



Structure–property relationships of energetic nitrogen-rich salts composed of triaminoguanidinium or ammonium cation and tetrazole-based anions

Yuling Shao, Weihua Zhu*, Heming Xiao

Institute for Computation in Molecular and Materials Science and Department of Chemistry, Nanjing University of Science and Technology, Nanjing 210094, China

ARTICLE INFO

Article history:

Received 25 July 2012

Received in revised form

10 December 2012

Accepted 10 December 2012

Available online 21 December 2012

Keywords:

Density functional theory

Crystal density

Heats of formation

Detonation properties

Thermodynamics of salt formation

ABSTRACT

Density functional theory and volume-based thermodynamics calculations have been performed to study the crystal densities, heats of formation (HOFs), energetic properties, and thermodynamics of formation for a series of ionic salts composed of triaminoguanidinium or ammonium cations and tetrazole-based anions. Substitution with $-\text{NF}_2$, $-\text{CH}_2\text{NF}_2$, $-\text{CF}_2\text{NF}_2$, or $-\text{C}(\text{NO}_2)_2\text{NF}_2$ groups increased the densities of the salts. The densities of the tetrazole-based salts are affected not only by different substituents but also by different cations. The $-\text{CN}$ or $-\text{N}_3$ groups are effective substituents for increasing the HOFs of the salts. The triaminoguanidinium cation is more effective than the ammonium cation for increasing the HOF of the tetrazole-based salts. Substitution with $-\text{NO}_2$, $-\text{NF}_2$, or $-\text{C}(\text{NO}_2)_2\text{NF}_2$ groups enhances the explosive properties of the salts. The thermodynamics of formation of the salts reveal that all of the tetrazole-based salts with the triaminoguanidinium or ammonium cation could be synthesized using the proposed reactions. Our calculated methods provide a straightforward and inexpensive route for screening a large number of potentially energetic ionic salts.

© 2012 Elsevier Inc. All rights reserved.

1. Introduction

High-nitrogen energetic compounds, which are a new type of energetic material, have attracted considerable interest because of its large positive heat of formation [1,2] and good thermal stability [3,4]. These materials can be used as highly energetic, stable explosives [5], solid fuel for small propulsion systems, and other applications [6–8]. Energetic nitrogen-rich ionic salts are classified as high-nitrogen energetic compounds. These salts often possess many advantages over energetic nonionic compounds because they are intrinsically nonvolatile, typically thermally stable under normal conditions, and denser than nonionic molecules [9]. In addition, the decomposition of ionic compounds results in the generation of nitrogen gas, with potential to be environmentally friendly energetic materials for industrial or military applications [10]. Therefore, energetic ionic salts are frequently considered to be a new and unique class of energetic materials.

In recent years, considerable attention has been focused on studying high-nitrogen tetrazole-based energetic materials. The aromatic ring structures impart outstanding energetic properties and good thermal stability to the tetrazole-based derivatives. The large heat of formation of these materials is directly attributable to a considerable number of energetic N–N and C–N bonds [11,12]. Because tetrazole-based energetic salts possess unique properties,

such as high-nitrogen contents, large positive heats of formation [13], and surprisingly high thermal stabilities [14–16], many studies on tetrazole-based molecules [17–20] and tetrazole-based salts [21–25] are reported. However, systematic and comparative studies on N,N-(bistetrazolide-5-yl)amine and furazan-functionalized tetrazolideionic salts are still lacking.

In this work, we performed density functional theory (DFT) and volume-based thermodynamics calculations to study the densities, heats of formation (HOFs), energetic properties, and thermodynamics of formation for a series of energetic N,N-(bistetrazolide-5-yl)amine and furazan-functionalized tetrazolideionic salts. The volumes of the cations and anions were calculated in order to obtain the crystal densities of the salts from electronic structure calculations. The HOFs of these materials were calculated by designing isodesmic reactions. Based on the calculated HOFs and densities, the detonation velocities and pressures of these materials were predicted. Finally, the lattice enthalpies and entropies were used to construct a thermodynamic cycle for the formation of the salts to predict a possible synthesis of the salts.

The remainder of this paper is organized as follows. A brief description of our computational method is provided in Section 2. The results and discussion are presented in Section 3, which is followed by a summary of our conclusions in Section 4.

2. Computational method

The calculations were performed using the Gaussian 03 [26] suite of programs. All optimized structures were characterized as

* Corresponding author. Tel.: +86 25 84303919; fax: +86 25 84303919.
E-mail address: zhuwh@njust.edu.cn (W. Zhu).

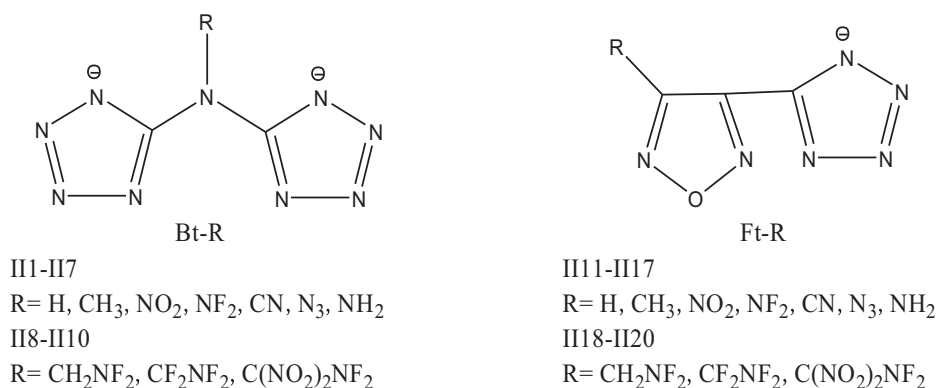


Fig. 1. Structures of a series of substituted N,N-(bistetrazolide-5-yl)amine (Rt) (II1–II10) and furazan-functionalized tetrazolide (Ft) (II11–II20) anions.

true local energy minima on the potential energy surfaces without imaginary frequencies. To obtain more precise HOFs of the ions, geometric optimization of the structures and frequency analyses were performed at the B3LYP/6-31++G* level, and single point energies were calculated at the MP2/6-311++G** level. Fig. 1 shows the structures of a series of N,N-(bistetrazolide-5-yl)amine (Bt) anions (II1–II10) and furazan-functionalized tetrazolide (Ft) anions (II11–II20).

Density is one of the most important physical properties of energetic materials. Several methods [27–29] have been developed to accurately predict crystal density without a priori knowledge of the crystal structure. The developed methods have demonstrated that the molecular volume is sufficient to predict crystal density. The density of a compound can be obtained using the following formula:

$$\rho = \frac{M}{V} \quad (1)$$

where M is the chemical formula mass of the compound, and V is the volume of the compound.

The volume of an ionic compound with the formula M_pX_q is simply the sum of the volumes of the ions contained in the formula [30]:

$$V = pV_{M^+} + qV_{X^-} \quad (2)$$

where V_{M^+} is the volume of the cation M^+ , and V_{X^-} is the volume of the anion X^- . Because the volumes of the individual ions can be evaluated using the DFT procedure, we simply used Eq. (2) to calculate the formula unit volumes for the ionic crystals. For the compounds that contain hydrogen atoms, a “corrected” molecular volume using a molecular structure optimized at the DFT level can be calculated using the following [30]:

$$V_{(\text{corrected})\text{Opt}} = V_{(\text{uncorrected})\text{Opt}} - [0.6763 + 0.9418 \times (\text{no. of hydrogen atoms in the ion})] \quad (3)$$

A previous report [30] stated that the formula unit volumes calculated using the optimized geometries at the B3LYP/6-31G** level and corrected for the number of hydrogen atoms produces average and RMS deviations from the experimental values of 1.3% and 5.0%, respectively, which are in much better agreement than the uncorrected values (5.6% and 7.3%, respectively). Therefore, we used the B3LYP/6-31G** method to calculate the molecular volumes for the tetrazole-based ionic salts in this study. The volume of each ion was defined as the inside of a contour of 0.001 electrons/bohr³ density that was evaluated using a Monte Carlo integration. We performed 100 single-point calculations for the optimized structure of each ion to obtain an average volume. For the ionic salts, the theoretical density was obtained by dividing the molecular weight with

the average molecular volume. This method has been successfully applied to high-nitrogen compounds and ionic salts [30–33].

