Theoretical Study of High-nitrogen Salts Composed of Ammonium Cations and Pyrazole-derived Anions

Abstract: A series of energetic salts, which consist of simple ammonium cations (NH_4^+, $N_2H_5^+$ and $^+NH_3OH$) and pyrazole-derived anions were designed. The anions were attached by substituents of $–NH_2$, $–NO_2$, $–N_3$, $–NF_2$ or –CN. The densities and heats of formation (HOFs) of the salts were predicted by using DFT-B3LYP and volume-based thermodynamics methods. The detonation performance and impact sensitivity of the salts were also studied by several empirical formulas. The results show that for the promotion of energetic performance of the salts, $^+NH_3OH$ is the best cation among the three cations. When one substituent is $-NO_2$, another substitution of the $–NO_2$, $–N_3$ or $–NF_2$ group is helpful for enhancing the densities of the salts and the substitution of $–NF_2$ group presents the best density. The attachment of $–NO_2$ group in combination with the $–NO_2$, $–N_3$, $–NF_2$ or –CN group is favorable for improving the HOFs of the salts and the incorporation of $–N_3$ shows the greatest HOFs. The synergy of $–N_3$ and $–NF_2$ group also exhibits the potential to improve the detonation performance of the salts. By comparing with the commonly used explosives RDX and HMX, we screened out the salts with high energy and acceptable sensitivity.

Comment [SMHAPD1]: Study design? Results? Conclusion? Methodology? Place and duration of study?

Keywords: Crystal density, Density functional theory, Detonation properties, Heats of formation

1. Introduction

Comment [SMHAPD2]: Research objective should be stated in introduction

Along with the growing demand of a new generation of advanced energetic materials to replace some conventional explosives, extensive studies have been focused on finding N-heterocycles with lower impact sensitivity and better detonation performance as well as environmentally friendly[1-4]. This is because N-heterocycles have higher nitrogen content, densities and heats of formation than carbocyclic energetic compounds and are compatible with many energetic groups. By incorporating different energetic functionalized group with heterocyclic backbone, we can get advanced energetic materials to meet ever-changing criteria, such as reducing pollution for the environment, low cost and safe storage.

Comment [SMHAPD3]: Incorrect format.

In the text, citations should be indicated by the reference number in brackets

Over the past years, energetic salts have received a substantial amount of interest as a new class of energetic materials[5-8]. As the cations and anions in the salts can be modified independently, we can produce a large amount of different salts by combining different potential cations and anions[9]. Usually, ionic compounds have regular molecular sorting and compact crystal structure, thus have higher densities than atomically similar nonionic molecules[10]. Furthermore, forming salts is a promising strategy in modifying the sensitivity for energetic materials with strong acidity, such as nitroazoles[11]. Therefore, when the neutral molecules are converted to salts, the detonation performance can be improved significantly.

In the design of high energy density molecules, combing various energetic substituents with a variety of backbone is the most popular strategy[12-14]. Among explosophore groups, nitro[15], nitramino[16], dinitromethyl[17] and trinitromethyl[18] groups have been proved excellent to enhance the detonation performance of the backbone since they are favorable for increasing the density and the oxygen balance value. Recently, the polynitromethyl energetic derivatives based on N-heterocycles have aroused a large amount of interest. And in the N-heterocyclic structures, the three linked carbon atoms of the pyrazole provide a unique opportunity for the skeleton to be diversified functionalized[3]. For example, Shreeve and co-workers synthesized a new family of pyrazole with three induced hydrogen bonds by incorporating various energetic functional groups[19]. Therefore, different substituents of pyrazole can produce a variety of properties and finally enhance the detonation performance. What's more, the N-H of the pyrazole can be a reaction site for functionalization and some N-polynitromethyl-substituted pyrazoles have been synthesized[20-21]. Considering the advantages of explosophore groups and pyrazole in improving the detonation properties, their combination is certainly an ideal strategy for designing high energy density materials (HEDMs). However, there is still lacking a good understanding of energetic substituents of pyrazole and various counter ions on their property.

On the account of above situations, the salts composed of pyrazole-derived anions containing different substituents (–NH_2, –NO_2, –N_3, –NF_2, –CN) with some simple energetic cations (NH_4^+, $N_2H_5^+$, $^+NH_3OH$) were designed in Figure 1. We performed density functional theory (DFT)[22] and volume-based thermodynamics calculations[23] to search potential salts with high energy and good stability. Our main purpose is investigating the important role of simple ammonium cations, different substituents and their synergetic effect in the design of efficient pyrazole-derived salts.

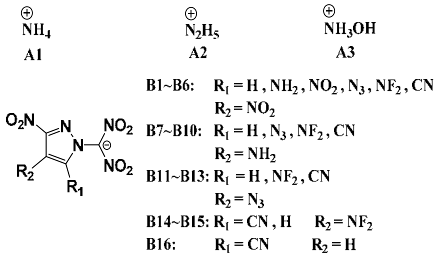


Figure 1. Frameworks of cations and pyrazole-derived anions.

2. Computational method

The Gaussian 09 program package were used to perform the calculations[24]. The geometries of all pyrazole-derived salts were fully optimized at the DFT (B3LYP) level with 6-31++G(d) basis set which was successfully applied to calculate the properties of energetic salts[25-26]. Since density is the key parameter to predict energetic performance, some approaches have been evolved in order to predict the crystal density more accurately[27-29]. According to these methods, we need to take intermolecular interactions within the crystal into account since the traditional M/V procedure often leads to large errors. Therefore, the formula for calculating the crystal density of salts has improved as follows[30]:

$$\rho(\mathrm{g/cm^3}) = 1.0260(M/V) + 0.0514(V_s^+/A_s^+) + 0.0419(V_s^-/A_s^-) + 0.0277 \qquad (1)$$

where, M is the molecular mass of the ionic compound and V is the volume of that compound. A_s^+ is the positive electrostatic potential of the cation and V_s^+ is the average value of the potential, while A_s^- and V_s^- are the analogous quantities for an anion. The electrostatic potential was calculated by the Multiwfn program[31].

