra	Raman spectra
526	$\rho NO_2$		528
594	ω N2H		
725	ωCN	769	
784	$\delta_s NO_2$		782
940	$\delta_s NO_2$		972
976	vs N4C4N5		1006
996	ω N1H	1003	
1035	$v_{as}$ C4N5N6	1069	1060
1153	v C1N2, N2C3		1164
1174	v N1C3N2	1172	1187
1223	v <sub>as</sub> N3N4C4		1204
1242	$v_{as} NO_2$		
1315	v <sub>s</sub> N6N5H	1293	
1364	δ C4N5H		1331
1445	v <sub>as</sub> C1C2N2		1455
1523	NO <sub>2</sub>		
1575	v C1C2		
1598	$v_{as} NO_2$	1592	
1700	v CO	1710	1715
2730	v N1H	2878	
3133	v C3H	3161	
3480	v N5H		
3529	v N2H		

at 769 cm<sup>-1</sup>. For the cationic vibrations, only those of C—H and N—H bonds were observed in the IR spectrum. For example, the in-plane rocking vibrations of C1—H and N2—H were assigned at 1172 cm<sup>-1</sup>. These stretching vibrations were confirmed within 2880–3235 cm<sup>-1</sup>.

The skeletal stretching vibrations were mainly exhibited in the Raman spectrum. The strong band at  $1187 \text{ cm}^{-1}$  was assigned to the symmetric stretching vibration of N1–C3–N2 bonds in the cation. Another strong band at 1006 cm<sup>-1</sup> was associated with the symmetric stretching vibration of N4–C4–N5 bonds in the anion. The rocking vibrations of –NO<sub>2</sub> were assigned at 528, 782, and 972 cm<sup>-1</sup>. The asymmetric stretching vibrations of C4–N5–N6, N3–N4–C4, and C1–C2–N2 were associated at 1060, 1204, and 1455 cm<sup>-1</sup>, respectively.

## 3.3. Non-isothermal kinetic analysis

The methods of Kissinger [25] (Eq. (1)) and Ozawa [26] (Eq. (2)) were applied to study the kinetic parameters of the energetic materials [42–44]. The related equations were:

$$\frac{d[\ln(\beta/T_m^2)]}{d(1/T_m)} = -\frac{E}{R},$$
(1)

$$\log \beta + \frac{0.4567E}{RT_m} = C,$$
 (2)

$$A = \frac{E\beta}{RT_m^2} \exp\left(\frac{E}{RT_m}\right),\tag{3}$$

$$k = A \exp\left(-\frac{E}{RT}\right),\tag{4}$$

where  $T_m$  is the peak temperature (K); *R* is the gas constant, 8.314 J/(mol K);  $\beta$  is the linear heating rate (K/min); *A* is the pre-exponential factor; and *k* is the rate constant.

Thermogravimetric (TG)/DTA analysis was carried out at the heating rates of 2, 5, 10, 15, and 20 °C/min. The calculated results and TG/DTA plot of [IMI][DNU] are shown in Table 3 and the thermal analysis plots are listed in Supporting information. The calculated apparent activation energies were 161.6 kJ/mol by the Kissinger method and 159.7 kJ/mol by the Ozawa method. The average of these two values is 160.7 kJ/mol. The values of *A* and *k* calculated with this average number were all within the normal range of the kinetic parameters of the thermal decomposition reaction of solid materials [15].

## 3.4. Compatibility of [IMI][DNU] with PEG10000

Compatibility is an important safety property of energetic materials related to their production, storage and application [45–47]. Differential scanning calorimetry (DSC), TG, and DTA curves are effective methods for evaluating the effect of contact

#### Table 3

Peak temperature of the exothermic stage at different heating rates and the kinetic parameters of pure [IMI][DNU].

$\beta^{a}$	$T_m^{\mathbf{b}}$	A <sup>c</sup>	$k^{\mathrm{d}}$
2	370	$\textbf{2.99}\times \textbf{10}^{-4}$	$\textbf{2.84}\times \textbf{10}^{-4}$
5	375	$7.27 imes10^{-4}$	$6.90 imes10^{-4}$
10	380	$1.42  imes 10^{-3}$	$1.35  imes 10^{-3}$
20	387	$2.74 imes10^{-3}$	$\textbf{2.60}\times \textbf{10}^{-3}$
$E_k^e$		161.6	
$E_o^{f}$		159.7	
$E_a^g$		160.7	

<sup>a</sup> Heating rate (°C/min).

<sup>b</sup> Peak temperature (K).

<sup>c</sup> Pre-exponential factor (s<sup>-1</sup>).

<sup>d</sup> Rate constant at  $T_m$ .

<sup>e</sup> Activation energy in Kissinger method (kJ/mol).

<sup>f</sup> Activation energy in Ozawa method (kJ/mol).