Based on the Born–Haber energy cycle (Scheme 1), the heat of formation of a salt can be simplified according to Eq. (4):

$$\Delta H_f^\circ(\text{salt}, 298 \text{ K}) = \Delta H_f^\circ(\text{cation}, 298 \text{ K}) + \Delta H_f^\circ(\text{anion}, 298 \text{ K}) - \Delta H_L \quad (4)$$

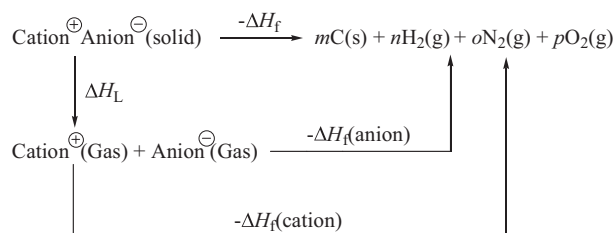
where ΔH_L is the lattice energy of the salt. The lattice energy can be determined from the lattice potential energy (U_{POT}) and the measure of the cohesive energy of the ionic crystal [34]:

$$\Delta H_L = U_{\text{POT}} + \left[p \left(\frac{n_M}{2-2} \right) + q \left(\frac{n_X}{2-2} \right) \right] RT \quad (5)$$

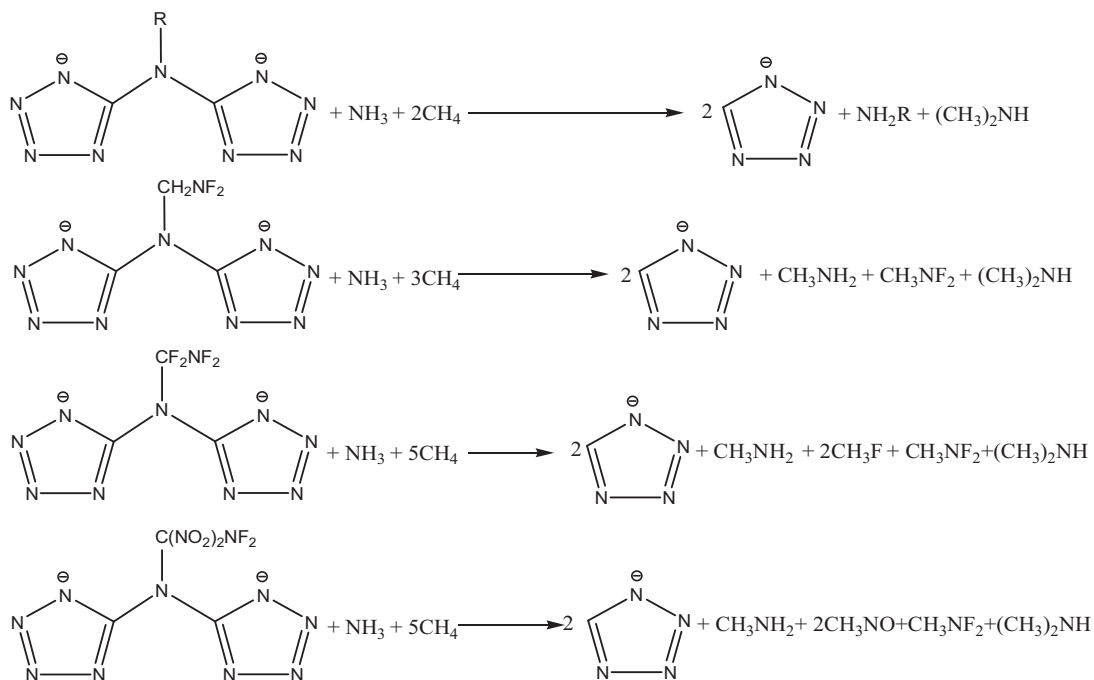
where n_M and n_X depend on the nature of the ions, M_{p^+} and X_{q^-} , respectively, and are equal to 3 for monatomic ions, 5 for linear polyatomic ions, and 6 for nonlinear polyatomic ions. The equation for the lattice potential energy U_{POT} (kJ mol^{−1}) has the following form:

$$U_{\text{POT}} = \gamma \left(\frac{\rho}{M} \right)^{1/3} + \delta \quad (6)$$

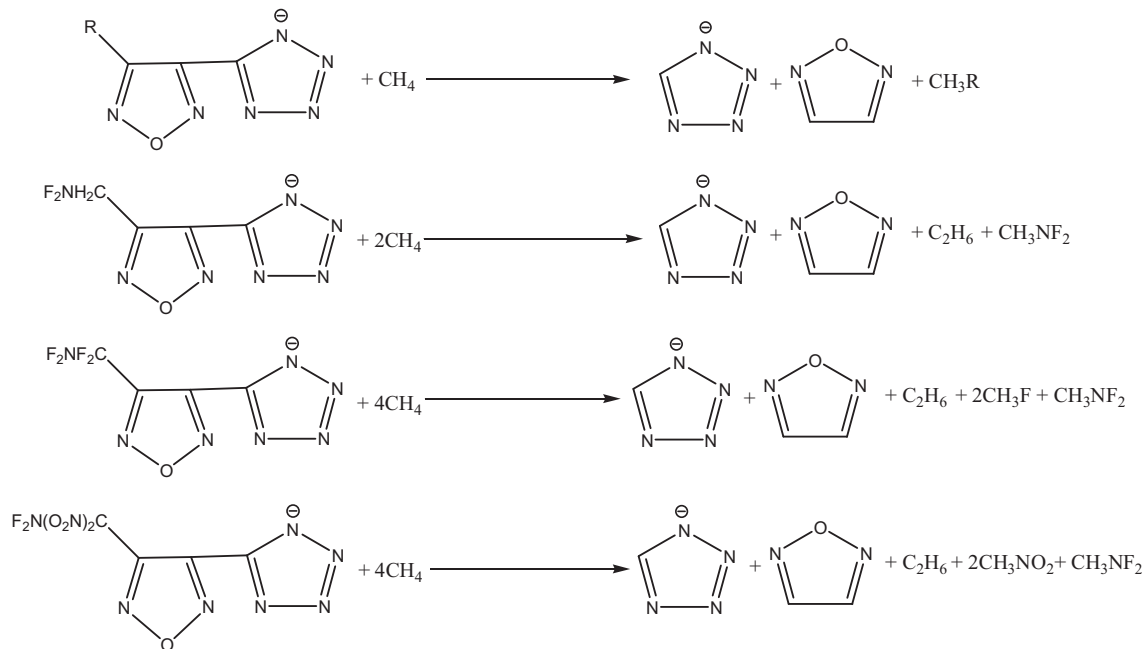
where ρ (g cm³) is the density, M (g mol^{−1}) is the chemical formula mass of the ionic material, and coefficients; $\gamma = 1981.2$ kJ mol^{−1} cm, and $\delta = 103.8$ kJ mol^{−1} [34]. The HOFs of the ions were computed using the isodesmic reactions method. The isodesmic reactions used to obtain the HOFs of the substituted Bt and Ft anions at 298 K are presented in Schemes 2 and 3, respectively. The isodesmic reaction for triaminoguanidinium is presented in Scheme 4. The protonation reactions were calculated at the G2 level. Because the experimental HOFs of some small molecules, such as NH₂CN and NH₂NF₂, are unavailable, additional calculations were performed for the atomization reaction: $C_aH_bO_cN_dFe \rightarrow aC(g) + bH(g) + cO(g) + dN(g) + eF(g)$ using G2 theory to obtain the HOFs.



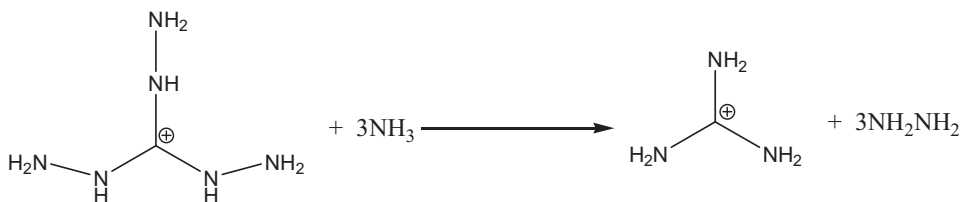
Scheme 1. Born–Haber cycle for the formation of energetic salts.



Scheme 2. Isodesmic reactions for the substituted Bt anions (II1–II10).



Scheme 3. Isodesmic reactions for the substituted Ft anions (II11–II20).



Scheme 4. Isodesmic reaction for triaminoguanidinium.

The detonation velocity and detonation pressure were estimated using the Kamlet–Jacobs equations [35]:

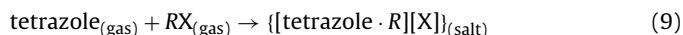
$$D = 1.01(\overline{NM}^{1/2}Q^{1/2})^{1/2}(1 + 1.30\rho) \quad (7)$$

$$P = 1.558\rho^2\overline{NM}^{1/2}Q^{1/2} \quad (8)$$

where each term in Eqs. (7) and (8) is defined as follows: D is the detonation velocity (km s^{-1}); P is the detonation pressure (GPa); N is the number of moles of detonation gases per gram of explosive; \overline{M} is the average molecular weight of these gases (g mol^{-1}); Q is the heat of detonation (cal g^{-1}); and ρ is the loaded density of explosives (g cm^{-3}). For known explosives, the values of Q and ρ can be measured experimentally; therefore, their D and P values can be calculated using Eqs. (7) and (8). However, for unknown compounds, the Q and ρ values cannot be evaluated from experimental measurements. Therefore, to estimate the D and P values, we first need to calculate the Q and ρ values.