When the ionic crystal has the formula unit M_pX_q, its volume is simply the sum of the volumes of the ions and can be calculated in the following equation[27]:

$$V = pV_M^+ + qV_X^- \qquad (2)$$

where M denotes the cation and X denotes the anion.

Based on Born-Haber cycle (Scheme 1), the heats of formation of energetic salts were predicted using Eq. (3):

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

in above equation, ΔH_L is the lattice energy of the salts which can be predicted by the formula proposed by Jenkins et al[32] as:

$$\Delta H_L = U_{\mathrm{POT}} + [p(n_{\mathrm{M}}/2 - 2) + q(n_{\mathrm{X}}/2 - 2)]RT \qquad (4)$$

the n_{M} and n_{X} values depend on the nature of the cation M_p^{+} and anion X_q^{-}, respectively. U_{POT} (kJ/mol) is the lattice potential energy which can be calculated by the following expression:

$$U_{\mathrm{POT}} = \gamma(\rho/M)^{1/3} + \delta \qquad (5)$$

where ρ is the predicted density (g/cm^3), M is the chemical formula mass (g/mol) of salts and the coefficients γ and δ for our designed 1:1(charge ratio) salts are 1981.2kJ·mol^{-1}·cm and 103.8 kJ/mol, respectively.

The detonation velocity and detonation pressure of the salts were computed using the empirical Kamlet−Jacobs as shown in the following equations[33]:

$$D\ (km/s) = 1.01(NM^{1/2}Q^{1/2})^{1/2}(1+1.30\rho) \qquad (6)$$

$$P\ (GPa) = 1.558\rho^2 NM^{1/2}Q^{1/2} \qquad (7)$$

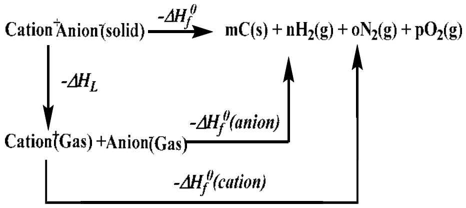
in which, N stands for the moles of detonation gases which is produced by per gram explosive, M represents the average molecular weight of these gases (g/mol), Q denotes the heat of detonation (cal/g) which is related to the HOF difference between products and explosives according to the principle of exothermic reactions, and ρ stands for the predicted density of salts (g/cm^3) here.

As the impact sensitivity become increasingly important for energetic materials, there is a simple method developed by Keshavarz[34] to estimate the h_{50} (cm) as follows:

$$(\log h_{50})_{\mathrm{core}} = -0.584 + 61.62a + 21.53b + 27.96c \qquad (8)$$

$$(\log h_{50}) = (\log h_{50})_{\mathrm{core}} + 84.47F^{+}/MW - 147.1F^{-}/MW \qquad (9)$$

where $(\log h_{50})_{\mathrm{core}}$ is the core function for prediction of impact sensitivity based on the elemental composition; MW is the molecular mass of the energetic compound; a, b, and c are the number of carbon, hydrogen, and nitrogen atoms divided by molecular mass of the energetic compound, respectively. The data of F^{+} and F^{-} were selected from Ref[34].



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

3. Results and Discussion

3.1 Crystal Density

Density is one of the most significant factor for energetic materials as higher density means that more energy will be packed per unit volume of these materials. Specifically, crystal density can directly influence the detonation performance which is shown in the K-J equation. Here, we investigate a series of energetic salts and study the impact of different combinations of substituents and simple cations on the densities of pyrazole-derived salts. The volumes, densities and other related data were listed in Table 1, while Figure 2 displayed a comparison of the densities of different pyrazole-derived salts.

As shown in Table 1, some salts possess high densities over 1.9 g/cm^3. When the pyrazole-derived anions coupled with **A1** or **A3** cation, the densities of the salts are all higher than RDX (1.80 g/cm^3)[35]. Meanwhile, the salts of **A2** cation also have comparable densities. For the same cation, **B12** anion shows the largest potential for enhancing the densities of the salts as it has the highest density when incorporated with the cation **A1**. And the salts of **B7**, **B10** or **B16** anion have the lowest densities in the salts of the same cation. For the **B1**~**B6** anions, all have same $–NO_2$ group and **B2**~**B6** anions have another different substitution groups. When the other substituent is $–NO_2$, $–N_3$ or $–NF_2$ group, the salt contained **B3**, **B4** or **B5** anion has high density as compared to the salts including **B1** anion. This is because the π conjugation between pyrazole and substituents can not only stabilize the structure of energetic materials, but also increase the crystal density. Compared to **B3** and **B4** anions, **B5** anion plays a more important role in enhancing the crystal density since its $-NF_2$ group significantly increases the mass of the salts but affects the molecular volume relatively little. However, when the H atom of the pyrazole is replaced by $–NH_2$ or –CN group, a decrease of the density can be observed in the salts of **B2** and **B6** anions in comparison to the salts of **B1** anion. This suggests that these two groups are not beneficial for improving the densities of the salts. For the **B7**~**B16** anions, the influences of substituents on the densities of the pyrazole-derived anions are further elaborated. When the $–NF_2$ group is associated with other groups, their densities greatly increase. It is noteworthy that the combination of $–N_3$ and $–NF_2$ group has the greatest effect for the promotion of the crystal densities as the salts of **B12** anion possess the largest density when incorporated with the same cation. This proves that the $–NF_2$ group is the most effective group among the five groups for increasing the densities of the pyrazole-derived salts.

Figure 2 exhibits a comparison of the densities of three series of energetic salts with anions of different combinations of substituents and cations. By comparing the **A1**, **A2**, **A3** series, it is obvious that their change trends are similar. Among three cations, **A1** is the best cation to increase the densities of the pyrazole-derived salts, while **A2** is not so good for promoting the densities of these salts. This is because the ammonium cation has smaller size, resulting in better packing of the salts and less molecular volume than the hydrazine cation.

