

Theoretical studies of energetic nitrogen-rich ionic salts composed of substituted 5-nitroiminotetrazolate anions and various cations

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Abstract We have performed density functional theory and volume-based thermodynamics calculations to study the effects of different combinations of energetic anions and cations on the crystal densities, heats of formation, energetic properties, and thermodynamics of formation for a series of 5-nitroiminotetrazolate-based ionic salts. The results show that the substitution of the $-\text{NO}_2$, $-\text{NF}_2$, $-\text{N}_3$, or $-\text{C}(\text{NO}_2)_3$ group is helpful for increasing the densities of the salts. Incorporating every substituent ($-\text{NH}_2$, $-\text{NO}_2$, $-\text{NF}_2$, $-\text{N}_3$, or $-\text{C}(\text{NO}_2)_3$) into the salt is favorable for improving its HOF and detonation performance. Incorporating the cation B1, B2, B10, or B11 into the salts is helpful for improving its detonation properties. Increasing negative charge for the 5-nitroiminotetrazolate-based salts is unfavorable for enhancing the density and detonation performance, but is helpful for increasing the HOFs. Many salts present comparable detonation performance with commonly used explosives RDX or HMX. Among them, 21 salts have near or better properties than HMX. The thermodynamics of formation of the salts show that the majority of the 5-nitroiminotetrazolate salts with the cation B1, B3, B9, B10, B12 could be synthesized by the proposed reactions.

Keywords Crystal density · Density functional theory · Detonation properties · Heats of formation · Thermodynamics of salt formation

Introduction

The development of nitrogen-rich heterocycle compounds as high-energy density materials (HEDMs) have received considerable attention because of their high heat of formation (HOF) [1, 2], high density, and good thermal stability [3, 4]. To meet the continuing need for improved energetic materials, many studies have been focused on the development and synthesis of energetic salts as a special class of highly energetic materials [5–10]. Energetic ionic salts often possess better properties than their atomically similar molecular analogues owing to their lower vapor pressures, higher densities, lower melting points, and higher cohesive energy densities. One of the main decomposition products of the ionic compounds is nitrogen gas that makes them become environmentally acceptable [11]. Therefore, the energetic salts form a new and unique class of HEDMs that have attracted a substantial amount of interest in recent years [12–14].

The present research for energetic salts is mainly aimed at the modification of cations, the synthesis of organic anions, or a combination of different kinds of energetic cations and anions that yield a large number of energetic salts. The tetrazole-based energetic salts have high nitrogen contents, high positive HOF [15–17], and good thermal stability [18–20]. This shows that the tetrazole cation (tetrazolium) [15, 21] or tetrazole anion (tetrazolide) [22, 23] is an efficient unit to enhance the physical and chemical properties of the energetic salts. In addition, the parent tetrazole ring can be easily modified by incorporating different functional groups to obtain a desired set of energetic properties [24–26]. Therefore, further development of energetic tetrazole-based salts requires potential ions with high nitrogen content.

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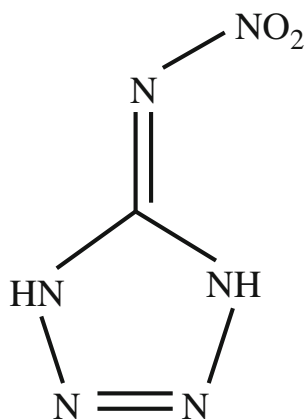
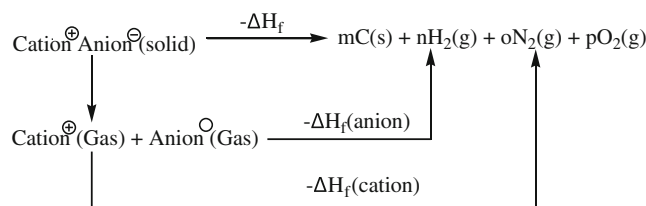


Fig. 1 Framework of 5-nitroiminotetrazole

Among the tetrazole-based salts, 5-nitroiminotetrazole (Fig. 1) derivatives have received considerable attention [5, 23, 27–29] because of high nitrogen content. The substitution of the nitroimino group can improve the crystal densities, heats of formation, and oxygen balances of the energetic materials [13]. It is well known that the hydrogen bonds of energetic compounds have a special effect on the physical and chemical properties. Such hydrogen-bonding interactions in the 5-nitroiminotetrazole derivatives can help to substantially stabilize the compounds, to decrease toxicities and solubility in common solvents, and to enhance the densities [27]. In addition, incorporating different groups into 5-nitroiminotetrazole can improve its properties. For example, the substitution of the $-\text{CH}_3$ group can decrease the sensitivity of the 5-nitroiminotetrazole derivatives [15, 27, 30] or its corresponding salts [31, 32] compared with unsubstituted ones. 5-Nitroiminotetrazole is characterized as a dibasic acid [27], indicating that both hydrogen atoms on the tetrazole ring are acidic. Thus, it can react as a monoprotic or diprotic acid. So 5-nitroiminotetrazoles can be deprotonated to yield thermally stable anions, which are favorable of producing a great deal of energetic salts [23, 33–35].

In this work, we performed density functional theory (DFT) and volume-based thermodynamics calculations to study the densities, HOFs, energetic properties, and thermodynamics of formation for a series of energetic salts composed of substituted 5-nitroiminotetrazolate anions containing different substituents ($-\text{NH}_2$, $-\text{NO}_2$, $-\text{NF}_2$, $-\text{N}_3$, $-\text{C}(\text{NO}_2)_3$) and energetic cations. The combination of 5-nitroiminotetrazolate anions with various nitrogen-rich chained and heterocyclic cations was made to establish the broad relative potential to comprehensively evaluate their performances and thermodynamics of formation. Our main purpose is to investigate different substituents and various cations in the design of efficient 5-nitroiminotetrazolate-based high-energy salts.

The remainder of this paper is organized as follows. A brief description of our computational method is given in the



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

“Computational methods” section. The results and discussion are presented in the “Results and discussion” section, followed by a summary of our conclusions in the “Conclusions” section.

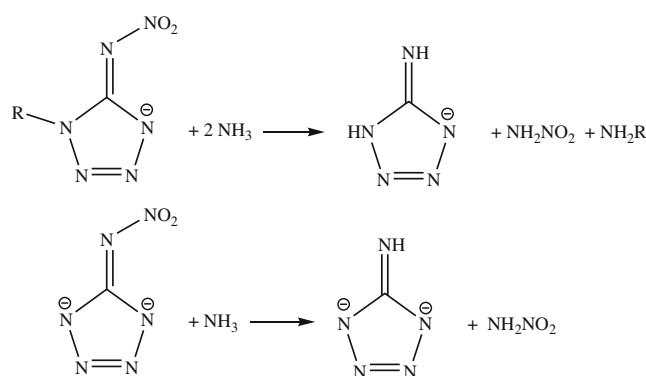
Computational methods

Density is one of the most important physical properties of a solid energetic material. Some approaches [36–40] have been developed to accurately predict the crystal density without a prior knowledge of the crystal structure. The traditional M/V procedure for predicting densities often leads to large errors, because it completely ignores intermolecular interactions within the crystal. The crystal density of ionic crystals can be improved by [41]:

$$\rho = \alpha \left(\frac{M}{V} \right) + \beta \left(\frac{V_S^+}{A_S^+} \right) + \gamma \left(\frac{V_S^-}{A_S^-} \right) + \delta, \quad (1)$$

where M is the chemical formula mass of the compound and V is the volume of the isolated gas molecule. A_S^+ is the portion of a cation’s surface that has a positive electrostatic potential. V_S^+ is the average value of that potential. A_S^- and V_S^- are the analogous quantities for an anion. The values of the coefficients α , β , γ , and δ are 1.026, 0.0514, 0.0419, and 0.0227, respectively [41].