For the tetrazole-based salts, the theoretical density was suggested as ρ , and Q was evaluated by the HOF difference between the products and the explosives according to the principle of exothermic reactions. Based on the ρ and Q values, the corresponding D and P values can be evaluated. In practice, the D and P values obtained from ρ can be regarded as their upper limits (maximum values) because the value of ρ from this method is slightly greater than the loading density of the explosive.

To have the formation reaction of a salt be thermodynamically favorable, the free energy change, ΔG_{rxn} , must be less than or equal to zero. The generalized reaction for forming a salt is written as follows:



Because two free gas-phase particles in reaction (9) react to form a solid, the entropy change for this process is negative, which makes the term $-T\Delta S$ positive, which provides a destabilizing contribution. Therefore, the ability of the salt to form will be governed by the negative magnitude of the enthalpy. The estimated entropies ($\text{J K}^{-1} \text{mol}^{-1}$) of the tetrazole-based ionic salts were calculated using the relationship developed by Glasser and Jenkins [36] for organic solids (OS):

$$S_{298}^0(\text{OS}) = (1.285M/\rho) + 57 \quad (10)$$

where ρ and M are defined as in the lattice energy Eq. (6) above.

3. Results and discussion

3.1. Crystal density

A high density is desirable for energetic materials because more energy will be contained in each unit volume. Therefore, density is a critical factor that influences the performance of energetic materials. In this section, we investigate the effects of different substituents and cations (triaminoguanidinium and ammonium) on the densities of the tetrazole-based (II1–II20) salts. The formula unit volumes used for predicting the crystal densities of the ionic crystals were determined using Eq. (1). The volumes of the cations and anions contained in the salts were calculated using the optimized structures. The densities of the ionic salts composed of the triaminoguanidinium or ammonium cation and the substituted tetrazolidide-based (II1–II20) anions and experimental and other calculated values are listed in Table 1. Our calculations are credible because the calculated results are close to other calculated [37] and experimental values [38].

For the triaminoguanidinium or ammonium salts containing the Bt anions (II1–II10), all of the substituted Bt salts have greater densities than the corresponding unsubstituted Bt (II1) salt, except for

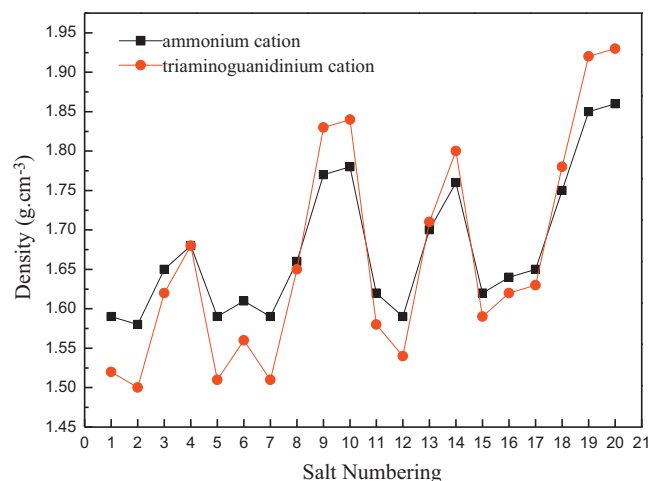
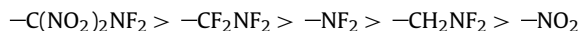


Fig. 2. Comparison of the densities of the ionic salts composed of the triaminoguanidinium or ammonium cations and tetrazole-based anions (II1–II20).

the salt that contains the II2, II5, or II7 anions. The same is true of the Ft-based salts, except for the salt that contains the II2 or II5 anion. In the same series (II1–II10 or II11–II20), the salts that contain the $\text{C}(\text{NO}_2)_2\text{NF}_2$ -substituted Bt or Ft anions have the largest densities. This result indicates that the $-\text{NF}_2$, $-\text{CH}_2\text{NF}_2$, $-\text{CF}_2\text{NF}_2$, and $-\text{C}(\text{NO}_2)_2\text{NF}_2$ substituents increase the densities of the Bt- and Ft-based salts. The primary reasons for this result may be because incorporating the $-\text{NF}_2$ group into the tetrazole ring could significantly enhance its mass but not have much effect on the volume.

Fig. 2 presents a comparison of the densities of the ionic salts composed of the triaminoguanidinium or ammonium cations and the tetrazole-based anions (II1–II20). With the variation of the salt numbering, the evolution pattern of ρ for the ammonium salts is very similar to that for the corresponding triaminoguanidinium salts. Generally speaking, the Ft-based (II10–II20) salts have greater densities than the Bt-based (II1–II10) salts with the same cation. Fig. 2 reveals that the cations have different effects on the densities of the ionic salts. When the substituent is $-\text{CF}_2\text{NF}_2$ or $-\text{C}(\text{NO}_2)_2\text{NF}_2$, the density of the salt containing triaminoguanidinium and Bt-based anions is slower than those that contain ammonium and Bt-based anions, whereas for other substituents, the situation is the opposite. For the salts that contain NO_2^- , NF_2^- , CH_2NF_2^- , CF_2NF_2^- , or $\text{C}(\text{NO}_2)_2\text{NF}_2^-$ -substituted Ft (II3, II4, II18–II20), the densities of the triaminoguanidinium salts are slower than those of ammonium salts, whereas for other substituents, the opposite is observed. This result indicates that the densities of the tetrazole-based salts are affected not only by different substituents but also by different cations. In addition, involving different substituents has a significant effect on the densities of the tetrazole-based salts. Substitution with $-\text{C}(\text{NO}_2)_2\text{NF}_2$, $-\text{CF}_2\text{NF}_2$, $-\text{NF}_2$, $-\text{CH}_2\text{NF}_2$, or $-\text{NO}_2$ groups greatly enhances the density of salts containing the substituted Bt or Ft, and the order is as follows:



3.2. Heats of formation

HOF is frequently used as indicator of the “energy content” of an energetic compound. Therefore, it is very important to predict the HOF of a material. The calculated HOFs of the reference compounds in the isodesmic reactions are listed in Table 2 along with available experimental and other calculated values. The results indicate that the HOF values of small compounds are very close to their corresponding experimental values [20,39]. In addition, the calculated HOF values of the ammonium and triaminoguanidinium cations

Table 1
Volumes (cm³ mol^{−1}) and densities (g cm^{−3}) of the ionic salts composed of the triaminoguanidinium or ammonium cations and tetrazole-based anions (II1–II20).

Salt	Anion	Cation			
		Triaminoguanidinium		Ammonium	
No.	No.	^a V _{corrected} (cm ³ mol ^{−1})	ρ _{corrected} (g cm ^{−3})	^a V _{corrected} (cm ³ mol ^{−1})	ρ _{corrected} (g cm ^{−3})
1	II1	227.6	1.59 (1.60 ^b)	123.3	1.52 (1.60 ^b)
2	II2	237.6	1.58	134.2	1.50
3	II3	246.3	1.65	142.9	1.62
4	II4	244.8	1.68	141.4	1.68
5	II5	243.5	1.59	140.1	1.51
6	II6	249.2	1.61	145.8	1.56
7	II7	237.2	1.59	133.7	1.51
8	II8	256.4	1.66	153.0	1.65
9	II9	260.7	1.77	157.2	1.83
10	II10	289.8	1.78	186.4	1.84
11	II11	149.9	1.62	98.2	1.58
12	II12	161.2	1.59	109.5	1.54
13	II13	168.4	1.70	116.7	1.71
14	II14	166.1	1.76	114.4	1.80
15	II15	165.1	1.62	113.4	1.59
16	II16	173.0	1.64	121.3	1.62
17	II17	156.3	1.65 (1.62 ^c)	104.6	1.63 (1.62 ^c)
18	II18	175.6	1.75	123.9	1.78
19	II19	185.1	1.85	133.4	1.92
20	II20	213.3	1.86	161.6	1.93

^a The average volumes are from 100 single-point calculations.
^b The calculated value was taken from Ref. [37].
^c The experimental value was taken from Ref. [38].

are in agreement with the measured results [41] within errors of 0.03% and 0.01%. Therefore, the HOF values from the G2 calculations are expected to be reliable in this work. Table 3 presents the HOFs of the substituted tetrazole-based anions (II1–II20) and their triaminoguanidinium or ammonium salts as well as the lattice energies of these salts. It can be seen in Table 3 that our calculated HOFs of the ions and the salts are close to other calculated values [38,40–42]. This result means that our calculated results are reliable.