Table 1. Volumes (cm^3/mol) and densities (g/cm) of the pyrazole-derived salts

Cation	Anion	V	A_s^+	V_s^+	A_s^-	V_s^-	ρ
A1	B1	182.00	47.50	171.70	240.43	–72.88	1.95
A1	B2	154.58	47.50	171.70	246.67	–72.54	1.94
A1	B3	172.90	47.50	171.70	260.69	–70.75	2.02
A1	B4	175.47	47.50	171.70	256.96	–71.54	2.01
A1	B5	163.32	47.50	171.70	259.26	–71.40	2.05
A1	B6	169.91	47.50	171.70	260.62	–70.28	1.94
A1	B7	180.60	47.50	171.70	225.04	–77.21	1.85
A1	B8	182.87	47.50	171.70	248.48	–73.83	1.89
A1	B9	178.68	47.50	171.70	244.45	–74.94	1.99
A1	B10	179.94	47.50	171.70	246.93	–73.30	1.85
A1	B11	173.35	47.50	171.70	246.26	–72.15	1.86
A1	B12	171.34	47.50	171.70	263.57	–71.05	2.08
A1	B13	170.18	47.50	171.70	265.17	–70.05	1.91
A1	B14	178.10	47.50	171.70	258.75	–70.96	2.03
A1	B15	163.30	47.50	171.70	236.95	–74.15	1.99
A1	B16	160.69	47.50	171.70	235.95	–74.52	1.85
A2	B1	192.53	61.68	152.51	240.43	–72.88	1.86

A2	B2	165.11	61.68	152.51	246.67	−72.54	1.85
A2	B3	183.43	61.68	152.51	260.69	−70.75	1.93
A2	B4	186.00	61.68	152.51	256.96	−71.54	1.92
A2	B5	173.85	61.68	152.51	259.26	−71.40	1.95
A2	B6	180.44	61.68	152.51	260.62	−70.28	1.85
A2	B7	191.13	61.68	152.51	225.04	−77.21	1.76
A2	B8	193.40	61.68	152.51	248.48	−73.83	1.80
A2	B9	189.21	61.68	152.51	244.45	−74.94	1.90
A2	B10	190.47	61.68	152.51	246.93	−73.30	1.76
A2	B11	183.88	61.68	152.51	246.26	−72.15	1.77
A2	B12	181.87	61.68	152.51	263.57	−71.05	1.98
A2	B13	180.71	61.68	152.51	265.17	−70.05	1.82
A2	B14	188.63	61.68	152.51	258.75	−70.96	1.94
A2	B15	173.83	61.68	152.51	236.95	−74.15	1.89
A2	B16	171.22	61.68	152.51	235.95	−74.52	1.76
A3	B1	188.51	67.18	146.42	240.43	−72.88	1.92
A3	B2	161.09	67.18	146.42	246.67	−72.54	1.91
A3	B3	179.41	67.18	146.42	260.69	−70.75	1.99
A3	B4	181.98	67.18	146.42	256.96	−71.54	1.98
A3	B5	169.83	67.18	146.42	259.26	−71.40	2.01
A3	B6	176.42	67.18	146.42	260.62	−70.28	1.91
A3	B7	187.11	67.18	146.42	225.04	−77.21	1.82
A3	B8	189.38	67.18	146.42	248.48	−73.83	1.86
A3	B9	185.19	67.18	146.42	244.45	−74.94	1.96
A3	B10	186.45	67.18	146.42	246.93	−73.30	1.82
A3	B11	179.86	67.18	146.42	246.26	−72.15	1.83
A3	B12	177.85	67.18	146.42	263.57	−71.05	2.04
A3	B13	176.69	67.18	146.42	265.17	−70.05	1.88
A3	B14	184.61	67.18	146.42	258.75	−70.96	2.00
A3	B15	169.81	67.18	146.42	236.95	−74.15	1.96
A3	B16	167.20	67.18	146.42	235.95	−74.52	1.82

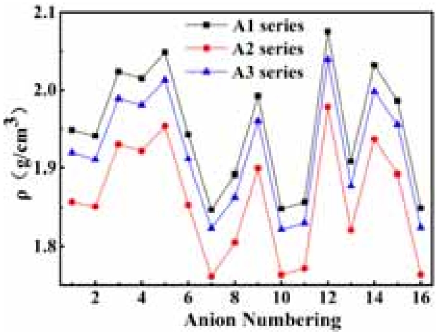


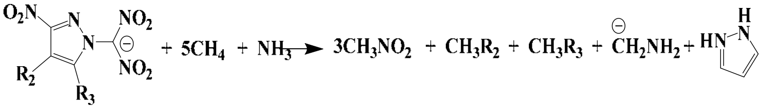
Figure 2. Comparison of the densities of the pyrazole-derived salts.

3.2 Heats of Formation (HOFs)

The heats of formation are usually important for evaluating energetic material because higher HOFs means greater energy content[36]. The designed isodesmic reactions for the anions are given in Scheme 2. Table 2 lists the calculated and experimental gas-phase HOFs of small molecules and ions at 298 K and the calculated values are very close to the literature values[9, 37]. The G2 method was used to calculate the HOFs of small molecules and ions[38].

It is seen in Table 3 that the HOFs of cations are all large, while the anions are not so beneficial for improving the HOFs of the pyrazole-derived salts except for **B4**, **B8**, **B11**, **B12** or **B13** anion. Especially, for the same cation, the salt containing **B4** anion has the greatest HOF. This indicates that the $–N_3$ group is the best substituent to enhance the HOFs of anions among the five groups. When the other substituent is $–NO_2$, $–NF_2$ or –CN, its substituted pyrazole-derived salts have slightly higher HOFs than its unsubstituted one, while for the substituent $–NH_2$, the HOFs of the salts are lower. However, when the $–NH_2$ group is coupled with the $–N_3$ group, it can promote the HOFs of the salts significantly. By comparing the **B11**, **B12** and **B13** anions, **B11** anion has less substituents but possess higher HOFs than **B12** anion when they form salts with the same cation. It is interesting that the combination of $–N_3$ group and $–NF_2$ group is not so good for the HOFs of the salts.