For an ionic crystal with formula unit M_pX_q , its volume is simply the sum of the volumes of the ions contained in the formula unit [39]:



Scheme 2 Isodesmic reactions for the substituted 5-nitroiminotetrazolate anions (A1–A7)

Scheme 3 Isodesmic reactions for different cations

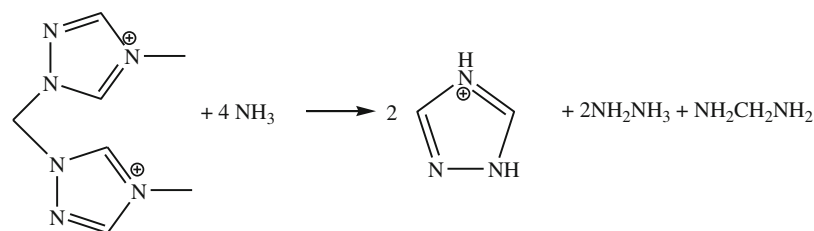
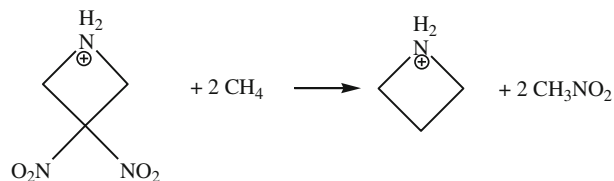
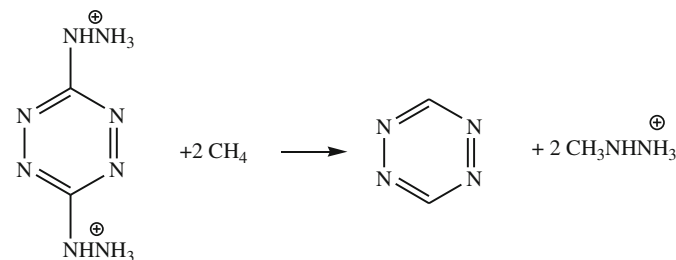
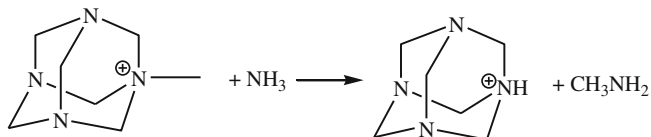
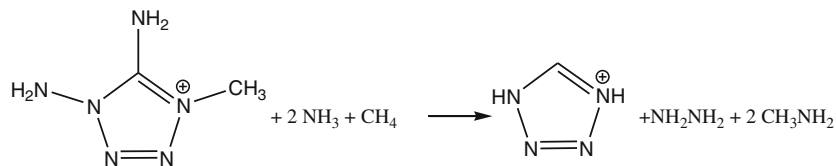
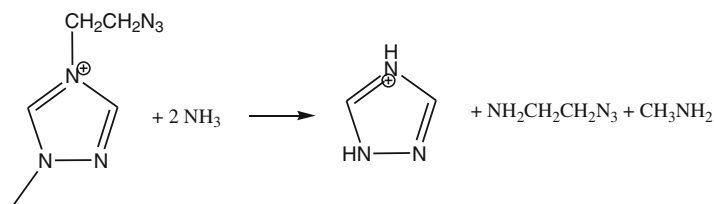
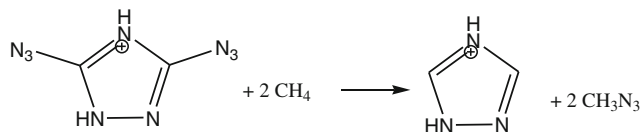
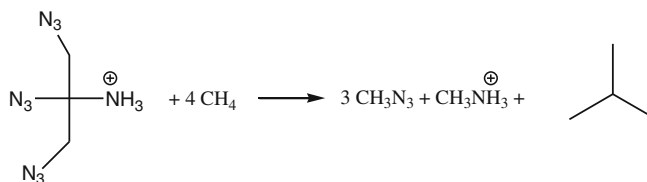
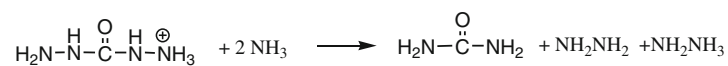
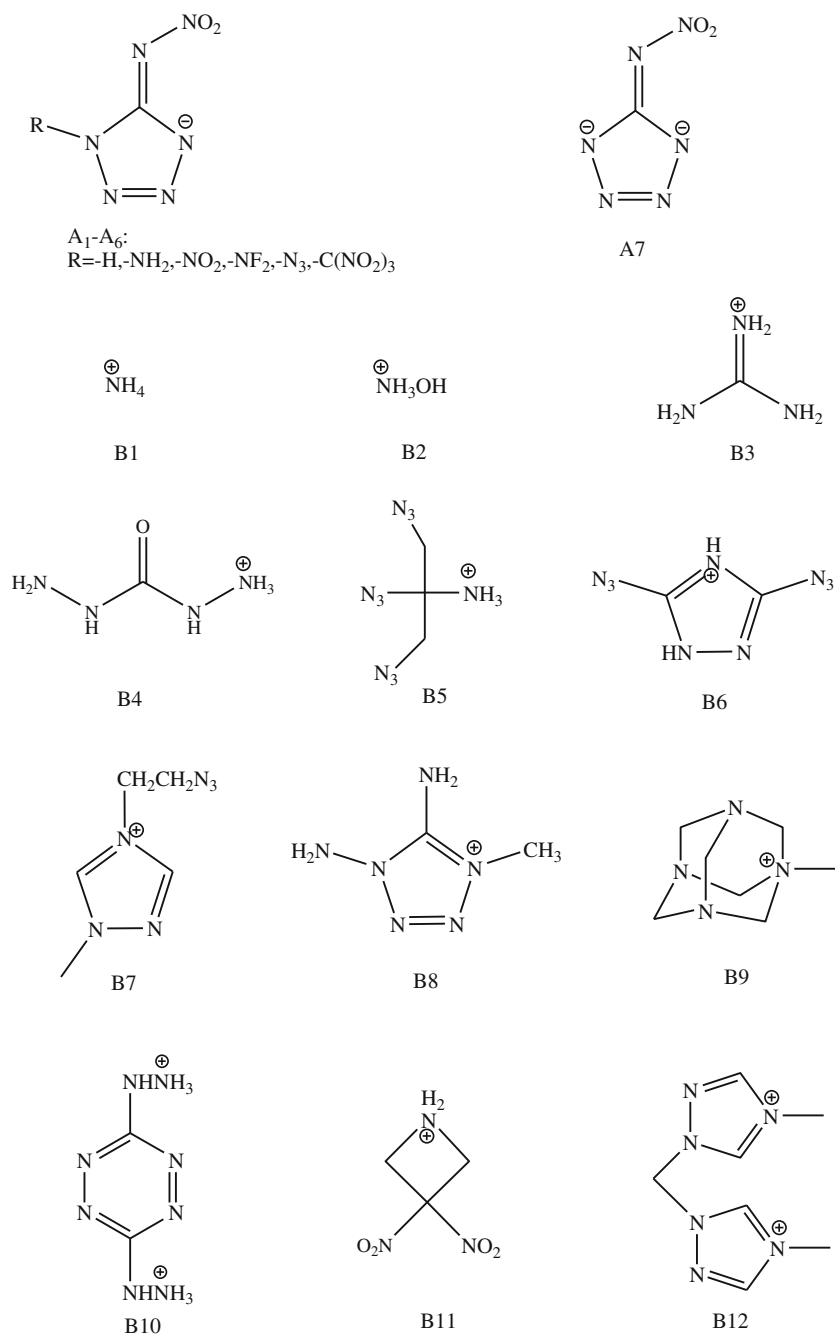


Fig. 2 Frameworks of a series of substituted 5-nitroiminotetrazolate anions and various cations



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

where V_{M^+} is the volume of the cation M^+ and V_{X^-} is the volume of the anion X^- . Since the volumes of individual ions are able to be estimated using the DFT procedure, we can use Eq. (2) to calculate formula unit volumes for ionic salts.

Rice et al. [39] reported that the formula unit volumes calculated using the optimized geometries at the B3LYP/6-31G** level and corrected for the number of hydrogen atoms produce average and RMS deviations from experimental values of 1.3 % and 5.0 %, respectively, in much

better agreement than the uncorrected values (5.6 % and 7.3 %, respectively). So we used the B3LYP/6-31G** method to calculate the molecular volumes for the 5-nitroiminotetrazolate-based ionic salts here. The volume of each ion was defined as inside 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 get an average volume [39]. For the ionic salts, the theoretical density was obtained from the molecular weight divided by the average molecular volume. This method has been

Table 1 Volumes ($\text{cm}^3\cdot\text{mol}^{-1}$) and densities ($\text{g}\cdot\text{cm}^{-3}$) of the substituted 5-nitroiminotetrazolate-based ionic salts