For the ionic salts that contain Bt-based anions (II1–II10), substitution with −NO₂, −NF₂, −CN, −N₃, or −NH₂ increases its HOF value compared to the triaminoguanidinium (HOF = 1205.2 kJ mol^{−1}) or ammonium (HOF = 404.0 kJ mol^{−1}) salts that contain the unsubstituted anion (II1). However, the case is quite the opposite for the −CH₃, −CH₂NF₂, and −CF₂NF₂ groups. The same relationship is observed for salts that contain Ft-based anions (II11–II20), except for the salt containing NH₂-substituted Ft (II17). Among the Bt-based (II1–II10) salts, the salt that contains N₃-substituted Bt (II6) has the largest HOF with both the triaminoguanidinium or ammonium cation. The salt that contains CN-substituted Bt (II5) has the

second largest HOF. However, for the Ft-based (II1–II10) salts, the situation is different. The salt that contains CN-substituted Ft (II15) has the largest HOF, and the salt that contains N₃-substituted Ft (II16) has the second largest HOF. Therefore, the −CN or −N₃ group is an effective substituent for increasing the HOFs of the tetrazole-based salts.

Fig. 3 displays a comparison of the HOF values of the ionic salts composed of triaminoguanidinium or ammonium cations and tetrazole-based anions (II1–II20). For the Bt-based (II1–II10) anions, their triaminoguanidinium salts have considerably greater HOFs than the corresponding ammonium salts because the Bt-based anions have two negative charges and can combine with two cations. Furthermore, the triaminoguanidinium cation has a higher HOF than the ammonium cation. However, for the Ft-based (II11–II20) anions, the situation is different because the Ft-based anions have a single negative charge. In addition, the evolution pattern of the HOFs for the triaminoguanidinium salts is very similar to that of their corresponding ammonium salts, as shown in Fig. 3. This result indicates that the character of the different substituents determines the HOFs of their substituted salts, regardless

Table 2
Calculated and experimental gas-phase heats of formation (kJ mol^{−1}) for small molecules and ions at 298 K.

Molecules	ΔH _f ^o (calc.) ^a	ΔH _f ^o (expt.)	Molecules/ions	ΔH _f ^o (calc.)	ΔH _f ^o (expt.)
NH ₃	−45.2	−46.1 ^b	CH ₄	−76.5 ^a	−74.6 ^b
NH ₂ NO ₂	−3.8	−3.9 ^b	CH ₃ NO ₂	−84.9 ^a	−80.8 ^b
NH ₂ NF ₂	−23.3 (−20.0 ^d)		CH ₃ NF ₂	−109.2 ^a (−110.6 ^e)	
NH ₂ N ₃	436.0 (453.1 ^d)		CH ₃ N ₃	298.3 ^a (296.5 ^e)	
NH ₂ CN	137.8		CH ₃ CN	75.2 ^a	−74.0 ^b
NH ₂ NH ₂	96.2	95.4 ^b	CH ₃ NH ₂	−23.2 ^a	−22.5 ^b
CH ₃ CH ₂ NH ₂	−48.4		H ⁺		1536.2 ^b
(CH ₃) ₂ NH	−20.1		NO ₃ [−]	−308.6 ^c	−306.4 ^d
CH ₃ F	−244.2		NH ₄ ⁺	626.6 ^c (626.4 ^f)	
Furazan	196.2		Triaminoguanidinium	871.6 ^c (871.5 ^f)	

^a The data were calculated at the G2 level.
^b Ref. [39].
^c The data were calculated by protonation reactions: NO₃[−] + H⁺ → HNO₃, NH₃ + H⁺ → NH₄⁺.
^d Ref. [20].
^e Ref. [40].
^f Ref. [41].

Table 3

Heats of formation of the tetrazole-based anions (II1–II20) and their triaminoguanidinium and ammonium salts and the lattice energies of these salts.

Salt	Anion	Cation				
No.	No.	ΔH_f° (kJ mol ⁻¹)	Triaminoguanidinium	Ammonium		
			ΔH_L (kJ mol ⁻¹)	calc ΔH_f° (kJ mol ⁻¹)	ΔH_L (kJ mol ⁻¹)	calc ΔH_f° (kJ mol ⁻¹)
1	II1	662.5	1200.4	1205.2(1195 ^a)	1511.6	404.0(356 ^a)
2	II2	642.3	1180.9	1204.5	1464.5	430.9
3	II3	653.0	1164.8	1231.4	1430.8	475.4
4	II4	692.6	1167.5	1268.2	1436.4	509.4
5	II5	774.1	1170.0	1347.3	1441.4	585.8
6	II6	905.1	1159.6	1488.7	1420.0	738.2
7	II7	766.9	1181.7	1328.3	1466.4	553.6
8	II8	556.5	1147.0	1152.7	1394.6	415.1
9	II9	123.6	1139.8	727.0	1380.4	-3.6
10	II10	518.4	1094.3	1167.2	1295.0	476.6
11	II11	345.3	481.7	735.1(703.5 ^b)	538.2	433.6(411.5 ^b)
12	II12	302.7	472.8	701.5	522.9	406.4
13	II13	345.9	467.5	750.0	514.1	458.4
14	II14	336.6	469.2	739.1	516.9	446.3
15	II15	1217.9	469.9	1619.7	518.0	1326.5
16	II16	681.6	464.3	1088.9	508.9	799.2
17	II17	328.1	476.6	723.1	529.3	425.4
18	II18	256.0	461.6	666.1	506.2	376.4
19	II19	-125.35	460.6	285.6	496.5	4.7
20	II20	286.4	440.4	717.6	472.5	440.4

^a The calculated value was taken from Ref. [42].^b The calculated value was taken from Ref. [38].

of whether the cation is triaminoguanidinium or ammonium. The triaminoguanidinium salts have higher HOFs than the ammonium salts with the same tetrazole-based anion (II1–II20). Therefore, the triaminoguanidinium cation is more suitable for increasing the HOF of the tetrazole-based salts than the ammonium cation. These findings suggest that the rational combination of different substituents and cations may increase the HOFs of the ionic salts.

3.3. Energetic properties

Detonation velocity and detonation pressure are two important performance parameters for an energetic material. The calculated heats of detonation (Q), detonation velocities (D), detonation pressures (P), and oxygen balance (OB) for the ionic salts composed of the triaminoguanidinium or ammonium cations and tetrazole-based anions (II1–II20) are provided in Table 4. Previous studies have shown that the Kamelet–Jacobs formula is appropriate for

predicting the detonation properties of energetic nitrogen-rich compounds [43–45].

For the Bt-based (II1–II10) ionic salts, substitution with the $-\text{NO}_2$, $-\text{NF}_2$, $-\text{N}_3$, $-\text{CN}$, $-\text{NH}_2$, or $-\text{C}(\text{NO}_2)_2\text{NF}_2$ groups increases its Q value compared to its parent II1 salt, with both the triaminoguanidinium and ammonium cations. However, the Ft-based (II11–II20) salts are different. Substitution with $-\text{NH}_2$ decreases the Q value of the parent II11 salt, whereas for the $-\text{CH}_2\text{NF}_2$, or $-\text{CF}_2\text{NF}_2$ group, the relationship is the opposite. Among the Bt-based (II1–II10) salts, the $\text{C}(\text{NO}_2)_2\text{NF}_2$ -substituted Bt (II10) salt has the largest Q value, and the next largest is that of is the NF_2 -substituted Bt (II4) salt. However, for the Ft-based (II11–II20) salts, the CN-substituted Ft (II15) salt has the largest Q value, and the $\text{C}(\text{NO}_2)_2\text{NF}_2$ -substituted Ft (II20) salt has the next largest value. Of the tetrazole-based (II1–II20) salts, the salt composed of ammonium and the CN-substituted Ft (II15) anion has the largest Q value (2082.2 J g⁻¹). Therefore, the $-\text{NF}_2$, $-\text{CN}$, or $-\text{C}(\text{NO}_2)_2\text{NF}_2$ group is an effective substituent for increasing the Q value of the tetrazole-based salts.