Figure 3 presents a comparison of the HOFs for the salts composed of pyrazole-derived anions and ammonium, hydrazine and hydroxylamine cations. It is seen that the variation trends of the salts of the three cations are unanimous. This shows that incorporating different cations hardly affects the change trends of the HOFs of the salts even if they have anions with different substituents. When the cation is $N_2H_5^+$, its corresponding salts with the same anion have the largest HOFs among the salts. This is because this cation has higher nitrogen content than the other two.



Scheme 2. Isodesmic reactions for the anions.

Table 2. Calculated and experimental gas-phase heats of formation (kJ/mol) for small molecules and ions at 298 K

Molecules/ions	ΔH^o_f (calculated)	ΔH^o_f (literature)
CH_4	−73.6[a]	−74.4[c]
NH_3	−45.3[a]	−46.1[c]
CH_3NO_2	−85.9[a]	−80.8[c]
CH_3NH_2	−23.2[a]	−22.5[c]
CH_3N_3	295.8[a]	296.5[c]
CH_3NF_2	−109.2[a]	
CH_3CN	75.2[a]	74[c]
H^+		1536.2[c]
$CH_2NH_2^-$	196.11[b]	
NH_4^+	630.51[b]	626.4[f]
$N_2H_5^+$	760.37[b]	759.7[f]
$^+NH_3OH$	668.58[b]	664.4[f]
pyrazole	183.01[a]	

[a] The values were calculated at G2 level. [b] The values were calculated by protonation reactions: $CH_2NH_2^- + H^+ \rightarrow CH_3NH_2$, $NH_3 + H^+ \rightarrow NH_4^+$, $N_2H_4 + H^+ \rightarrow N_2H_5^+$, $NH_2OH + H^+ \rightarrow {}^+NH_3OH$. [c] The values

were taken from Ref [36]. [f]The values were taken from Ref [9]

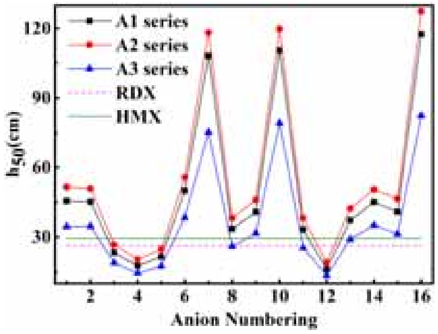


Figure 3. Comparison of the HOFs of the pyrazole-derived salts.

Table 3. Heats of formation ((kJ/mol) for the pyrazole-derived anions, ammonium cations, and their salts and lattice energies of these salts

Cation	Anion	ΔH^{o}_{f}(cation)	ΔH^{o}_{f}(anion)	Lattice energy	ΔH^{o}_{f}(salt)
A1	B1	630.51	–197.54	487.45	–54.49
A1	B2	630.51	–233.43	480.41	–83.33
A1	B3	630.51	–168.88	473.61	–11.98
A1	B4	630.51	528.80	474.59	684.72
A1	B5	630.51	–191.14	472.86	–33.49
A1	B6	630.51	–42.28	476.41	111.81
A1	B7	630.51	–179.13	495.12	–43.75
A1	B8	630.51	294.75	478.93	446.33
A1	B9	630.51	–220.46	481.14	–71.09
A1	B10	630.51	–64.15	483.07	83.29
A1	B11	630.51	159.83	483.21	307.13
A1	B12	630.51	94.38	475.93	248.96
A1	B13	630.51	297.24	475.82	451.93
A1	B14	630.51	–67.63	479.52	83.36
A1	B15	630.51	–216.12	487.17	–72.79
A1	B16	630.51	–55.93	490.23	84.34
A2	B1	760.37	–197.54	477.67	85.16
A2	B2	760.37	–233.43	471.05	55.90
A2	B3	760.37	–168.88	464.85	126.64
A2	B4	760.37	528.80	465.75	823.42
A2	B5	760.37	–191.14	464.20	105.03
A2	B6	760.37	–42.28	467.30	250.79
A2	B7	760.37	–179.13	484.56	96.68
A2	B8	760.37	294.75	469.54	585.58
A2	B9	760.37	–220.46	471.85	68.05
A2	B10	760.37	–64.15	473.30	222.92
A2	B11	760.37	159.83	473.46	446.75
A2	B12	760.37	94.38	467.15	387.60
A2	B13	760.37	297.24	466.66	590.95

A2	B14	760.37	–67.63	470.43	222.31
A2	B15	760.37	–216.12	477.50	66.75
A2	B16	760.37	–55.93	480.00	224.43
A3	B1	668.58	–197.54	475.95	–4.91
A3	B2	668.58	–233.43	469.50	–34.35
A3	B3	668.58	–168.88	463.41	36.30
A3	B4	668.58	528.80	464.29	733.09
A3	B5	668.58	–191.14	462.76	14.69
A3	B6	668.58	–42.28	465.85	160.45
A3	B7	668.58	–179.13	482.72	6.73
A3	B8	668.58	294.75	468.06	495.27
A3	B9	668.58	–220.46	470.25	–22.14
A3	B10	668.58	–64.15	471.76	132.67
A3	B11	668.58	159.83	471.91	356.51
A3	B12	668.58	94.38	465.62	297.34
A3	B13	668.58	297.24	465.24	500.58
A3	B14	668.58	-67.63	468.84	132.11
A3	B15	668.58	–216.12	475.75	–23.30
A3	B16	668.58	–55.93	478.29	134.36

3.3 Energetic properties and sensitivity

According to our predicted densities and HOFs, we calculated the corresponding energetic parameters which were summarized in Table 4. Meanwhile, commonly used explosives RDX and HMX were also listed for comparison[39].