Salt		V	A_S^-	\bar{V}_S^-	A_S^+	V_S^+	ρ
Anion	Cation						
A1	B1	92.61	142.93	-97.03	48.08	170.81	1.81
A1	B2	99.61	142.93	-97.03	61.80	152.27	1.80
A1	B3	122.16	142.93	-97.03	346.50	0.19	1.58 (1.61 ^b)
A1	B4	136.54	142.93	-97.03	121.07	109.10	1.69
A1	B5	209.03	142.93	-97.03	230.25	86.06	1.61
A1	B6	166.75	142.93	-97.03	169.49	95.97	1.75
A1	B7	186.49	142.93	-97.03	200.67	89.95	1.56
A1	B8	155.36	142.93	-97.03	145.16	102.53	1.64
A1	B9	191.78	142.93	-97.03	176.48	93.38	1.54
A1	B10	240.39	142.93	-97.03	162.98	184.37	1.77
A1	B11	162.16	142.93	-97.03	156.13	102.22	1.78
A1	B12	278.23	142.93	-97.03	223.82	164.57	1.65
A2	B1	103.92	157.25	-92.45	48.08	170.81	1.78
A2	B2	110.93	157.25	-92.45	61.80	152.27	1.77
A2	B3	133.48	157.25	-92.45	346.50	0.19	1.57
A2	B4	147.86	157.25	-92.45	121.07	109.10	1.68
A2	B5	220.34	157.25	-92.45	230.25	86.06	1.61
A2	B6	178.07	157.25	-92.45	169.49	95.97	1.73
A2	B7	197.80	157.25	-92.45	200.67	89.95	1.55
A2	B8	166.68	157.25	-92.45	145.16	102.53	1.63
A2	B9	203.10	157.25	-92.45	176.48	93.38	1.54
A2	B10	263.01	157.25	-92.45	162.98	184.37	1.74
A2	B11	173.47	157.25	-92.45	156.13	102.22	1.76
A2	B12	300.86	157.25	-92.45	223.82	164.57	1.63
A3	B1	111.81	170.22	-88.37	48.08	170.81	1.95
A3	B2	118.82	170.22	-88.37	61.80	152.27	1.92
A3	B3	141.37	170.22	-88.37	346.50	0.19	1.70
A3	B4	155.75	170.22	-88.37	121.07	109.10	1.79
A3	B5	228.23	170.22	-88.37	230.25	86.06	1.69
A3	B6	185.96	170.22	-88.37	169.49	95.97	1.83
A3	B7	205.69	170.22	-88.37	200.67	89.95	1.65
A3	B8	174.57	170.22	-88.37	145.16	102.53	1.74
A3	B9	210.99	170.22	-88.37	176.48	93.38	1.63
A3	B10	278.79	170.22	-88.37	162.98	184.37	1.87
A3	B11	181.36	170.22	-88.37	156.13	102.22	1.86
A3	B12	316.64	170.22	-88.37	223.82	164.57	1.75
A4	B1	109.52	170.64	-88.86	48.08	170.81	2.04
A4	B2	116.53	170.64	-88.86	61.80	152.27	2.01
A4	B3	139.08	170.64	-88.86	346.50	0.19	1.77
A4	B4	153.46	170.64	-88.86	121.07	109.10	1.86
A4	B5	225.94	170.64	-88.86	230.25	86.06	1.73
A4	B6	183.67	170.64	-88.86	169.49	95.97	1.88
A4	B7	203.40	170.64	-88.86	200.67	89.95	1.69
A4	B8	172.28	170.64	-88.86	145.16	102.53	1.79
A4	B9	208.70	170.64	-88.86	176.48	93.38	1.68
A4	B10	274.21	170.64	-88.86	162.98	184.37	1.95
A4	B11	179.07	170.64	-88.86	156.13	102.22	1.91

Table 1 (continued)

Salt		V	A _S ⁻	\bar{V}_S^-	A _S ⁺	V _S ⁺	ρ
Anion	Cation						
A4	B12	312.06	170.64	-88.86	223.82	164.57	1.81
A5	B1	114.64	175.23	-87.91	48.08	170.81	1.87
A5	B2	121.64	175.23	-87.91	61.80	152.27	1.85
A5	B3	144.19	175.23	-87.91	346.50	0.19	1.64
A5	B4	158.57	175.23	-87.91	121.07	109.10	1.74
A5	B5	231.06	175.23	-87.91	230.25	86.06	1.65
A5	B6	188.78	175.23	-87.91	169.49	95.97	1.78
A5	B7	208.52	175.23	-87.91	200.67	89.95	1.60
A5	B8	177.39	175.23	-87.91	145.16	102.53	1.69
A5	B9	213.81	175.23	-87.91	176.48	93.38	1.59
A5	B10	284.45	175.23	-87.91	162.98	184.37	1.81
A5	B11	184.19	175.23	-87.91	156.13	102.22	1.81
A5	B12	322.29	175.23	-87.91	223.82	164.57	1.70
A6	B1	158.94	232.30	-76.84	48.08	170.81	2.10
A6	B2	165.95	232.30	-76.84	61.80	152.27	2.06
A6	B3	188.50	232.30	-76.84	346.50	0.19	1.85
A6	B4	202.88	232.30	-76.84	121.07	109.10	1.92
A6	B5	275.37	232.30	-76.84	230.25	86.06	1.80
A6	B6	233.09	232.30	-76.84	169.49	95.97	1.93
A6	B7	252.83	232.30	-76.84	200.67	89.95	1.77
A6	B8	221.70	232.30	-76.84	145.16	102.53	1.86
A6	B9	258.12	232.30	-76.84	176.48	93.38	1.76
A6	B10	373.06	232.30	-76.84	162.98	184.37	1.99
A6	B11	228.50	232.30	-76.84	156.13	102.22	1.96
A7	B12	410.91	232.30	-76.84	223.82	164.57	1.88
A7	B1	111.57	149.11	-194.12	48.08	170.81	1.66
A7	B2	125.58	149.11	-194.12	61.80	152.27	1.70
A7	B3	170.69	149.11	-194.12	346.50	0.19	1.46 (1.50 ^b)
A7	B4	199.45	149.11	-194.12	121.07	109.10	1.61
A7	B5	344.42	149.11	-194.12	230.25	86.06	1.54
A7	B6	259.87	149.11	-194.12	169.49	95.97	1.70
A7	B7	299.34	149.11	-194.12	200.67	89.95	1.47
A7	B8	237.09	149.11	-194.12	145.16	102.53	1.55
A7	B9	309.92	149.11	-194.12	176.48	93.38	1.45
A7	B10	166.74	149.11	-194.12	162.98	184.37	1.70
A7	B11	250.68	149.11	-194.12	156.13	102.22	1.74
A7	B12	204.59	149.11	-194.12	223.82	164.57	1.55

^a The average volumes are from 100 single-point calculations

^b The calculated values are taken from ref. [23]

successfully applied to high-nitrogen compounds and ionic salts [39, 42–44].

Based on a Born–Haber energy cycle (Scheme 1), the HOF of a salt can be simplified by Eq. (3):

$$\Delta H_f^\circ(\text{salt}, 298\text{K}) = \Delta H_f^\circ(\text{cation}, 298\text{K}) + \Delta H_f^\circ(\text{anion}, 298\text{K}) - \Delta H_L, \quad (3)$$

where ΔH_L is the lattice energy of the salts that can be predicted by the formula suggested by Jenkins et al. [45] as

$$\Delta H_L = U_{\text{POT}} + [p(n_M/2 - 2) + q(n_X/2 - 2)]RT, \quad (4)$$

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

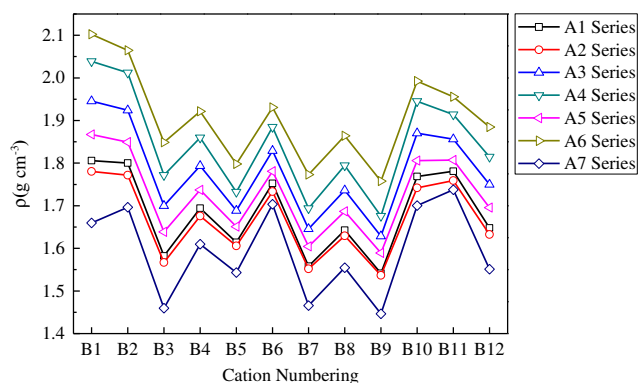


Fig. 3 Comparison of the densities of the ionic salts composed of substituted 5-nitroiminotetrazolate anions and different cations

equation for lattice potential energy U_{POT} ($\text{kJ}\cdot\text{mol}^{-1}$) is as follows:

$$U_{\text{POT}} = \gamma(\rho/M)^{1/3} + \delta, \quad (5)$$

where ρ ($\text{g}\cdot\text{cm}^{-3}$) is the density and M ($\text{g}\cdot\text{mol}^{-1}$) is the chemical formula mass of the ionic material. For 1:1 (charge ratio) salts, the coefficients γ and δ are $1981.2 \text{ kJ}\cdot\text{mol}^{-1}\cdot\text{cm}$ and

$103.8 \text{ kJ}\cdot\text{mol}^{-1}$; for 1:2 salts, they are $8375.6 \text{ kJ}\cdot\text{mol}^{-1}\cdot\text{cm}$ and $-178.8 \text{ kJ}\cdot\text{mol}^{-1}$; for 2:1 salts, they are $6764.3 \text{ kJ}\cdot\text{mol}^{-1}\cdot\text{cm}$ and $365.4 \text{ kJ}\cdot\text{mol}^{-1}$; for 2:2 salts, they are $6864.0 \text{ kJ}\cdot\text{mol}^{-1}\cdot\text{cm}$ and $732.0 \text{ kJ}\cdot\text{mol}^{-1}$, respectively [45].

The isodesmic reactions used to obtain the HOFs of substituted 5-nitroiminotetrazolate anions and cations at 298 K are illustrated in Schemes 2 and 3, respectively. For some small molecules such as NH_2N_3 , NH_2NF_2 , and so on, the experimental HOFs are unavailable, additional calculations were carried out for the atomization reaction: $\text{C}_a\text{H}_b\text{O}_c\text{N}_d\text{F}_e \rightarrow a\text{C}(\text{g}) + b\text{H}(\text{g}) + c\text{O}(\text{g}) + d\text{N}(\text{g}) + e\text{F}(\text{g})$ using the G2 theory to get their HOFs. To obtain more accurate HOFs of the ions, the geometric optimization of the structures and frequency analyses were carried out at the B3LYP/6-311++G* level, and single point energies were calculated at the MP2/6-311++G** level.