For the Bt-based (II1–II10) salts, substitution with $-\text{NO}_2$, $-\text{NF}_2$, $-\text{N}_3$, $-\text{NH}_2$, or $-\text{C}(\text{NO}_2)_2\text{NF}_2$ groups increases the D and P values compared to the parent II1 salt, with both the triaminoguanidinium ($D = 7.69 \text{ km s}^{-1}$ and $P = 24.27 \text{ GPa}$) and ammonium ($D = 6.65 \text{ km s}^{-1}$ and $P = 17.60 \text{ GPa}$) cations. The NO_2 -, NF_2 -, CN -, N_3 -, CH_2NF_2 -, CF_2NF_2 -, or $\text{C}(\text{NO}_2)_2\text{NF}_2$ -substituted Ft salts have higher D and P values than the parent II11 salt, with both the triaminoguanidinium ($D = 7.62 \text{ km s}^{-1}$ and $P = 24.09 \text{ GPa}$) and ammonium ($D = 7.27 \text{ km s}^{-1}$, $P = 21.61 \text{ GPa}$) cations. Therefore, different substituents have different effects on the explosive properties of the substituted tetrazole-based ionic salt. The majority of the substituted Ft-based (II13–II20) salts have higher D and P values than their corresponding Bt-based (II3–II10) salts. Of the salts (II1–II20), the $\text{C}(\text{NO}_2)_2\text{NF}_2$ -substituted Ft (II20) salt has the largest D (9.20 km s^{-1}) and P (39.10 GPa) values.

Oxygen balance (OB) is an index of the deficiency or excess of oxygen in a compound required to convert all of the C into CO_2 and all of the H into H_2O . OB is a parameter that indicates the degree to which an explosive can be oxidized. OB values near to or greater than zero are desirable for reducing toxic fume gases. In other words, compounds with higher OB values have more improved energetic properties. Therefore, OB is another important

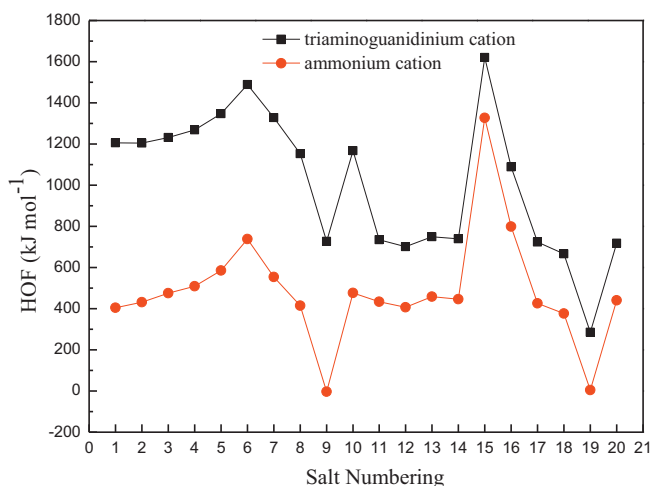


Fig. 3. Comparison of the HOFs of the ionic salts composed of the triaminoguanidinium or ammonium cations and tetrazole-based anions (II1–II20).

Table 4
Predicted heats of detonation (*Q*), detonation velocities (*D*), detonation pressures (*P*), and oxygen balance (OB) of the ionic salts composed of triaminoguanidinium or ammonium cations with tetrazole-based anions (II1–II20).^a

Salt No.	Anion No.	Triaminoguanidinium				Ammonium			
		<i>Q</i> (cal g ^{−1})	<i>D</i> (km s ^{−1})	<i>P</i> (GPa)	^b OB (%)	<i>Q</i> (cal g ^{−1})	<i>D</i> (km s ^{−1})	<i>P</i> (GPa)	^b OB (%)
1	II1	797.5	7.69	24.27	−77.5	516.3	6.65	17.60	−72.7
2	II2	767.2	7.56	23.33	−87.4	512.2	6.52	16.77	−91.5
3	II3	1009.1	8.17	28.05	−59.1	987.9	7.81	25.39	−41.4
4	II4	1259.3	8.09	27.87	−66.0	1192.5	8.06	27.65	−53.8
5	II5	833.8	7.60	23.67	−78.7	660.4	6.76	18.15	−75.5
6	II6	884.6	7.90	25.87	−67.6	773.7	7.36	22.02	−56.1
7	II7	843.8	7.83	25.12	−76.6	654.9	7.09	19.93	−71.3
8	II8	646.4	6.70	18.97	−75.1	393.6	5.89	14.58	−69.8
9	II9	585.7	6.60	19.16	−65.8	146.6	4.76	10.14	−55.6
10	II10	1323.2	8.13	29.15	−46.5	1357.0	8.13	29.65	−28.1
11	II11	964.4	7.62	24.09	−79.3	1041.4	7.27	21.61	−77.4
12	II12	880.3	7.34	22.10	−93.7	916.5	6.93	19.36	−99.4
13	II13	1228.4	8.13	28.33	−52.9	1414.7	7.92	26.99	−40.0
14	II14	1334.5	8.09	28.67	−62.8	1428.3	8.18	29.69	−54.4
15	II15	1665.6	8.46	29.71	−80.9	2082.2	8.26	27.99	−80.0
16	II16	1123.4	7.92	26.22	−65.0	1269.3	7.72	24.73	−57.1
17	II17	896.9	7.66	24.60	−77.8	937.9	7.39	22.73	−75.3
18	II18	1251.9	8.40	30.76	−75.5	1310.4	8.05	28.53	−72.7
19	II19	1171.0	8.28	30.93	−63.0	1201.9	8.48	33.14	−56.2
20	II20	1445.8	8.88	35.67	−38.3	1541.5	9.20	39.10	−25.6

^a Oxygen balance (%) for C_aH_bO_cN_d: ^b 1600 × (c − 2a − b/2)/M_w; M_w, molecular weight of the corresponding compounds.

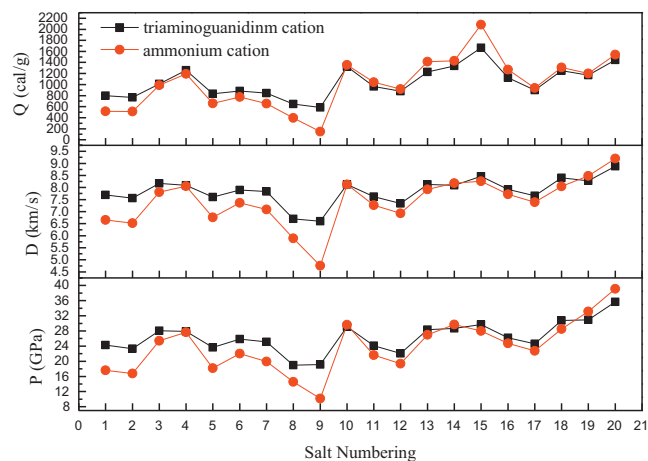
criterion for selecting potential high energy compounds. As shown in Table 4, all of the salts possess negative OB values in the range from −25.6 to −99.4. The triaminoguanidinium salts have smaller OB values than their corresponding ammonium salts, except for the CH₃-substituted (II2 and II12) tetrazole salts. Substitution with the −NO₂, −NF₂, −N₃, −CH₂NF₂, or −C(NO₂)₂NF₂ groups decreases the OB value compared with the parent II1 or II11 salt. Because the additional oxygen atoms in the derivatives will produce additional O₂ that takes away a great deal of energy during the explosion of high energy materials, too much oxygen is unfavorable for increasing the explosive performance. Therefore, one must maintain the value of the oxygen balance around zero when designing high-energy salts.

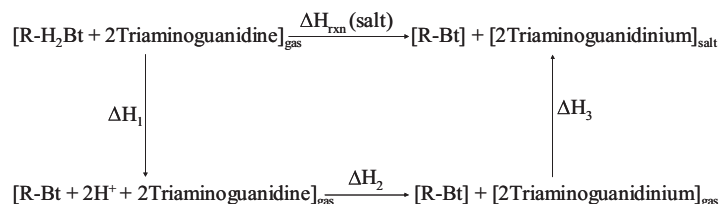
Fig. 4 presents a comparison of the calculated *Q*, *D*, and *P* values of the ionic salts composed of the triaminoguanidinium or ammonium cations and the tetrazole-based anions (II1–II20). For the Bt-based (II1–II10) anions, the triaminoguanidinium salts have higher *Q*, *D*, and *P* values than the corresponding ammonium salts, except for the salt that contains II5 or II10. For the Ft-based

(II11–II20) anions, the triaminoguanidinium salts have higher *Q* values than their corresponding ammonium salts. However, the case is quite different for the *D* and *P* values. The ammonium salts that contain the Ft-based anions (II14, II19, or II20) have higher *D* and *P* values than the corresponding triaminoguanidinium salts, whereas other Ft-based anions show the opposite. This result indicates that the combination of different substituents possessing the furazan ring determines the energetic properties of the Ft-based salts. With the triaminoguanidinium cation, all of the Ft-based salts have higher *D* and *P* values than the Bt-based salts with the same substituent. A similar situation is also observed with the ammonium salts, except for the CH₃- or NH₂-substituted Ft salt. These findings indicate that the rational combination of different cations and substituents may improve the explosive properties of the energetic salts. When the anion number increases, the evolution pattern of the *D* and *P* values for the triaminoguanidinium salts is very similar to that of the corresponding ammonium salts with the same anion. The substituent −C(NO₂)₂NF₂ is the best group for increasing the explosive properties of the salts.