The calculated heat of detonation (Q) in Table 4 show that for the **B1**~**B6** anions, the substitution of the –NO$_2$, –N$_3$ and –NF$_2$ group increases the Q value of its salts as compared to the salts incorporated with **B1** anion (which doesn't have the other substituent), whereas for the substituent –NH$_2$ and –CN, the case is quite the contrary. Especially, **B4** anion presents the best potential for enhancing the Q value among the six anions and the salts of **B4** anion even has larger Q than HMX. By comparing the **B7**~**B16** anions, the influences of different substituents on the Q value are further presented. When the two substituents are –N$_3$ and –NF$_2$ group (anion **B12**), the Q of its salt is the best among the ten anions but is lower than **B3**, **B4** and **B5** anions. When the two substituents are –NH$_2$ and –CN (anion **B10**), the Q value of its salt is the lowest. This indicates that the –NO$_2$, –N$_3$ and –NF$_2$ groups are effective substituents for enhancing the Q of the pyrazole-derived salts.

As is shown in Table 4, for the **B1**~**B6** anions, the salts of **B3**~**B5** have larger D and P than the salts of B1. On the contrary, the salts of **B2** and **B6** anions have smaller ones. This indicates that the substitution of group –NO$_2$, –N$_3$ and –NF$_2$ can enhance the D and P of the salts. Among the six anions, the salts of **B4** has relatively larger D and P values which means that the substituent –N$_3$ is the best group for increasing the D and P. For the **B7**~**B16** anions, the combination of different substituents slightly enhances D and P of their salts except **B9**, **B12** and **B15** anions, indicating that the –NO$_2$ group is important for increasing the energetic properties. When the two substituents are –N$_3$ and –NF$_2$ group (anion **B12**), the D and P of its salts is the largest among **B7**~**B16** anions and only slightly lower than the **B4** and **B5** anions. It is concluded that the –NO$_2$, –N$_3$ or –NF$_2$ group is favorable for increasing the detonation properties of its salts and the combination of –N$_3$ and –NF$_2$ group is also beneficial for enhancing the energetic properties.

Figure 4 exhibits a comparison of the calculated Q, D and P values of the pyrazole-derived salts. The **A1**, **A2** and **A3** cations hardly influence the detonation properties. Among **A1**~**A3** cations, **A3** cation has the largest potential to enhance the detonation properties. By comparing the detonation properties of these salts with RDX and HMX, we can find that the salts of **B3**, **B4**, **B5** and **B12** anion have better energetic properties than RDX and HMX.

Impact sensitivity has been more and more important in the field of high energy density materials. The impact sensitivity is generally reported as the height in cm, designated h_{50} [40]. The higher the h_{50} is, the less sensitive the explosive is. Figure 5 presents the influence of different combination of substituents and ammonium cations on the h_{50} of the pyrazole-derived salts. When the anion is same, the salts of **A2** series have the largest h_{50} among the three series salts, the middle is the salts of **A1** series and the salts of **A3** series have the lowest h_{50}. This indicates that the **A2** cation is good for reducing the impact sensitivity of the salts. For the salts of **B1**~**B6** anions and the same cation, the h_{50} of salts containing **B6** anion are larger than the salts of **B1** anion, while the h_{50} of the salts of **B3**, **B4** and **B5** anion are smaller. Among the **B7**~**B16** anions, when the cation is same, the salts of **B12** anion have the smallest h_{50}. As a whole, incorporating $-N_3$, $-NO_2$ or $-NF_2$ group into pyrazole-derived salts is not helpful for reducing the impact sensitivity while incorporating $-NH_2$ or –CN group can reduce the impact sensitivity. When the two substituents are $-N_3$ and $-NF_2$, it is also not so good for reducing the impact sensitivity of the pyrazole-derived salts. Furthermore, it can be found that the better the detonation properties are, the larger the sensitivity is.

Table 4. Predicted heats of detonation (Q), detonation velocities (D) and pressures (P), and sensitivity for the pyrazole-derived salts

Cation	Anion	Q(cal/g)	D(km/s)	P(GPa)	h_{50}(cm)
A1	B1	1397.79	9.06	38.10	45.62
A1	B2	1321.41	8.95	37.16	45.23
A1	B3	1508.45	9.58	43.53	23.31
A1	B4	1753.67	9.85	45.94	17.57
A1	B5	1558.54	9.77	45.62	21.48
A1	B6	1279.46	8.65	34.74	49.95
A1	B7	1242.37	8.40	31.76	108.20
A1	B8	1451.81	8.93	36.42	33.42
A1	B9	1407.12	9.29	40.62	40.80
A1	B10	1091.02	7.95	28.49	110.58
A1	B11	1390.44	8.67	33.94	33.16
A1	B12	1496.30	9.70	45.28	16.26
A1	B13	1254.02	8.43	32.64	37.33
A1	B14	1331.86	9.06	39.06	45.11
A1	B15	1460.81	9.31	40.73	40.92
A1	B16	1134.34	7.97	28.61	117.52
A2	B1	1458.31	8.89	35.75	51.63
A2	B2	1382.37	8.80	34.90	50.91
A2	B3	1555.32	9.37	40.57	26.74
A2	B4	1790.18	9.62	42.61	20.44
A2	B5	1602.35	9.55	42.41	24.67
A2	B6	1340.30	8.52	32.77	55.76
A2	B7	1319.30	8.29	30.12	118.25
A2	B8	1507.18	8.76	34.11	38.24
A2	B9	1462.79	9.11	37.96	46.05
A2	B10	1168.50	7.88	27.22	119.80
A2	B11	1452.15	8.53	31.94	38.22
A2	B12	1543.45	9.49	42.15	18.93
A2	B13	1316.88	8.31	30.86	42.31
A2	B14	1389.15	8.90	36.67	50.49