The detonation velocity and detonation pressure were calculated by the Kamlet–Jacobs formulas [46]:

$$D = 1.01 \left(N\bar{M}^{1/2} Q^{1/2} \right)^{1/2} (1 + 1.30\rho) \quad (6)$$

$$P = 1.558\rho^2 N\bar{M}^{1/2} Q^{1/2}, \quad (7)$$

Table 2 Calculated and experimental heats of formation ($\text{kJ}\cdot\text{mol}^{-1}$) for small molecules and ions at 298 K

Molecules	ΔH_f° (calc.) ^a	ΔH_f° (expt.) ^b	Molecules/ions	ΔH_f° (calc.)	ΔH_f° (expt.) ^b
NH_3	-45.3	-46.1	H^+		1536.2
NH_2NO_2	-3.8	-3.9	NH_4^+	610.0 ^f (626.4 ^c)	
NH_2NF_2	-25.9 (-27.8 ^c)		NH_3OH^+	683.8 ^f (664.4 ^c)	
NH_2N_3	420.8 (418.8 ^c)		NH_2NH_3^+	760.9 ^f (759.7 ^c)	
NH_2NH_2	110.4	95.4	CH_3NH_3^+	617.2 ^f (611.0 ^c)	
NH_2OH	-45.0 (-45.0)		$\text{CH}_3\text{NHNH}_3^+$	756.4 ^f	
CH_4	-73.6	-74.4	1,2,4-triazole	193.4 ^a	193.7
CH_3N_3	295.8 (296.5 ^c)		1,2,4-triazolium	858.1 ^f (835.0 ^g)	
$\text{NH}_2\text{CH}_2\text{CH}_2\text{N}_3$	303.4		1H-tetrazole	334.6 ^a (334.6 ^d)	
CH_3NH_2	-23.2	-22.5	Tetrazolium	1044.6 ^f (1027.5 ^c)	
CH_3NO_2	-85.9	-80.8	5-iminotetrazole	377.5 ^a	
Isobutane	133.5	134.2	5-iminotetrazolate	228.3 ^f	
Urea	-244.5	-245.8	5-iminotetrazole-1,4-diide	569.1 ^f	
Guanidine	25.3 (25.3 ^d)		Guanidinium	582.9 ^f (575.9 ^g)	
1,3,5-triazinane	71.4		s-tetrazine	481.5 ^a (481.6 ^d)	
$\text{NH}_2\text{CH}_2\text{NH}_2$	-5.0		Urotropinium	841.9 ^f	
Azetidine	95.2	94.7			

^a The values are calculated at the G2 level

^b The experimental data are taken from ref. [53]

^c The calculated data are taken from ref. [17]

^d The calculated data are taken from ref. [50]

^f The values are calculated by protonation reactions: $\text{NH}_3 + \text{H}^+ \rightarrow \text{NH}_4^+$, $\text{NH}_2\text{OH} + \text{H}^+ \rightarrow \text{NH}_3\text{OH}^+$, $\text{NH}_2\text{NH}_2 + \text{H}^+ \rightarrow \text{NH}_2\text{NH}_3^+$, $\text{CH}_3\text{NH}_2 + \text{H}^+ \rightarrow \text{CH}_3\text{NH}_3^+$, $\text{CH}_3\text{NHNH}_2 + \text{H}^+ \rightarrow \text{CH}_3\text{NHNH}_3^+$, $1,2,4\text{-triazole} + \text{H}^+ \rightarrow 1,2,4\text{-triazolium}$, $1\text{H-tetrazole} + \text{H}^+ \rightarrow \text{tetrazolium}$, $5\text{-iminotetrazolate} + \text{H}^+ \rightarrow 5\text{-iminotetrazole}$, $5\text{-iminotetrazole-1,4-diide} + 2\text{H}^+ \rightarrow 5\text{-iminotetrazole}$, $\text{guanidine} + \text{H}^+ \rightarrow \text{guanidinium}$

^e The calculated data are taken from ref. [15]

^g The calculated data are taken from ref. [51]

Table 3 Heats of formation of the 5-nitroiminotetrazolate-based anions and cations and their salts and lattice energies of these salts

Salt		ΔH_f° anion (kJ mol ⁻¹)	ΔH_f° cation (kJ mol ⁻¹)	Lattice energy (kJ mol ⁻¹)	calc'd ΔH_f° (kJ mol ⁻¹)
Anion	Cation				
A1	B1	161.6 (143.6 ^a)	601.0	565.9	205.6
A1	B2	161.6	683.9	549.9	295.5
A1	B3	161.6	582.9	511.0	233.5
A1	B4	161.6	669.3 (663.4 ^c)	500.0	330.9
A1	B5	161.6	1522.8	446.4	1238.0
A1	B6	161.6	1547.1 (1524.4 ^d)	473.4	1235.4
A1	B7	161.6	1181.5 (1074.1 ^d)	459.8	883.2
A1	B8	161.6	1072.7	482.8	751.5
A1	B9	161.6	824.8	456.9	529.5
A1	B10	161.6	2314.8	1481.1	1156.8
A1	B11	161.6	729.1	477.1	413.6
A1	B12	161.6	2028.4 (1880.0 ^d)	1424.7	926.8
A2	B1	270.9 (279.9 ^a)	609.9	549.2	331.6
A2	B2	270.9	683.9	534.9	419.9
A2	B3	270.9	582.9	499.6	354.2
A2	B4	270.9	669.3	490.0	450.2
A2	B5	270.9	1522.8	440.8	1352.9
A2	B6	270.9	1547.2	465.8	1352.3
A2	B7	270.9	1181.5	453.3	999.1
A2	B8	270.9	1072.7	474.4	869.2
A2	B9	270.9	824.8	450.6	645.2
A2	B10	270.9	2314.8	1449.4	1407.2
A2	B11	270.9	729.1	469.2	530.8
A2	B12	270.9	2028.4	1398.6	1171.7
A3	B1	227.8 (273.1 ^a)	609.9	537.5	300.3
A3	B2	227.8	683.9	524.6	387.1
A3	B3	227.8	582.9	492.4	318.3
A3	B4	227.8	669.3	483.5	413.7
A3	B5	227.8	1522.8	437.0	1313.6
A3	B6	227.8	1547.2	460.8	1314.3
A3	B7	227.8	1181.5	448.9	960.4
A3	B8	227.8	1072.7	468.9	831.6
A3	B9	227.8	824.8	446.4	606.3
A3	B10	227.8	2314.8	1428.4	1342.0
A3	B11	227.8	729.1	464.0	493.0
A3	B12	227.8	2028.4	1381.3	1102.8
A4	B1	227.5 (201.1 ^a)	609.9	539.7	297.7
A4	B2	227.5	683.9	526.9	384.5
A4	B3	227.5	582.9	494.5	315.9
A4	B4	227.5	669.3	485.2	411.6
A4	B5	227.5	1522.8	438.1	1312.2
A4	B6	227.5	1547.2	462.2	1312.5
A4	B7	227.5	1181.5	450.1	958.8
A4	B8	227.5	1072.7	470.4	829.8
A4	B9	227.5	824.8	447.5	604.8
A4	B10	227.5	2314.8	1433.8	1335.9
A4	B11	227.5	729.1	465.4	491.2

Table 3 (continued)

Salt		ΔH_f° anion (kJ mol ⁻¹)	ΔH_f° cation (kJ mol ⁻¹)	Lattice energy (kJ mol ⁻¹)	calc'd ΔH_f° (kJ mol ⁻¹)
Anion	Cation				
A4	B12	227.5	2028.4	1385.9	1097.5
A5	B1	636.5 (637.1 ^a)	609.9	534.6	711.8
A5	B2	636.5	683.9	521.8	798.5
A5	B3	636.5	582.9	489.9	729.4
A5	B4	636.5	669.3	481.4	824.4
A5	B5	636.5	1522.8	435.8	1723.5
A5	B6	636.5	1547.2	459.1	1724.6
A5	B7	636.5	1181.5	447.5	1370.5
A5	B8	636.5	1072.7	467.1	1242.1
A5	B9	636.5	824.8	445.0	1016.3
A5	B10	636.5	2314.8	1421.9	2165.8
A5	B11	636.5	729.1	462.3	903.3
A5	B12	636.5	2028.4	1375.7	1925.6
A6	B1	146.5	609.9	489.6	266.9
A6	B2	146.5	683.9	480.7	349.7
A6	B3	146.5	582.9	457.8	271.6
A6	B4	146.5	669.3	452.1	363.7
A6	B5	146.5	1522.8	417.5	1251.8
A6	B6	146.5	1547.2	435.6	1258.1
A6	B7	146.5	1181.5	426.7	901.3
A6	B8	146.5	1072.7	441.6	777.6
A6	B9	146.5	824.8	424.8	546.6
A6	B10	146.5	2314.8	1331.4	1276.4
A6	B11	146.5	729.1	438.0	437.6
A7	B12	146.5	2028.4	1298.2	1023.2
A7	B1	338.5 (338.3 ^b)	609.9	1640.0	-81.7
A7	B2	338.5	683.9	1548.2	158.1
A7	B3	338.5	582.9	1340.6	163.7
A7	B4	338.5	669.3	1278.8	398.3
A7	B5	338.5	1522.8	1030.5	2353.7
A7	B6	338.5	1547.2	1151.7	2281.2
A7	B7	338.5	1181.5	1088.9	1612.5
A7	B8	338.5	1072.7	1194.8	1289.0
A7	B9	338.5	824.8	1075.6	912.6
A7	B10	338.5	2314.8	2001.3	652.0
A7	B11	338.5	729.1	1168.9	627.9
A7	B12	338.5	2028.4	1913.3	453.6