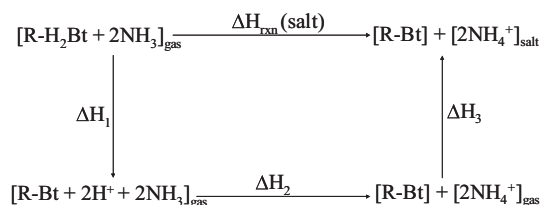
3.4. Thermodynamics of salt formation

Novel energetic ionic salts should not only have desirable explosive properties but should also be inexpensive and easy to synthesize. In this section, we predict the thermodynamics of formation for the salts composed of triaminoguanidinium or ammonium cations and the tetrazole-based anions II1–II20. The Born–Haber thermodynamic cycle for the formation of the tetrazole-based (II1–II20) salts is presented in Schemes 5–8. The overall enthalpy of reaction (ΔH_{rxn}) for the formation of the triaminoguanidinium or ammonium Bt-based (II1–II10) salt is given by the enthalpy for the reaction between a triaminoguanidine or ammonia base and a N-R-(N,N-bis-2H-tetrazole-5-yl)amino acid in the gas phase to form two ions plus the energy to form the salt in the solid state. The overall reaction enthalpy is given as $\Delta H_{\text{rxn}}(\text{salt}) = \Delta H_1 + \Delta H_2 + \Delta H_3$. ΔH_1 is the enthalpy for heterolytically dissociating the H–N bond in the N-R-(N,N-bis-2H-tetrazole-5-yl)amino. ΔH_2 is twice the proton affinity of the triaminoguanidine or ammonia. ΔH_3 is directly related to the lattice energy for the salt formation. The overall enthalpy of reaction

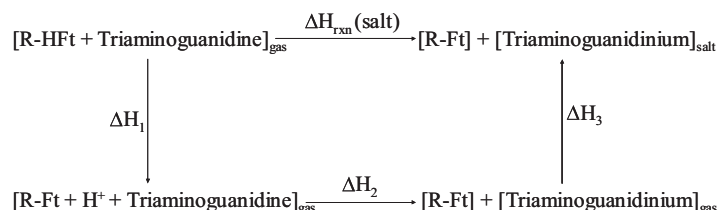
**Fig. 4.** Comparison of the heats of detonation, detonation velocities, and detonation pressures of the ionic salts composed of the triaminoguanidinium or ammonium cations and tetrazole-based anions (II1–II20).



Scheme 5. Born–Haber cycle for the formation of the ionic salts composed of the triaminoguanidinium cation and substituted Bt anions.



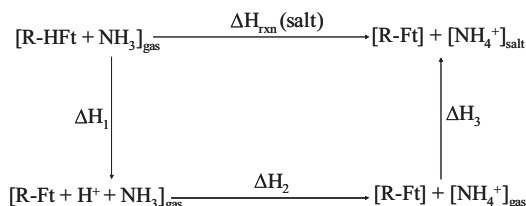
Scheme 6. Born–Haber cycle for the formation of the ionic salts composed of the ammonium cation and substituted Bt anions.



Scheme 7. Born–Haber cycle for the formation of the ionic salts composed of the triaminoguanidinium cation and substituted Ft anions.

(ΔH_{rxn}) for the formation of the triaminoguanidinium or ammonium Ft-based (II11–II20) salt is given by the enthalpy for the reaction between a triaminoguanidine or ammonia and a 4-R-3-(5-tetrazilyl)furan in the gas phase to form two ions plus the energy to form the salt in the solid state. The overall reaction enthalpy is given as $\Delta H_{\text{rxn}}(\text{salt}) = \Delta H_1 + \Delta H_2 + \Delta H_3$. ΔH_1 is the enthalpy for heterolytically dissociating the H–N bond in the 4-R-3-(5-tetrazilyl)furan. ΔH_2 is the proton affinity of the triaminoguanidine or ammonia. ΔH_3 is directly related to the lattice energy for the salt formation.

Table 5 gives the free energies of the reactions (ΔG_{rxn}) of all the salts. All of the free energies of reaction for the tetrazole-based salts are negative. This result indicates that the salts could be synthesized by the above proposed reactions. Among all the salts that contain triaminoguanidinium and substituted tetrazole-based anions (II1–II20), the salt composed of the CN-substituted Bt (II5) has the smallest ΔG_{rxn} values, followed by the NO_2 -substituted Bt (II3) salt and the NF_2 -substituted Bt (II4) salt. A similar situation is also observed for the corresponding ammonium salts. This result means that incorporating –CN, – NO_2 , or – NF_2 into the Bt (II1) or Ft (II11) anion makes the synthesis of these salts more favorable than the corresponding parent salts.



Scheme 8. Born–Haber cycle for the formation of the ionic salts composed of the ammonium cation and substituted Ft anions.

Fig. 5 presents ΔG_{rxn} for the formation of the Bt-based or Ft-based salts. As the anion numbering increases, the evolution pattern of the ΔG_{rxn} for the triaminoguanidinium tetrazolide-based (II1–II20) salts becomes very similar to that of the corresponding ammonium salts with the same anions: it fluctuates in magnitude. This result indicates that substitution with different substituents affects the value of ΔG_{rxn} for the formation of the salt. For the Bt-based (II1–II10) anions, the triaminoguanidinium salts have higher ΔG_{rxn} values than corresponding ammonium salts with the same anions. However, for the Ft-based (II11–II20) anions, the situation is the opposite. The particular combination of the tetrazole-based

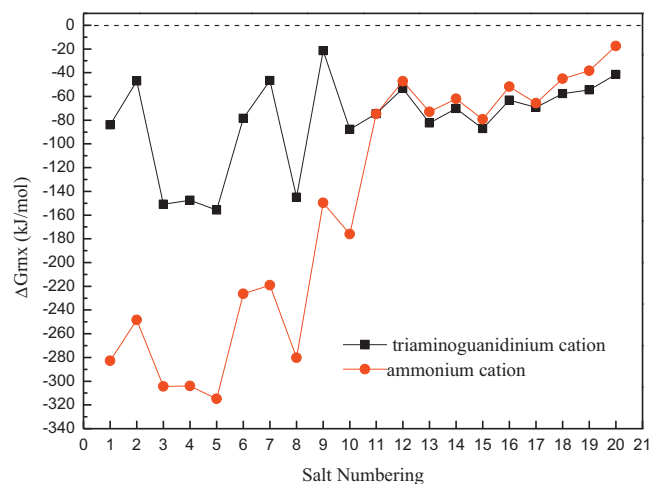


Fig. 5. The free energies of the reactions (ΔG_{rxn}) for the formation of the ionic salts composed of the triaminoguanidinium or ammonium cations and tetrazole-based anions (II1–II20).

Table 5
Proton acidities (ΔH_1), gas-phase proton affinities ($-\Delta H_2$), lattice enthalpies (ΔH_3), enthalpies of reaction ($\Delta H_{\text{rxn}}(\text{salt})$), entropies of reaction (ΔS_{rxn}), and free energies of reaction (ΔG_{rxn}) for the formation of the ionic salts composed of the triaminoguanidinium or ammonium cations with tetrazole-based anions (II1–II20).