A2	B15	1516.89	9.13	38.06	46.45
A2	B16	1214.08	7.90	27.37	127.45
A3	B1	1521.45	9.21	39.04	34.47
A3	B2	1442.56	9.10	38.03	34.66
A3	B3	1609.62	9.66	43.84	18.87
A3	B4	1844.43	9.90	45.99	14.38
A3	B5	1655.58	9.84	45.79	17.52
A3	B6	1398.67	8.81	35.63	38.41
A3	B7	1390.22	8.63	33.26	75.19
A3	B8	1567.70	9.06	37.15	25.93
A3	B9	1521.62	9.42	41.33	31.59
A3	B10	1233.58	8.19	29.93	79.20
A3	B11	1516.04	8.83	34.89	25.40
A3	B12	1597.52	9.79	45.62	13.40
A3	B13	1376.04	8.60	33.61	29.03
A3	B14	1446.39	9.20	39.88	35.03
A3	B15	1578.59	9.45	41.53	31.27
A3	B16	1282.70	8.21	30.17	82.36
RDX		1597.40	8.9(8.8[a])	34.8(34.7[a])	29.17(26.33[a]))
HMX		1633.90	9.3(9.1[a])	39.2(39.0[a])	31.28(29.36[a])

[a] The values were taken from Ref[38]

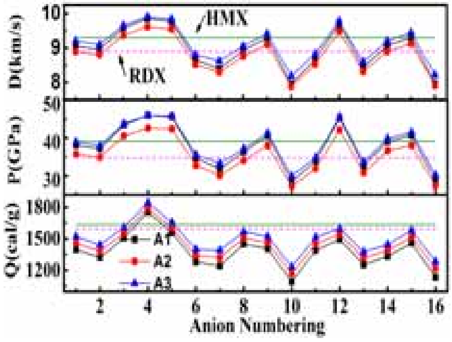


Figure 4. Heats of detonation, detonation velocities, and detonation pressures of the pyrazole-derived salts.

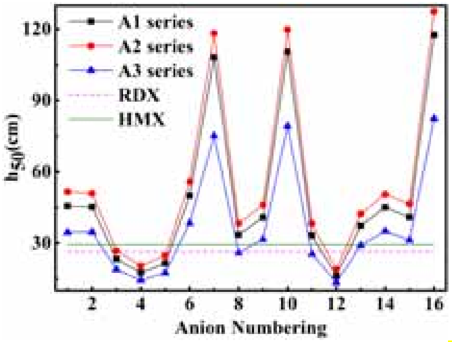


Figure 5. Comparison of the impact sensitivity of the pyrazole-derived salts.

4. Conclusion

A series of salts composed of simple ammonium cations (NH_4^+, $N_2H_5^+$ and $^+NH_3OH$) and pyrazole-derived anions were designed. The densities, heats of formation (HOFs) and energetic performance of the salts were studied. The impact sensitivity of the salts were predicted using the elemental composition and relevant correction factor. The results show that for the promotion of densities of the salts, NH_4^+ has the best among the three ammonium cations. When one substituent is $-NO_2$ group, another substitution of the $–NO_2$, $–N_3$ or $–NF_2$ group is helpful for increasing the densities of the salts. The substitution of $–NF_2$ group shows the best promotion for the densities of the salts, especially when the $–NF_2$ group attaches to the pyrazole ring with $–N_3$ group. The salts of $N_2H_5^+$ exhibit the best HOFs due to its highest nitrogen content. When one substituent is $–NO_2$ group, incorporating another $–NO_2$, $–N_3$, $–NF_2$ and –CN group into salts is favorable for improving the HOFs of the salts, with $–N_3$ group being the most favorable.

The detonation performance of these salts indicates that $^+NH_3OH$ has better detonation performance than the other two ammonium cations. When one substituent is $–NO_2$ group, introducing another $–NO_2$, $–N_3$ or $–NF_2$ group is an effective way for promoting the detonation properties of the salts. When the two substituents are $–N_3$ and $–NF_2$ group, there is a synergistic effect that is good for enhancing the detonation properties of the salts. By comparing with the commonly used explosives RDX and HMX, it can be found that the salts of **B3**, **B4**, **B5** or **B12** anion can be considered as potential high-energy salts.

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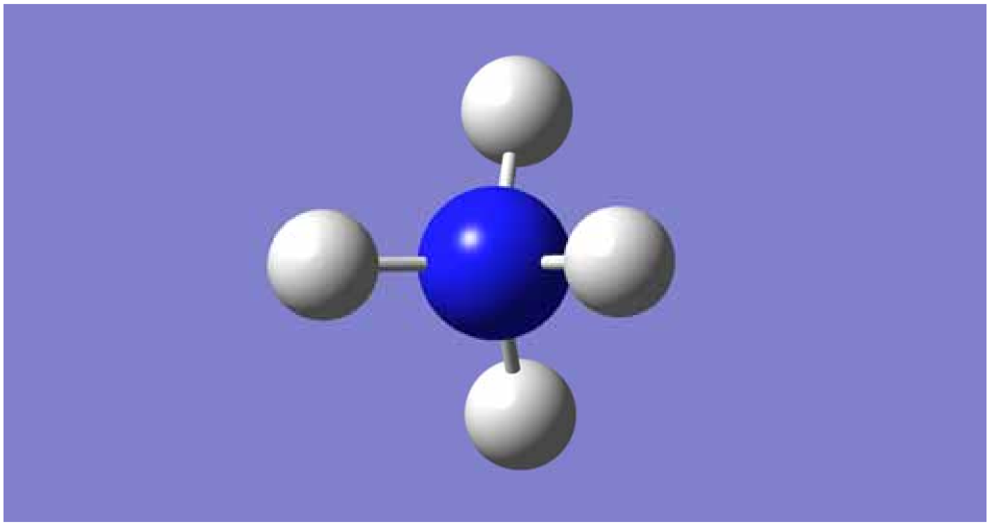