^a The calculated data are taken from ref. [29]

^b The calculated data are taken from ref. [23]

^c The calculated data are taken from ref. [51]

^d The calculated data are taken from ref. [33]

where each term in Eqs. (6) and (7) is defined as follows: D , the detonation velocity (km·s⁻¹); P , the detonation pressure (GPa); N , the moles of detonation gases per gram explosive; \bar{M} , the average molecular weight of these gases (g·mol⁻¹);

Q , the heat of detonation (cal·g⁻¹); and ρ , the loaded density of explosives (g·cm⁻³). For known explosives, their Q and ρ can be measured experimentally, thus their D and P can be calculated according to Eqs. (6) and (7). However, for

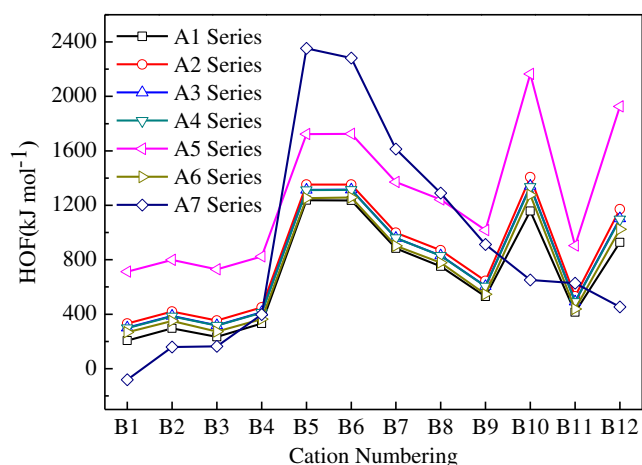
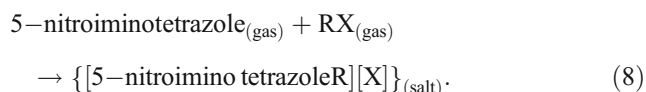


Fig. 4 Comparison of the HOFs of the ionic salts composed of substituted 5-nitroiminotetrazolate anions and different cations

unknown compounds, their Q and ρ cannot be evaluated from experimental measures. Therefore, to estimate their D and P , we first need to calculate their Q and ρ .

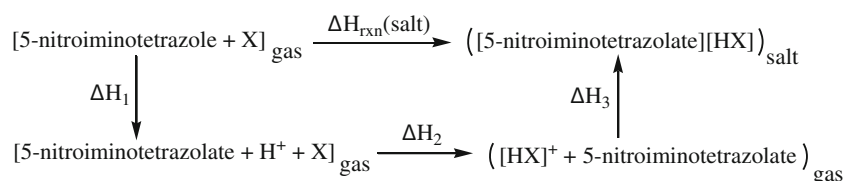
For the 5-nitroiminotetrazolate-based ionic salts, the theoretical density was suggested to ρ , and Q was estimated by the HOF difference between products and explosives according to the principle of exothermic reactions, i.e., all the N atoms turn into N_2 , F atoms form HF with H atoms or convert into F_2 without H atoms, and oxygen atoms go to H_2O before CO_2 . If the content of O is not enough to satisfy full oxidation of the H and C atoms, the remaining H atoms will convert into H_2 , and C atoms will exist as solid-state C. The detonation products are supposed to be CO_2 (or C), H_2O (or H_2 or HF or F_2), and N_2 , so released energy in the decomposition reaction reaches its maximum [47]. Based on the ρ and Q values, the corresponding D and P values can be evaluated. Practically, the D and P values gained from ρ can be regarded as their upper limits (maximum values) because ρ from this method is slightly greater than the loading density of the explosive.

To make 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 as follows:



Since two free gas-phase particles in reaction (8) react to form a solid, the entropy change for this process is negative

Scheme 4 Born–Haber cycle for the formation of the ionic salts composed of protonated cations and substituted 5-nitroiminotetrazolate anions. (X represents the cation base)



and this make the term $-T\Delta S$ positive, destabilizing contribution from the term. Therefore, the ability for the salt to form will be governed by how negative the enthalpy is. The estimated entropies ($J K^{-1} mol^{-1}$) of the 5-nitroiminotetrazolate-based ionic salts were calculated by using the relationship developed by Glasser and Jenkins [48] for organic solids (OS):

$$S_{298}^0(\text{OS}) = 1.285M/\rho + 57. \quad (9)$$

Here ρ and M are the same as employed in the lattice energy Eq. (5) above.

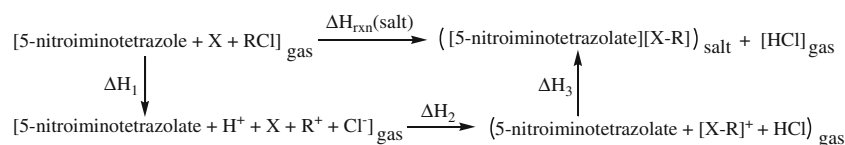
The calculations were performed with the Gaussian 03 [49] suite of programs. All of the optimized structures were characterized to be true local energy minima on the potential energy surfaces without imaginary frequencies. Figure 2 displays the frameworks of a series of 5-nitroiminotetrazolate-based anions and different cations studied here.

Results and discussion

Crystal density

High density is desirable for energetic materials because more energy will be packed per unit volume. In this section, we investigate the effects of different substituents and cations on the densities of the 5-nitroiminotetrazolate-based (A1–A7) salts. Formula unit volumes to be used in predicting the crystal densities of 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 uncorrected and corrected densities of the 5-nitroiminotetrazolate-based ionic salts along with available experimental and other calculated values are listed in Table 1.

It is found in Table 1 that for the same anion, when the cation is B1, B2, B10, or B11, its 5-nitroiminotetrazolate salt has relatively higher density than other salts. This shows that the cation B1, B2, B10, or B11 is favorable for enhancing the density of its 5-nitroiminotetrazolate salt. For the substituted 5-nitroiminotetrazolate anion (A1–A6), its salt containing the cation B1 has the highest densities among the salt series with the same anion, while for the anion A7, its salt including the cation B11 has the highest ones. The evolution pattern of the HOFs for the salts containing the anions A1–A7 is different. Therefore, the effects of different



Scheme 5 Born–Haber cycle for the formation of the ionic salts composed of methylated cations and substituted 5-nitroiminotetrazolate anions. (*X* represents the cation base, *R* represents methylate group)

cations on the density of their salts are coupled with those of different substituents.

Figure 3 illustrates a comparison of the densities for a series of 5-nitroiminotetrazolate-based salts. It is obvious that when the substituent is $-\text{NO}_2$, $-\text{N}_3$, $-\text{NF}_2$, or $-\text{C}(\text{NO}_2)_3$, the density value of its substituted 5-nitroiminotetrazolate-based salt is higher than corresponding unsubstituted one, while for the group $-\text{NH}_2$, the situation is quite the contrary. This may be owing to the big π bond formed between the tetrazole ring and substituent, which is favorable for molecular packing in crystal. It is well known that π bond interactions could not only help stabilize energetic compounds markedly but also enhance their densities substantially. Among the substituents, the substitution of the $-\text{NO}_2$, $-\text{NF}_2$, or $-\text{C}(\text{NO}_2)_3$ group could increase the density of its 5-nitroiminotetrazolate salt markedly; moreover, the salt containing the $-\text{C}(\text{NO}_2)_3$ group has the largest one among the same series, and the next one is $-\text{NF}_2$. This is since incorporating the $-\text{NF}_2$ or $-\text{C}(\text{NO}_2)_3$ group into the 5-nitroiminotetrazolate anion can enhance the mass of its salt intensively but affect its volume relatively little. On the whole, the $-\text{NO}_2$, $-\text{N}_3$, $-\text{NF}_2$, or $-\text{C}(\text{NO}_2)_3$ substituent is an effective group for enhancing the densities of the 5-nitroiminotetrazolate salts. The salts containing the 5-nitroiminotetrazolate anions with one negative charge (A1) have higher densities than the ones with two negative charges (A7). This is because the anion A7 can combine with more cations than the anion A1–A6, which leads to less effective molecular packing in the A7-based salts. Therefore, increasing negative charge for the 5-nitroiminotetrazolate anion is not favorable for enhancing the density of its salt.