Salt		Triaminoguanidinium					
No.	Anion No.	ΔS_{rxn} (J mol ⁻¹ K ⁻¹)	ΔH_1 (kJ mol ⁻¹)	^a ΔH_2 (kJ mol ⁻¹)	ΔH_3 (kJ mol ⁻¹)	ΔH_{rxn} (kJ mol ⁻¹)	ΔG_{rxn} (J mol ⁻¹ K ⁻¹)
1	II1	-765.0	2982.7	-2094.2	-1200.4	-311.9	-83.9
2	II2	-780.8	2995.3	-2094.2	-1180.9	-279.7	-47.0
3	II3	-800.6	2869.6	-2094.2	-1164.8	-389.4	-150.8
4	II4	-826.2	2868.1	-2094.2	-1167.5	-393.7	-147.5
5	II5	-781.6	2875.4	-2094.2	-1170.0	-388.7	-155.8
6	II6	-796.1	2938.2	-2094.2	-1159.6	-315.6	-78.4
7	II7	-774.8	2998.3	-2094.2	-1181.7	-277.6	-46.7
8	II8	-831.8	2848.4	-2094.2	-1147.0	-392.8	-144.9
9	II9	-843.1	2961.4	-2094.2	-1139.8	-272.6	-21.4
10	II10	-883.8	2837.3	-2094.2	-1094.3	-351.2	-87.8
11	II11	-467.2	1315.1	-1047.1	-481.7	-213.7	-74.5
12	II12	-487.3	1321.4	-1047.1	-472.8	-198.5	-53.3
13	II13	-514.3	1279.0	-1047.1	-467.5	-235.6	-82.4
14	II14	-517.8	1291.6	-1047.1	-469.2	-224.7	-70.3
15	II15	-489.5	1283.9	-1047.1	-469.9	-233.0	-87.2
16	II16	-501.1	1298.9	-1047.1	-464.3	-212.5	-63.2
17	II17	-482.6	1310.6	-1047.1	-476.6	-213.0	-69.2
18	II18	-540.4	1291.1	-1047.1	-462.6	-218.6	-57.6
19	II19	-554.2	1283.9	-1047.1	-456.4	-219.6	-54.4
20	II20	-591.4	1269.6	-1047.1	-440.4	-217.9	-41.6

No.		Ammonium					
No.	Anion No.	ΔS_{rxn} (J mol ⁻¹ K ⁻¹)	ΔH_1 (kJ mol ⁻¹)	^a ΔH_2 (kJ mol ⁻¹)	ΔH_3 (kJ mol ⁻¹)	ΔH_{rxn} (kJ mol ⁻¹)	ΔG_{rxn} (J mol ⁻¹ K ⁻¹)
1	II1	-433.0	2982.7	-1882.9	-1511.6	-411.9	-282.8
2	II2	-448.8	2995.3	-1882.9	-1494.5	-382.1	-248.4
3	II3	-468.6	2869.6	-1882.9	-1430.8	-444.1	-304.5
4	II4	-494.2	2868.1	-1882.9	-1436.4	-451.3	-304.0
5	II5	-449.6	2875.4	-1882.9	-1441.4	-448.9	-314.9
6	II6	-464.1	2938.2	-1882.9	-1420.0	-364.7	-226.4
7	II7	-442.8	2998.3	-1882.9	-1466.4	-351.0	-219.1
8	II8	-499.8	2848.4	-1882.9	-1394.6	-429.1	-280.2
9	II9	-511.1	2961.4	-1882.9	-1380.4	-302.0	-149.7
10	II10	-551.8	2837.3	-1882.9	-1295.0	-340.6	-176.1
11	II11	-301.2	1315.1	-941.5	-538.2	-164.6	-74.8
12	II12	-321.3	1321.4	-941.5	-522.9	-143.0	-47.3
13	II13	-348.3	1279.0	-941.5	-514.1	-176.7	-72.9
14	II14	-351.8	1291.6	-941.5	-516.9	-166.7	-61.9
15	II15	-323.5	1283.9	-941.5	-518.0	-175.6	-79.2
16	II16	-335.1	1298.9	-941.5	-508.9	-151.5	-51.7
17	II17	-316.6	1310.6	-941.5	-529.3	-160.1	-65.8
18	II18	-374.4	1291.1	-941.5	-506.2	-156.6	-45.0
19	II19	-388.2	1283.9	-941.5	-496.5	-154.1	-38.4
20	II20	-425.4	1269.6	-941.5	-472.5	-144.4	-17.6

^a Protonation reaction: triaminoguanidine + H⁺ → triaminoguanidinium, NH₃ + H⁺ → NH₄⁺.

(II1–II20) anions with different cations is a determining factor for the magnitude of the ΔG_{rxn} .

4. Conclusions

We investigated the densities, heats of formation, energetic properties, and thermodynamics of formation for a series of Bt- and Ft-based salts with triaminoguanidinium or ammonium cations using DFT and volume-based thermodynamics methods. The results reveal that substitution with the $-\text{NF}_2$, $-\text{CH}_2\text{NF}_2$, $-\text{CF}_2\text{NF}_2$, and $-\text{C}(\text{NO}_2)_2\text{NF}_2$ groups increases the densities of the Bt- and Ft-based salts. The densities of the tetrazole-based salts are affected by not only different substituents but also by different cations. The $-\text{CN}$ or $-\text{N}_3$ group is an effective substituent for increasing the HOFs of the tetrazole-based salts. Triaminoguanidinium is a better cation than ammonium for increasing the HOF.

The majority of the substituted Ft-based (II13–II20) salts have higher D and P values than corresponding Bt-based (II3–II10) salts with the same substituent. As for the Bt-based salts, triaminoguanidinium salts have higher D and P values than the corresponding ammonium salts, whereas the Ft-based salts behave differently. Substitution with the $-\text{NO}_2$, $-\text{NF}_2$, and $-\text{C}(\text{NO}_2)_2\text{NF}_2$

groups enhances the explosive properties of these salts. As the anion numbering increases, the evolution pattern of the D and P values for the triaminoguanidinium salts are very similar to that of the corresponding ammonium salts with the same anion.

The thermodynamics of formation of the salts reveal that all the tetrazole-based salts with triaminoguanidinium or ammonium cations could be synthesized using the proposed reactions.

Acknowledgments

This work has been supported by the NSAF Foundation of National Natural Science Foundation of China and China Academy of Engineering Physics (Grant No. 10876013) and the Fundamental Research Funds for the Central Universities (No. NUST2011YBXM08).

References

- [1] A.N. Ali, S.F. Son, M.A. Hiskey, D.L. Naud, Novel high nitrogen propellant use in solid fuel micro-propulsion, *Journal of Propulsion and Power* 20 (2004) 120–126.
- [2] J. Kerth, S. Löbbecke, Synthesis and characterization of 3,3'-azobis(6-amino-1,2,4,5-tetrazine) DAAT: a new promising nitrogen-rich compound, *Propellants Explosives Pyrotechnics* 27 (2002) 111–118.