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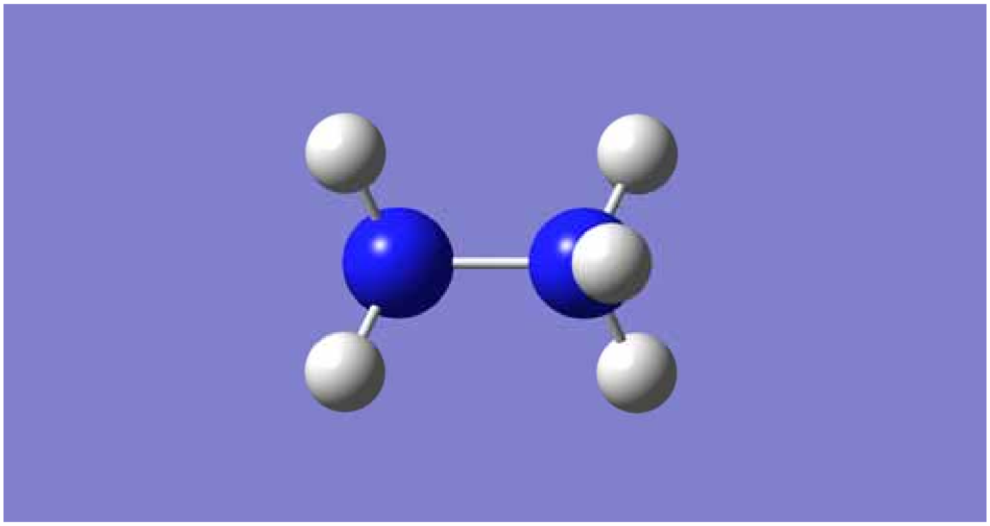

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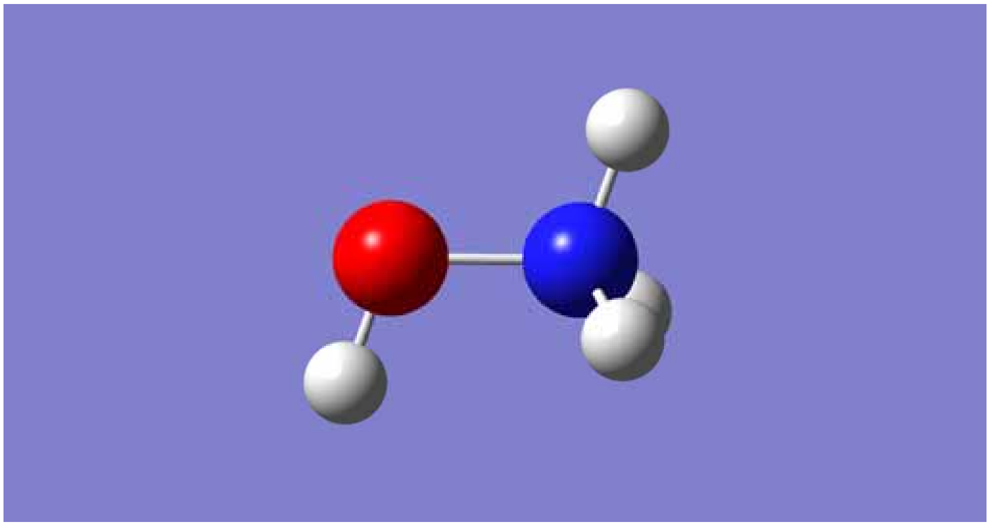

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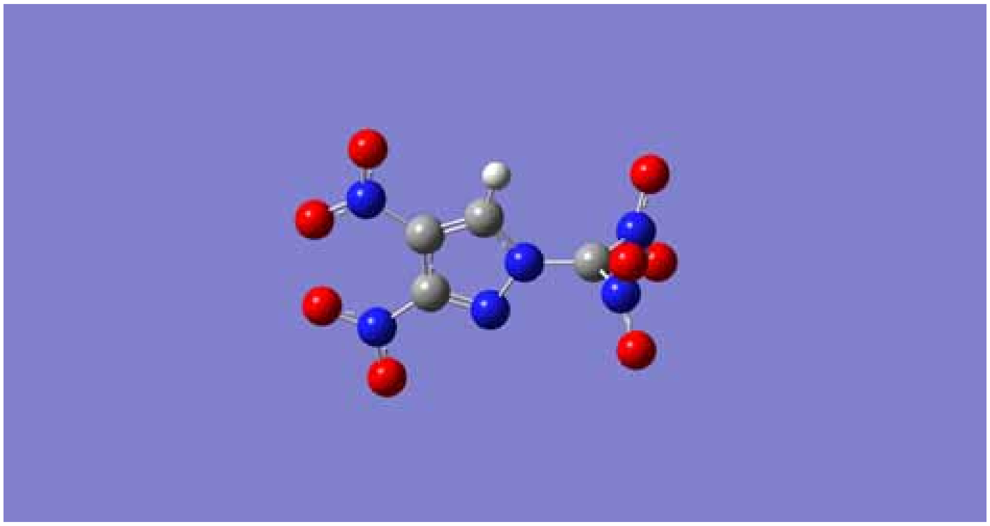

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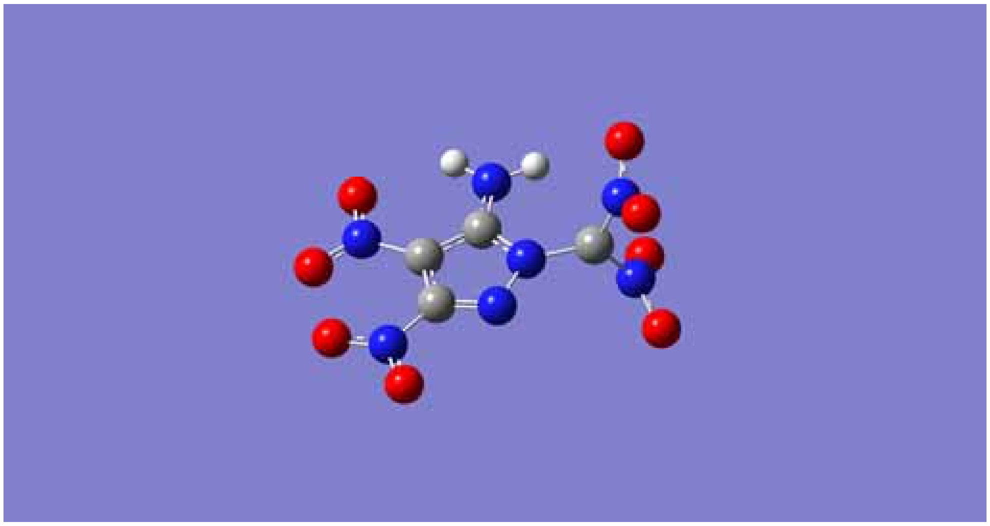