Heats of formation

As the HOF is frequently taken to be indicative of the “energy content” of an energetic compound, it is very important to predict its HOF. Table 2 lists the calculated HOFs of reference compounds in the isodesmic reactions along with available experimental and other calculated values. The calculated results indicate that the HOFs of small molecules are very close to corresponding experimental values [50]. In addition, the calculated HOFs of the reference anions and cations are in agreement with other calculated results [15, 17, 51, 52]. Table 3 presents the HOFs of the substituted 5-nitroiminotetrazolate-based anions, cations and their salts and lattice energies of

these salts. The results demonstrate that the calculated HOFs are very close to other calculated values [23, 29]. Therefore, our computational method to predict the HOFs is expected to be credible in this work.

As shown in Table 3, for the same anion, when the cation is B5, B6, B10, or B12, its 5-nitroiminotetrazolate-based salts have relatively larger HOFs than other salts. It means that containing the cation B5, B6, B10, or B12 is favorable for increasing the HOFs of the 5-nitroiminotetrazolate salts. The evolution pattern of the HOFs for the salts containing the anions A1–A7 is different. For example, for the anion A1 or A7, its salt containing the cation B5 has the highest HOFs among the salt series with the same anion; for the anion A2, A3, A4, A5, or A6, its salt containing the cation B10 has the highest ones. Consequently, the effects of different cations on the HOFs of their salts are combined with those of different substituents.

Figure 4 illustrates a comparison of the HOFs for a series of 5-nitroiminotetrazolate-based salts. The substituted 5-nitroiminotetrazolate salts have higher HOFs than corresponding unsubstituted ones. Among the substituted 5-nitroiminotetrazolate salts, the salts containing the $-\text{N}_3$ group has the highest HOF. When the cation is B1, B2, B3, B4, B9, B10, B11, or B12, the N_3 -substituted 5-nitroiminotetrazolate (A5) salt has the largest HOFs among the same series. Maybe it is because the N–N bond of energetic compound contributes more to a positive HOF than the C–N bond [33]. Some of the dianionic 5-nitroiminotetrazolate (A7) salts have larger HOF values than corresponding monoanionic 5-nitroiminotetrazolate (A1) salts. Even for the salts composed of the cation B5, B6, B7, or B8, the salts with two negative charges (A7) have the highest HOFs among the same series. It can be concluded that the substitution of each substituent ($-\text{NH}_2$, $-\text{NO}_2$, $-\text{NF}_2$, $-\text{N}_3$, $-\text{C}(\text{NO}_2)_3$) is favorable for improving the HOFs of its salts, and moreover, incorporating $-\text{N}_3$ into the salts exhibits the highest HOFs among the same series.

Energetic properties

Detonation velocity and detonation pressure are two important performance parameters for an energetic material. Table 4 lists the calculated heats of detonation (Q), detonation velocities (D), detonation pressures (P), and oxygen

Table 4 Predicted heats of detonation (Q), detonation velocities (D), detonation pressures (P), and oxygen balance (OB) of the 5-nitroiminotetrazolate-based salts

Salt	Q (cal g ⁻¹)	D (km s ⁻¹)	P (Gpa)	OB (%)	
Anion	Cation				
A1	B1	1120.3	8.6	32.9	-27.2
A1	B2	1463.7	9.1	36.8	-14.7
A1	B3	906.6	7.4 (8.1 ^b)	22.6 (22.1 ^b)	-46.5
A1	B4	1147.3	8.2	28.9	-36.4
A1	B5	1261.8	7.9	26.0	-63.8
A1	B6	1442.6	8.4	31.0	-31.3
A1	B7	1166.4	7.4	22.2	-85.7
A1	B8	1209.4	8.1	27.3	-52.4
A1	B9	852.2	6.8	18.8	-123.9
A1	B10	1262.5	8.5	31.4	-35.8
A1	B11	1511.3	8.6	32.9	-31.8
A1	B12	1033.2	7.3	22.5	-76.7
A2	B1	1202.3	8.8	34.3	-29.6
A2	B2	1537.5	9.1	36.7	-18.0
A2	B3	981.3	7.6	23.6	-47.0
A2	B4	1195.3	8.3	29.6	-37.4
A2	B5	1286.8	8.0	26.5	-63.3
A2	B6	1482.1	8.5	31.0	-32.4
A2	B7	1200.9	7.5	22.9	-84.0
A2	B8	1247.9	8.2	27.9	-52.5
A2	B9	901.8	7.0	19.7	-120.3
A2	B10	1313.3	8.6	32.0	-37.0
A2	B11	1548.0	8.7	32.9	-32.9
A2	B12	1092.0	7.5	23.6	-75.2
A3	B1	1465.4	9.6	43.1	0.0
A3	B2	1452.5	9.5	41.7	7.7
A3	B3	1266.8	8.3	29.3	-20.5
A3	B4	1402.3	8.9	35.0	-15.1
A3	B5	1469.0	8.3	29.2	-45.3
A3	B6	1573.3	9.0	36.1	-14.7
A3	B7	1417.3	7.9	25.9	-61.5
A3	B8	1468.7	8.6	31.9	-30.4
A3	B9	1142.7	7.5	23.4	-94.8
A3	B10	1503.9	9.2	38.3	-13.0
A3	B11	1634.4	9.2	38.1	-14.9
A3	B12	1374.6	8.1	28.7	-48.5
A4	B1	1543.8	10.1	48.8	-16.2
A4	B2	1745.1	10.4	50.9	-7.5
A4	B3	1336.6	8.6	32.8	-33.3
A4	B4	1461.5	9.2	38.5	-26.6
A4	B5	1525.2	8.4	30.9	-53.0
A4	B6	1618.8	9.3	39.0	-24.1
A4	B7	1482.1	8.0	27.7	-70.1
A4	B8	1521.9	8.9	34.8	-40.7
A4	B9	1308.2	7.5	23.6	-102.6

Table 4 (continued)

Salt	Q (cal g ⁻¹)	D (km s ⁻¹)	P (Gpa)	OB (%)	
Anion	Cation				
A4	B10	1564.1	9.6	42.4	-25.4
A4	B11	1679.3	9.5	41.2	-24.4
A4	B12	1394.2	8.4	31.3	-59.2
A5	B1	1519.3	9.3	39.5	-17.0
A5	B2	1732.3	9.6	41.9	-7.8
A5	B3	1260.2	8.1	27.8	-34.8
A5	B4	1418.8	8.7	33.0	-27.6
A5	B5	1436.9	8.3	28.7	-54.5
A5	B6	1605.3	8.8	34.0	-24.8
A5	B7	1380.1	7.9	25.5	-72.3
A5	B8	1446.7	8.5	31.0	-42.1
A5	B9	1102.6	7.4	22.8	-105.8
A5	B10	1546.8	8.9	35.5	-26.4
A5	B11	1667.6	9.0	35.9	-25.2
A5	B12	1329.3	8.0	27.0	-61.5
A6	B1	1241.4	9.6	44.6	10.8
A6	B2	1241.2	9.5	42.9	15.4
A6	B3	1400.5	9.0	36.4	-4.7
A6	B4	1484.5	9.4	41.0	-2.2
A6	B5	1523.7	8.7	33.8	-28.6
A6	B6	1599.1	9.4	40.9	-3.7
A6	B7	1491.9	8.4	31.4	-39.2
A6	B8	1525.9	9.1	37.8	-14.2
A6	B9	1356.8	8.0	28.0	-64.6
A6	B10	1572.1	9.7	44.4	0.0
A6	B11	1646.0	9.6	42.7	-3.8
A7	B12	1442.2	8.8	35.3	-26.1
A7	B1	716.9	7.6	24.4	-39.0
A7	B2	1371.9	8.7	32.5	-16.3
A7	B3	623.6	6.6 (7.6 ^b)	16.9 (18.1 ^b)	-64.5
A7	B4	1052.4	8.0	26.2	-46.4
A7	B5	1298.6	7.8	24.4	-76.6
A7	B6	1529.3	8.3	29.5	-37.0
A7	B7	1164.7	7.1	19.6	-107.9
A7	B8	1183.0	7.9	25.0	-67.0
A7	B9	761.4	6.3	15.5	-157.0
A7	B10	997.5	7.9	26.6	-47.0
A7	B11	1615.2	8.6	31.8	-37.7
A7	B12	727.0	6.4	16.5	-103.9
RDX		1597.4	8.9 (8.8 ^c)	34.8 (34.7)	-21.6
HMX		1633.9	9.3 (9.1)	39.2 (39.0)	-21.6

^a Oxygen balance (%) for $C_aH_bO_cN_d$: $1,600 \times (c-2a-b/2)/M_w$; M_w : molecular weight of the corresponding compounds

^b The experimental HOFs are taken from ref. [23]

^c The experimental HOFs are taken from refs. [52] and [54]

balance (OB) for the 5-nitroiminotetrazolate salts along with commonly used explosives RDX (1,3,5-trinitro-1,3,5-triazane) and HMX (1,3,5,7-tetranitro-1,3,5,7-tetrazocane). Figure 5 illustrates a comparison of Q , D and P values for a series of 5-nitroiminotetrazolate-based salts.