<sup>g</sup> Average activation energy in both method (kJ/mol).

materials on the decomposition temperatures of energetic materials [48,49]. PEG is widely used in explosives and propellants for reducing sensitivity [50] and improving mechanical properties [51]. Therefore, the compatibility of [IMI][DNU] with PEG10000 was studied by TG/DTA at the heating rates of 2, 5, 10, 15, and 20 K/min. The results are listed in Table 4. The kinetic parameters were calculated according to Eqs. (1)–(4). The peak temperature changes of [IMI][DNU] in the mixture decreased with increased heating rate, and its values ranged from -16 K to -5 K. The average apparent activation energy calculated from both Kissinger and Ozawa methods was 88.7 kJ/mol, which was lower than that of the pure products. These results meant that [IMI][DNU] was incompatible with PEG10000 [47,52,53], which decreased the thermal stability of [IMI][DNU]. However, the pre-exponential factor A and the rate constant k were still in the same order of magnitude as that of pure [IMI][DNU].

## 3.5. In situ IR analysis

In situ Fourier transform infrared (FT-IR) was used to analyze the thermal decomposition processes of energetic materials and other organic compounds [19,44,54,55]. The thermal decomposition process of [IMI][DNU] was analyzed from 20 °C to 200 °C. The curves of the characteristic band intensity for the condensed and gas phase products with different pyrolysis temperatures are shown in Figs. 2 and 3, respectively.

Fig. 2 shows that the band intensity of [IMI][DNU] at 1069 and 1293 cm<sup>-1</sup> initially weakened when the temperature was increased to 100 °C. At the same time, new bands within 2218–2371 cm<sup>-1</sup> were assigned to the vibrations of the -N=C=O group [56], which may have been formed by the breakage of one of the N—N bonds. The weakened intensities of these bands with increased temperature may be attributed to its further reaction. These reactions also enabled the blue shift of the in-plane rocking vibrations of C1—H and N2—H at 1172 cm<sup>-1</sup>. The stretching vibrations of C2=O (1710 cm<sup>-1</sup>) and N=O (1592 cm<sup>-1</sup>) weakened at high temperatures, which meant that these groups reacted or rearranged after the initial decomposition step. Nearly all the bands disappeared or weakened at 200 °C, indicating that the decomposition became complete at this temperature, in agreement with the TG results.

Fig. 3 shows nearly all the decomposition gas phase products of [IMI][DNU]. The gas products simultaneously appeared at around 105 °C, and reached the highest band intensity at about 150 °C. The dominant product from the [IMI][DNU] decomposition was  $N_2O$ , which can be assigned at about 2230, 2220, 1300, 1250, and

Table 4

Peak temperature of the exothermic stage at different heating rates and the kinetic parameters of [IMI][DNU] in mixture.

$\beta^{a}$	$T_{m1}^{\mathbf{b}}$	$T_m^c$	$\Delta T^{\mathbf{d}}$	A <sup>e</sup>	$k^{\mathrm{f}}$
2	370	354	-16	1.75  imes 10 - 4	$1.70  imes 10^{-4}$
5	375	362	-13	$4.19\times10^{-4}$	$4.07 imes10^{-4}$
10	380	370	-10	$8.02\times10^{-4}$	$7.79 imes10^{-4}$
15	384	375	-9	$1.17  imes 10^{-3}$	$1.14  imes 10^{-3}$
20	387	382	-5	$1.50  imes 10^{-3}$	$1.46  imes 10^{-3}$
$E_k^{\mathbf{g}}$			87.9		
$E_o^h$			89.4		
$E_{a}^{i}$			88.7		

<sup>a</sup> Heating rate (°C/min).

<sup>b</sup> Peak temperature of pure [IMI][DNU] (K).

<sup>c</sup> Peak temperature of [IMI][DNU] in mixture.

<sup>d</sup> change of peak temperature of [IMI][DNU] between pure and mixture.

<sup>e</sup> Pre-exponential factor (s<sup>-1</sup>).

<sup>f</sup> Rate constant at *T<sub>m</sub>*.

<sup>g</sup> Activation energy in Kissinger method (kJ/mol).

<sup>h</sup> Activation energy in Ozawa method (kJ/mol).

Average activation energy in both method (kJ/mol).



**Fig. 2.** IR spectra of the condensed phase products by thermal decomposition of [IMI][DNU] at various temperatures.



**Fig. 3.** IR spectra of the gas phase products by thermal decomposition of [IMI][DNU] at various temperatures.

 $670 \text{ cm}^{-1}$  [57]. This gas may have been formed from the rearrangement of anions after the breakage of one of the N–N bonds. The multi-peaks range from 2300 cm<sup>-1</sup> to 2400 cm<sup>-1</sup> can be attributed to the vibrations of NCO. Strong bands at 2189 and 2204 cm<sup>-1</sup> were the absorption spectra of HCNO [58,59]. These products may have also been formed from the breakage of the N–N bond. The broad band ranging from 2968 cm<sup>-1</sup> to 3416 cm<sup>-1</sup> was assigned to the vibrations of CH and NH in the cation [56].