- [3] M.H.V. Huynh, M. Hiskey, C.J. Pollard, 4,4',6,6'-Tetra-substituted hydrazo- and azo-1,3,5-triazines, *Journal of Energetic Materials* 22 (2004) 217–229.
- [4] M.H.V. Huynh, M. Hiskey, L. Ernest, P.M. Dennis, G. Richard, Polyazido high-nitrogen compounds: hydrazo and azo-1,3,5-triazine, *Angewandte Chemie International Edition* 43 (2004) 4924–4928.
- [5] J. Neutz, O. Grosshardt, S. Schäufele, H. Schuppler, Synthesis, characterization and thermal behavior of guanidinium-5-aminotetrazolate (GA): a new nitrogen-rich compound, *Propellants Explosives Pyrotechnics* 28 (2003) 181–188.
- [6] P.S. Khandhadia, S.P., Burns, G.K. Williams, High gas yield nonazide gas generators, US Patent No. 6,201,505, 2001.
- [7] H. Schmid, N. Eisenreich, Investigation of a two-stage airbag module with azide-free gas generators, *Propellants Explosives Pyrotechnics* 25 (2000) 230–235.
- [8] S.F. Son, H.L. Berghout, C.A. Bolme, D.E. Chavez, D. Naud, M.A. Hiskey, Burn rate measurements of HMX, TATB, DHT, DAAF and BTATz, *Proceedings of the Combustion Institute* 28 (2000) 919–924.
- [9] G. Drake, T. Hawkins, A. Brand, L. Hall, M. McKay, A. Vij, I. Ismail, Energetic, Low-melting salts of simple heterocycles, *Propellants Explosives Pyrotechnics* 28 (2003) 174–180.
- [10] Y.R. Mirzaei, B. Twamley, J.M. Shreeve, Syntheses of 1-alkyl-1,2,4-triazoles and the formation of quaternary 1-alkyl-4-polyfluoroalkyl-1,2,4-triazolium salts leading to ionic liquids, *Journal of Organic Chemistry* 67 (2002) 9340–9345.
- [11] T.M. Klapötke, P. Mayer, J. Schulz, J.J. Weigand, 1,5-Diamino-4-methyltetrazolium dinitramide, *Journal of the American Chemical Society* 127 (2005) 2032–2033.
- [12] K.E. Gutowski, R.D. Rogers, D.A. Dixon, Accurate thermochemical properties for energetic materials applications. II. Heats of formation of imidazolium-, 1,2,4-triazolium-, and tetrazolium-based energetic salts from isodesmic and lattice energy calculations, *Journal of Physical Chemistry B* 111 (2007) 4788–4800.
- [13] V.A. Ostrovskii, M.S. Pevzner, T.P. Kofman, I.V. Tselinskii, Energetic 1,2,4-triazoles and tetrazoles synthesis, structure and properties, *Targets in Heterocyclic Systems* 3 (1999) 467–526.
- [14] A.I. Lesnikov, O.A. Ivashkevich, S.V. Levchik, A.I. Balabanovich, P.N. Gaponik, A.A. Kulak, Thermal decomposition of aminotetrazoles, *Thermochimica Acta* 388 (2002) 233–251.
- [15] S.V. Levchik, A.I. Balabanovich, O.A. Ivashkevich, P.N. Gaponik, Thermal decomposition of tetrazole-containing polymers. V. Poly-1-vinyl-5-aminotetrazole, *Polymer Degradation and Stability* 47 (1995) 333–338.
- [16] V. Ernst, T.M. Klapötke, J. Stierstorfer, Alkali salts of 5-aminotetrazole-structures and properties, *Zeitschrift für Anorganische und Allgemeine Chemie* 633 (2007) 879–887.
- [17] W.H. Zhu, C.C. Zhang, T. Wei, H.M. Xiao, Computational study of energetic nitrogen-rich derivatives of 1,1'- and 5,5'-bridged ditetrazoles, *Journal of Computational Chemistry* 32 (2011) 2298–2312.
- [18] Z.X. Chen, J.M. Xiao, H.M. Xiao, Y.N. Chiu, Studies on heats of formation for tetrazole derivatives with density functional theory B3LYP method, *Journal of Physical Chemistry A* 103 (1999) 8062–8066.
- [19] F. Himo, Z.P. Demko, L. Noodleman, K.B. Sharpless, Mechanisms of tetrazole formation by addition of azide to nitriles, *Journal of the American Chemical Society* 124 (2002) 12210–12216.
- [20] C.C. Zhang, W.H. Zhu, H.M. Xiao, Density functional theory studies of energetic nitrogen-rich derivatives of substituted carbon-bridged diaminotetrazoles, *Computational and Theoretical Chemistry* 967 (2011) 257–264.
- [21] X.W. Zhang, W.H. Zhu, T. Wei, C.C. Zhang, H.M. Xiao, Densities, heats of formation, energetic properties, and thermodynamics of formation of energetic nitrogen-rich salts containing substituted protonated and methylated tetrazolecations: a computational study, *Journal of Physical Chemistry C* 114 (2010) 13142–13152.
- [22] W.H. Zhu, Q.L. Yan, J.S. Li, B.B. Cheng, Y.L. Shao, X.L. Xia, H.M. Xiao, Prediction of the properties and thermodynamics of formation for energetic nitrogen-rich salts composed of triaminoguanidinium cation and 5-nitroiminotetrazolate-based anions, *Journal of Computational Chemistry* 33 (2012) 1781–1789.
- [23] H. Xue, H.X. Gao, B. Twamley, J.M. Shreeve, Energetic salts of 3-nitro-1,2,4-triazole-5-one, 5-nitroaminotetrazole, and other nitro-substituted azoles, *Chemistry of Materials* 19 (2007) 1731–1739.
- [24] R.P. Singh, R.D. Verma, D.T. Meshri, J.M. Shreeve, Energetic nitrogen-rich salts and ionic liquids, *Angewandte Chemie International Edition* 45 (2006) 3584–3601.
- [25] M.W. Schmidt, M.S. Gordon, J.A. Boatz, Triazolium-based energetic ionic liquids, *Journal of Physical Chemistry A* 109 (2005) 7285–7295.
- [26] M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, V.G. Zakrzewski, J.A. Montgomery, R.E. Stratmann, J.C. Burant, S. Dapprich, J.M. Millam, A.D. Daniels, K.N. Kudin, M.C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G.A. Petersson, P.Y. Ayala, Q. Cui, K. Morokuma, D.K. Malick, A.D. Rabuck, K. Raghavachari, J.B. Foresman, J. Cioslowski, J.V. Ortiz, A.G. Baboul, B.B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R.L. Martin, D.J. Fox, T. Keith, M.A. Al-Laham, C.Y. Peng, A. Nanayakkara, C. Gonzalez, M. Challacombe, P.M.W. Gill, B. Johnson, W. Chen, M.W. Wong, J.L. Andres, C. Gonzalez, M. Head-Gordon, E.S. Replogle, J.A. Pople, Gaussian 03, Revision B. 03, Gaussian Inc., Pittsburgh, PA, 2003.
- [27] A.F. Jalbout, Z.Y. Zhou, X. Li, M. Solimannejad, Y. Ma, Density functional theory response to the calculation of electrode potentials of quinones in non-aqueous solution of acetonitrile, *Journal of Molecular Structure: Theochem* 664–665 (2003) 273–278.
- [28] L. Qiu, H.M. Xiao, X.D. Gong, X.H. Ju, W.H. Zhu, Crystal density predictions for nitramines based on quantum chemistry, *Journal of Hazardous Materials* 141 (2007) 280–288.
- [29] N. Bouhmaida, N.E. Ghermani, Elusive contribution of the experimental surface molecular electrostatic potential and promolecule approximation in the empirical estimate of the crystal density, *Journal of Chemical Physics* 122 (2005) 114101.
- [30] B.M. Rice, J.J. Hare, E.F.C. Byrd, Accurate predictions of crystal densities using quantum mechanical molecular volumes, *Journal of Physical Chemistry A* 111 (2007) 10874–10879.
- [31] X.W. Zhang, W.H. Zhu, H.M. Xiao, Comparative theoretical studies of energetic substituted carbon- and nitrogen-bridged difurazans, *Journal of Physical Chemistry A* 114 (2010) 603–612.
- [32] E.F.C. Byrd, B.M. Rice, A comparison of methods to predict solid phase heats of formation of molecular energetic salts, *Journal of Physical Chemistry A* 113 (2009) 345–352.
- [33] T. Wei, W.H. Zhu, X.W. Zhang, Y.F. Li, H.M. Xiao, Molecular design of 1,2,4,5-tetrazine-based high-energy density materials, *Journal of Physical Chemistry A* 113 (2009) 9404–9412.
- [34] H.D.B. Jenkins, D. Tudela, L. Glasser, Lattice potential energy estimation for complex ionic salts from density measurements, *Inorganic Chemistry* 41 (2002) 2364–2367.
- [35] M.J. Kamlet, S.J. Jacobs, Chemistry of detonation. I. A simple method for calculation detonation properties of C—H—N—O explosives, *Journal of Chemical Physics* 48 (1968) 23–35.
- [36] L. Glasser, H.D.B. Jenkins, Standard absolute entropies, S_{298}^0 , from volume or density: Part II. Organic liquids and solids, *Thermochimica Acta* 414 (2004) 125–130.
- [37] C.F. Ye, J.M. Shreeve, Rapid and accurate estimation of densities of room-temperature ionic liquids and salts, *Journal of Physical Chemistry A* 111 (2007) 1456–1461.
- [38] R.H. Wang, Y. Guo, Z. Zeng, B. Twamley, J.M. Shreeve, Furazan-functionalized tetrazolate-based salts: a new family of insensitive energetic materials, *Chemistry: A European Journal* 15 (2009) 2625–2634.
- [39] R.L. David, *Handbook of Chemistry and Physics*, 84th ed., CRC Press, Boca Raton, 2003–2004 (Section 5).
- [40] T. Wei, W.H. Zhu, J.J. Zhang, H.M. Xiao, DFT study on energetic tetrazolo-[1,5-b]-1,2,4,5-tetrazine and 1,2,4-triazolo-[4,3-b]-1,2,4,5-tetrazine derivatives, *Journal of Hazardous Materials* 179 (2010) 581–590.
- [41] H.X. Gao, C.F. Ye, C.M. Piekarski, J.M. Shreeve, Computational characterization of energetic salts, *Journal of Physical Chemistry C* 111 (2007) 10718–10731.
- [42] Y. Guo, H.X. Gao, B. Twamley, J.M. Shreeve, Energetic nitrogen rich salts of N,N-bis[1(2)H-tetrazol-5-yl]amine, *Advanced Materials* 19 (2007) 2884–2888.
- [43] J.C. Gálvez-Ruiz, G. Holl, K. Karaghiosoff, T.M. Klapötke, K. Löhnitz, P. Mayer, H. Nöth, K. Polborn, C.J. Rohbogner, M. Suter, J.J. Weigand, Derivatives of 1,5-diamino-1H-tetrazole: a new family of energetic heterocyclic-based salts, *Inorganic Chemistry* 44 (2005) 4237–4253.
- [44] L. Türker, T. Atalar, S. Gümmüs, Y. Camur, A DFT study on nitrotriazines, *Journal of Hazardous Materials* 167 (2009) 440–448.
- [45] M.W. Smith, M.D. Cliff, NTO-based explosive formulations: a technology review, DSTO-TR-0796, Australia, 1999. <http://hdl.handle.net/1947/3884>