It is seen in Fig. 5 that all the substituted 5-nitroiminotetrazolate salts possess higher Q than corresponding unsubstituted ones except for the NO_2 - and $\text{C}(\text{NO}_2)_3$ -substituted salts containing the cation B2. For the same anion, when the cation is B2, B6, B10, or B11, its 5-nitroiminotetrazolate salts have relatively larger Q than other salts among the salt series with the same anion. This means that incorporating the cation B2, B6, B10, or B11 is favorable for increasing the Q values of 5-nitroiminotetrazolate salts. Most of the salts containing the 5-nitroiminotetrazolate anions with one negative charge (A1) have higher Q than the ones with two negative charges (A7) except for the salts containing the cation B5, B6, or B11.

As shown in Fig. 5, all of the substituted 5-nitroiminotetrazolate salts have higher D and P than corresponding unsubstituted ones except for the salts containing the cation B2 or B11, and furthermore, the $\text{C}(\text{NO}_2)_3$ -substituted 5-nitroiminotetrazolate salt (A6) has the largest D and P among the same series except for the salts containing the cation B1 or B2. For the cation B1 or B2, the NF_2 -substituted 5-nitroiminotetrazolate (A4) salt has the largest D and P among the same series. For the same anion, when the cation is B1, B2, B10, or B11, its 5-nitroiminotetrazolate salts have relatively higher D and P than other salts. The salts containing the 5-nitroiminotetrazolate anions with one negative charge (A1) have higher D and P than the one with two negative charges (A7).

Oxygen balance (OB) is a parameter that indicates the degree to which an explosive can be oxidized and classifies energetic materials as either oxygen-deficient or oxygen-rich systems. OB values near or greater than zero are desirable to reduce toxic fume gases. In other words, the higher the OB, the better the energetic property. Therefore, OB is another important criterion for selecting potential high energy compounds. As is shown in Table 4, when the substituent is $-\text{NO}_2$, $-\text{NF}_2$, $-\text{N}_3$, or $-\text{C}(\text{NO}_2)_3$, its substituted 5-nitroiminotetrazolate salts have higher OB than corresponding unsubstituted ones. However, for the group $-\text{NH}_2$, the case is quite the contrary. Almost all of the salts containing the 5-nitroiminotetrazolate anions with one negative charge (A1) have higher OB than the ones with two negative charges (A7) except for the salts containing the cation B2. The majority of the A3- and A6-based salts (NO_2 - and $\text{C}(\text{NO}_2)_3$ -substituted salts) have close or greater OB values than RDX or HMX. Therefore, it can be concluded that $-\text{NO}_2$ or $-\text{C}(\text{NO}_2)_3$ is an effective substituent for improving OB in designing potential 5-nitroiminotetrazolate-based high-energy salts. It is known that too much oxygen is unfavorable for advancing their explosive performance for high energy materials. The reason is that additional oxygen will generate additional O_2 that takes away a great deal of energy during the explosion of high energy materials. Therefore, one had better keep the value of oxygen balance around zero in designing high-energy salts.

It is found that 31 salts have detonation performance that are near or better than RDX. Among them, 21 compounds exhibit striking detonation performance (D and P) that are near or better than HMX. Incorporating the substitution of $-\text{NO}_2$, $-\text{NF}_2$, $-\text{N}_3$, or $-\text{C}(\text{NO}_2)_3$ into the 5-nitroiminotetrazolate

Fig. 5 Comparison of the heats of detonation, detonation velocities, and detonation pressures of the ionic salts composed of substituted 5-nitroiminotetrazolate anions and different cations

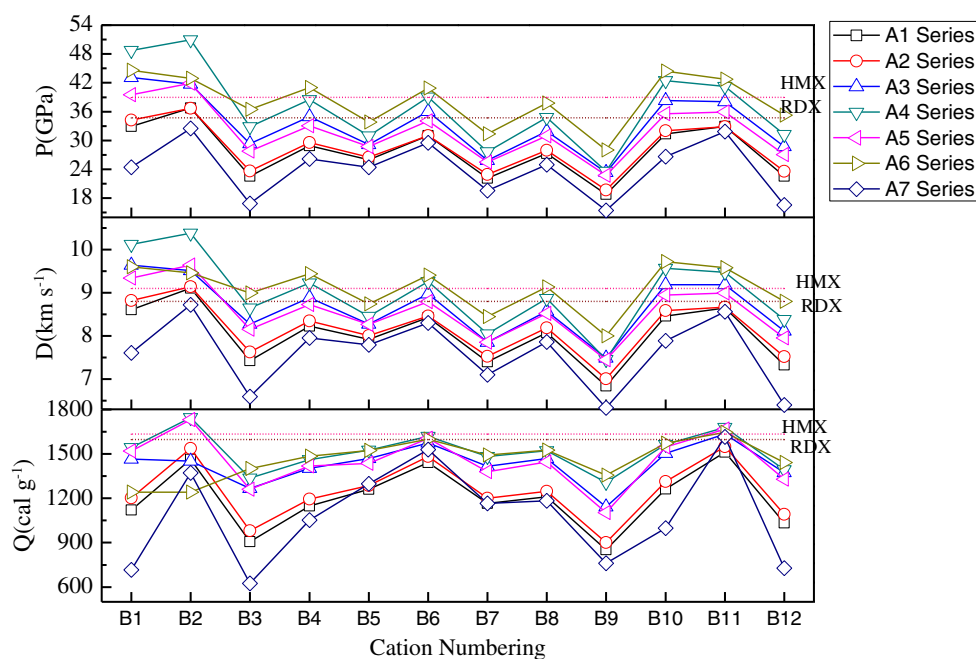


Table 5 Estimated entropies (ΔS_{salt}), enthalpies of reaction ($\Delta H_{\text{rxn}}(\text{salt})$), entropies of reaction (ΔS_{rxn}), and free energies of reaction (ΔG_{rxn}) for the formation of the 5-nitroiminotetrazolate-based salts

Salt		S_{salt}	ΔS_{rxn}	ΔH_{rxn}	ΔG_{rxn}
Anion Cation		(J mol ⁻¹ K ⁻¹)	(J mol ⁻¹ K ⁻¹)	(kJ mol ⁻¹)	(kJ mol ⁻¹)
A1	B1	166.7	-387.9	-119.9	-2.1
A1	B2	175.5	-412.0	-35.7	88.5
A1	B3	201.5	-438.5	-179.0	-50.1
A1	B4	218.4	-473.2	-103.3	37.1
A1	B5	307.3	-572.3	-50.0	119.4
A1	B6	262.4	-488.9	-1.2	145.5
A1	B7	278.9	-492.1	-79.3	66.1
A1	B8	242.1	-441.4	-117.8	13.2
A1	B9	278.5	-413.2	-147.7	-27.7
A1	B10	346.7	-770.9	-287.4	-56.6
A1	B11	251.9	-524.4	3.7	159.7
A1	B12	389.6	-725.1	-401.3	-185.8
A2	B1	179.8	-404.8	-106.0	17.2
A2	B2	188.6	-429.0	-23.3	106.1
A2	B3	214.6	-455.4	-170.0	-36.1
A2	B4	231.5	-490.2	-95.8	49.7
A2	B5	320.3	-589.3	-46.8	127.7
A2	B6	275.4	-505.9	3.6	155.4
A2	B7	292.0	-509.0	-75.1	75.3
A2	B8	255.2	-458.3	-111.8	24.2
A2	B9	291.5	-430.1	-143.5	-18.4
A2	B10	372.8	-804.8	-259.9	-19.0
A2	B11	264.9	-541.4	9.1	170.1
A2	B12	415.7	-759.0	-379.1	-153.5
A3	B1	192.1	-437.2	-135.0	-1.4
A3	B2	200.9	-461.3	-53.4	86.4
A3	B3	226.9	-487.7	-202.6	-58.3
A3	B4	243.8	-522.5	-129.7	26.3
A3	B5	332.6	-621.6	-84.2	100.8
A3	B6	287.7	-538.2	-32.4	129.9
A3	B7	304.2	-541.4	-111.7	49.2
A3	B8	267.5	-490.7	-147.0	-0.5
A3	B9	303.8	-462.5	-180.1	-44.5
A3	B10	397.4	-869.5	-321.1	-59.2
A3	B11	277.2	-573.7	-26.5	145.0
A3	B12	440.3	-823.7	-443.8	-197.3
A4	B1	189.2	-439.4	-139.2	-5.2
A4	B2	198.0	-463.6	-57.4	82.9
A4	B3	224.0	-490.0	-206.0	-61.0
A4	B4	240.9	-524.7	-132.8	23.7
A4	B5	329.7	-623.8	-86.5	99.0
A4	B6	284.8	-540.5	-35.1	127.8
A4	B7	301.4	-543.6	-114.3	47.3
A4	B8	264.6	-492.9	-149.9	-2.8
A4	B9	300.9	-464.7	-182.7	-46.5