## 3.6. Electron impact ionization (EI) analysis

The mass spectral fragmentation could represent the thermal decomposition pathway [22,58,60]. Hence, mass spectroscopy (MS) was conducted to confirm the final decomposition products of [IMI][DNU] (Fig. 4). The most intensive peak of m/z 68 was assigned to the products of iminazole ( $C_3N_2H_4$ ), which indicated that the cation ( $C_3N_2H_5$ ) decomposed into iminazole by hydrogen migration with temperature increase. The m/z of 69 was assigned to the cation ( $C_3N_2H_5$ ) fragment. The m/z of 67 ( $C_3N_2H_3$ ) may have been formed by the further delocalization of one hydrogen atom from iminazole. The m/z of 44, 41, 40, 39, and 30 may have been formed from the decomposition of the anion. The corresponding products were assigned to  $N_2O$ ,  $CN_2H$ ,  $CN_2$ ,  $C_2NH$ , and NO. Most of them were also found in the DNU mass spectrum, which meant



Fig. 4. Mass spectra of [IMI][DNU].

Table 5 Computed BDE (kcal/mol, 298 K, with the 6-311G+(d, p) basis set) for initial decomposition of [IMI][DNU].

Bonds	BDE
N1(2)—H C3—H C1(2)—H	112.7 126.3 125.9
N3–N4	57.6
N5—N6	47.7
N5—н С4—N5	92.8 88.3
C4–N4	87.1

that DNU and [IMI][DNU] had similar decomposition pathways [22].

#### 3.7. Quantum chemical computation

BDE is frequently and successfully used to measure the bond strength and relative stability of a compound, as well as those of the corresponding radicals [61–65]. In the present study, the geometries of molecules and related radical species were optimized at the B3LYP/6-311+G (d, p) level. The optimized structures were demonstrated to be ground states without imaginary frequencies (NI<sub>mag</sub> = 0) with the help of subsequent frequency calculations at the same level.

Therefore, BDEs were calculated using the thermo-chemical scheme shown in the following equation:

$$BDE(R_1 - R_2) = [\Delta_f H(R_1) + \Delta_f H(R_2)] - \Delta_f H(R_1 - R_2).$$

where  $R_1-R_2$  stands for the neutral molecules.  $\Delta_f H$  ( $R_1$ ),  $\Delta_f H$  ( $R_2$ ), and  $\Delta_f H$  ( $R_1-R_2$ ) are the standard heats of formation for the molecule and radicals.

The experimental results showed that with increased temperature, the bonds in the anion were most probably cleaved, and the cation lost a hydrogen atom by hydrogen migration. The corresponding BDEs were calculated, and the results are listed in Table 5. The minimum BDE was only 47.7 kcal/mol, indicating that the N5—N6 bond may have been the initial step in the thermolysis or explosion in the gas phase [63], in agreement with the RSFTIR analysis results. The BDE of N1(2)—H was 112.7 kcal/mol lower than that of the C—H bond, which meant that the *m/z* of 68 found from the EI spectrum may have been formed by one of the N—H bond that cleaved.

Therefore, the possible decomposition pathway of [IMI][DNU] was proposed according to Scheme 1. The thermal decomposition of [IMI][DNU] was initiated by hydrogen migration or N5—N6 bond



Scheme 1. Proposed decomposition pathway of [IMI][DNU].

homolysis forming stable iminazole  $(C_3N_2H_4)$  and unstable intermediate derivatives  $(CN_3H_2O_3^{-} \text{ and } NO_2^{-})$ . The intermediate  $CN_3H_2O_3^{-}$  further decomposed into the products HNCO, N<sub>2</sub>O, and 'OH. The radicals 'OH and NO<sub>2</sub> then recombined to HNO<sub>3</sub>, which further decomposed into NO, NO<sub>2</sub>, and H<sub>2</sub>O.

## 4. Conclusions

The crystal structure and thermal behavior of [IMI][DNU] were fully investigated by experimental and theoretical methods. A slight twist or torsion was found in the cation and anion because of the interaction between them. This interaction also formed a stabilized hydrogen bond network. Non-isothermal studies showed that the average apparent activation energy from the methods of Kissinger and Ozawa was 160.7 kJ/mol. The corresponding value of [IMI][DNU] and the PEG10000 mixture was 88.7 kJ/mol. The peak temperature of [IMI][DNU] in the mixture decreased from -16 K to -5 K with increased heating rate. In situ IR analysis and BDE calculation results indicated that the initial decomposition step of [IMI][DNU] was the breakage of the N–N bond in the anion. The in situ IR of the gas phase products and mass spectral fragmentation also showed that the main final products of [IMI][DNU] decomposition were N<sub>2</sub>O and imidazole.

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## **Appendix A. Supplementary material**

Supporting online materials provides further details about the crystal parameters; the assignment of IR and Raman spectrum, the thermal analysis plots. These materials can be found in the online version. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.molstruc.2012. 02.001.

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