Table 5 (continued)

Salt		S_{salt}	ΔS_{rxn}	ΔH_{rxn}	ΔG_{rxn}
Anion Cation		(J mol ⁻¹ K ⁻¹)	(J mol ⁻¹ K ⁻¹)	(kJ mol ⁻¹)	(kJ mol ⁻¹)
A4	B10	391.6	-874.0	-329.4	-66.4
A4	B11	274.3	-576.0	-29.3	142.9
A4	B12	434.5	-828.2	-451.3	-203.6
A5	B1	195.6	-428.8	-105.2	26.2
A5	B2	204.4	-452.9	-23.9	113.6
A5	B3	230.4	-479.3	-173.8	-31.9
A5	B4	247.3	-514.1	-101.1	52.4
A5	B5	336.2	-613.2	-56.6	126.0
A5	B6	291.3	-529.8	-4.4	155.5
A5	B7	307.8	-533.0	-83.9	74.6
A5	B8	271.0	-482.3	-118.8	25.3
A5	B9	307.4	-454.0	-152.3	-19.1
A5	B10	404.5	-852.7	-261.5	-4.3
A5	B11	280.8	-565.3	1.6	170.7
A5	B12	447.4	-806.9	-385.3	-143.5
A6	B1	251.4	-509.6	-120.4	36.6
A6	B2	260.2	-533.8	-42.1	120.8
A6	B3	286.2	-560.2	-199.0	-32.3
A6	B4	303.1	-594.9	-129.9	48.7
A6	B5	391.9	-694.0	-96.6	111.0
A6	B6	347.0	-610.6	-39.9	145.0
A6	B7	363.5	-613.8	-121.2	62.3
A6	B8	326.8	-563.1	-151.6	17.6
A6	B9	363.1	-534.9	-189.6	-31.4
A6	B10	516.0	-1014.3	-288.1	19.3
A6	B11	336.5	-646.2	-32.5	161.6
A7	B12	558.9	-968.6	-423.6	-131.8
A7	B1	187.0	-569.1	-321.1	-149.8
A7	B2	204.7	-617.4	-104.6	80.0
A7	B3	256.7	-670.3	-283.3	-87.8
A7	B4	290.5	-739.7	-83.8	134.0
A7	B5	468.1	-937.9	161.9	437.0
A7	B6	378.3	-771.2	194.4	424.8
A7	B7	411.4	-777.5	71.6	298.8
A7	B8	337.8	-676.1	-63.7	135.1
A7	B9	410.5	-619.7	-57.7	118.7
A7	B10	256.4	-508.1	-152.7	-1.8
A7	B11	357.3	-842.2	194.2	443.2
A7	B12	299.3	-462.3	-251.7	-116.1

salts is favorable for enhancing the energetic properties of 5-nitroiminotetrazolate salts, and the NF₂- or C(NO₂)₃-5-nitroiminotetrazolate salts has the best performance. Although the NF₂- or C(NO₂)₃-substituted 5-nitroiminotetrazolate salts do not have outstanding HOFs among the energetic salts, their high densities compensate this disadvantage. And increasing

negative charge for the 5-nitroiminotetrazolate is unfavorable for increasing the Q , D , P , and OB of its salts.

Although many 5-nitroiminotetrazolate salts are sensitive, some belong to the insensitive or less sensitive classification, such as guanidine and aminoguanidine 5-nitroiminotetrazoles [23].

Thermodynamics of salt formation

New energetic ionic salts not only should have desirable explosive properties, but also should be cheap and easy to synthesize. In this section, we predict the thermodynamics of formation of the salts composed of 5-nitroiminotetrazolate-based anions and various cations. The Born–Haber thermodynamic cycle for the formation of the salts is exhibited in Schemes 4 and 5.

The overall enthalpy of reaction (ΔH_{rxn}) for formation of the salt composed of 5-nitroiminotetrazolate-based anion and protonated cation is given by the enthalpy for the reaction between a substituted 5-nitroiminotetrazolate base and a cation base 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 to dissociate the H–N bond in the 5-nitroiminotetrazolate heterolytically. ΔH_2 is the proton affinity. ΔH_3 is directly related to the lattice energy for salt formation. The overall enthalpy of reaction (ΔH_{rxn}) for formation of the salt composed of 5-nitroiminotetrazolate-based anion and methylated cation is given by the enthalpy for the reaction between a substituted 5-nitroiminotetrazolate base and a methylating agent (RCl) 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 to dissociate the C–Cl bond in the RCl heterolytically. ΔH_2 is the affinity of the cation base for R^+ . ΔH_3 is directly related to the lattice energy for salt formation.

Table 5 lists the thermodynamic data S_{salt} , ΔH_{rxn} , ΔS_{rxn} , and ΔG_{rxn} of a series of 5-nitroiminotetrazolate-based salts. The free energies of reaction for the salts containing the cation B3, B9, B10, or B12 are negative except for the salts containing the anion series A7. This means that the salts could be synthesized by the reactions proposed here. This is consistent with the experimental results [23]. According to our calculated free energies of reaction, the salts with positive free energies of reaction should not be easily synthesized. However, these salts might be possible under alternative experimental methods.

Figure 6 displays the free energies of reaction (ΔG_{rxn}) for formation of a series of 5-nitroiminotetrazolate-based salts. As the cation numbering increases, the evolution pattern of the ΔG_{rxn} for the salts containing different substituted 5-nitroiminotetrazolate with one negative charge is very

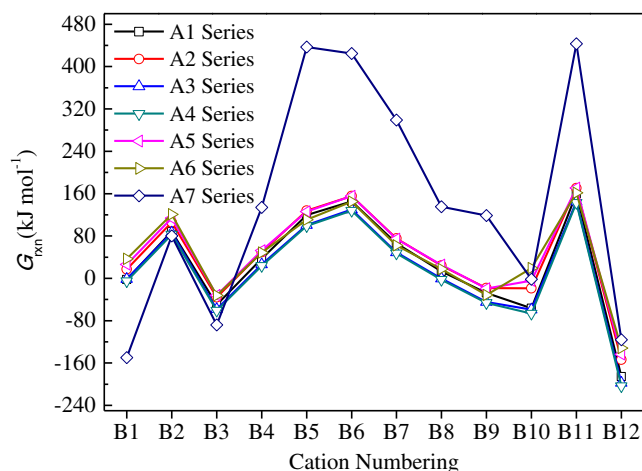


Fig. 6 Comparison of the free energies of the reactions (ΔG_{rxn}) for the formation of the ionic salts composed substituted 5-nitroiminotetrazolate anions and different cations

similar, but is different from those for the salts containing different substituted 5-nitroiminotetrazolate with two negative charges. It is found that the NO_2 - or NF_2 -substituted 5-nitroiminotetrazolate salts have lower free energies of reaction than corresponding unsubstituted ones. It means that incorporating the cation B1, B3, B9, B10, B12 and the group -NO_2 or -NF_2 are favorable for decreasing the free energies of reaction of the 5-nitroiminotetrazolate salts. As a result, the combination of the 5-nitroiminotetrazolate-based anions with different cations is a leading factor in determining the free energies of reaction.

Conclusions

In this work, we have studied the densities, HOFs, energetic properties, and thermodynamics of formation for a series of the 5-nitroiminotetrazolate salts by using DFT and volume-based thermodynamics methods. The results show that the substitution of the -NO_2 , -NF_2 , -N_3 , or $\text{-C(NO}_2)_3$ group is helpful for increasing the densities of the salts. Incorporating each group (-NH_2 , -NO_2 , -NF_2 , -N_3 , or $\text{-C(NO}_2)_3$) into the salt is favorable for increasing its HOFs.

The calculated energetic properties show that incorporating every substituent into the salts is favorable for improving its detonation performance. The NF_2 - or $\text{C(NO}_2)_3$ -substituted salts exhibits the best energetic performance among the same series. Incorporating the cation B1, B2, B10, or B11 into the salts is helpful for improving its detonation properties. Increasing negative charge for the 5-nitroiminotetrazolate salts is unfavorable for enhancing the density and detonation performance, but is helpful for improving the HOFs. Many salts present comparable detonation performance with commonly used explosives RDX or HMX. Among them, 21 salts have near or better properties than HMX.

The thermodynamics of formation of the salts show that the majority of the 5-nitroiminotetrazolate salts with the cation B1, B3, B9, B10, B12 could be synthesized by the proposed reactions. The densities, HOFs, energetic properties, and thermodynamics of the 5-nitroiminotetrazolate-based salts are affected not only by different substituents but also by different cations.

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