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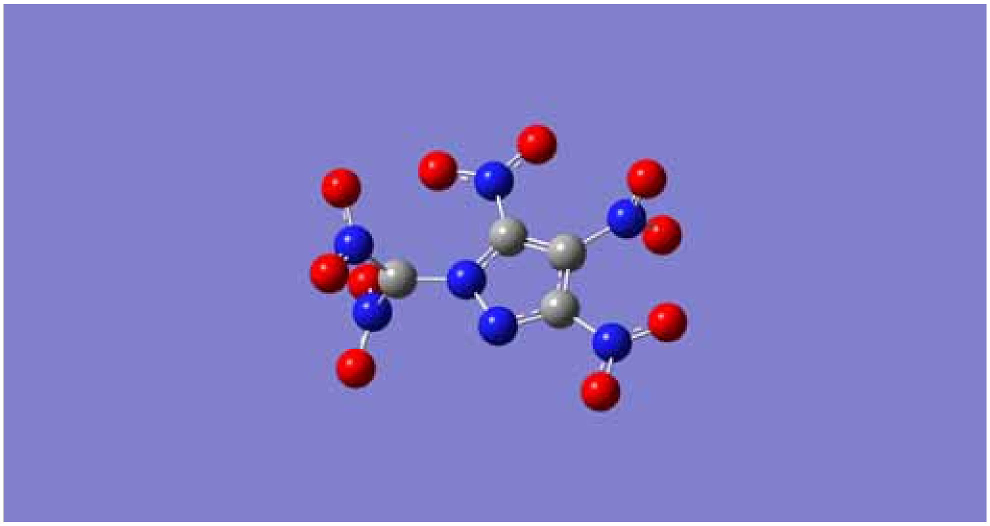

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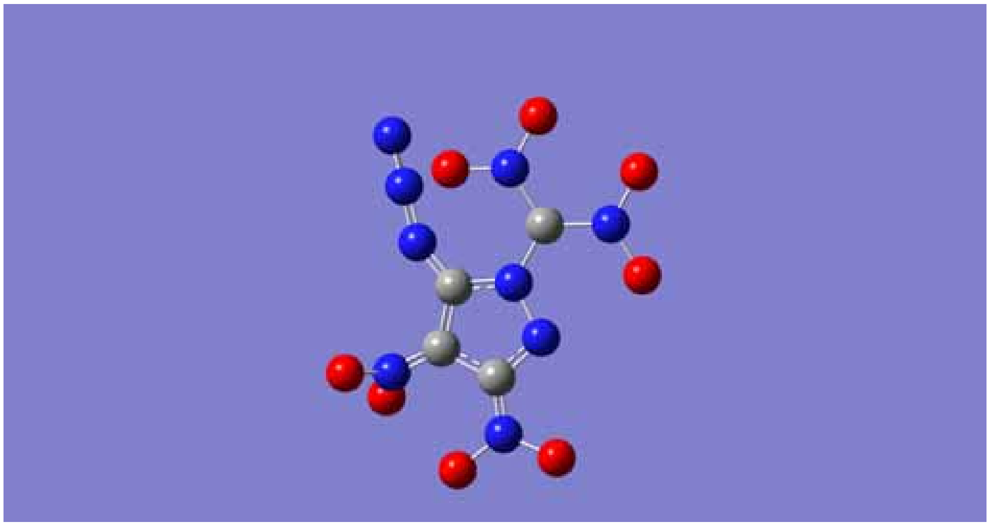

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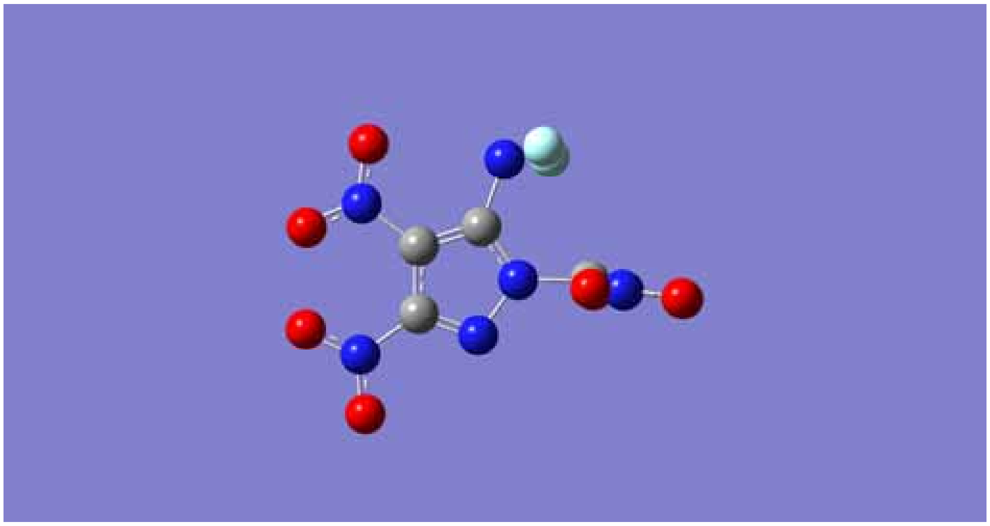

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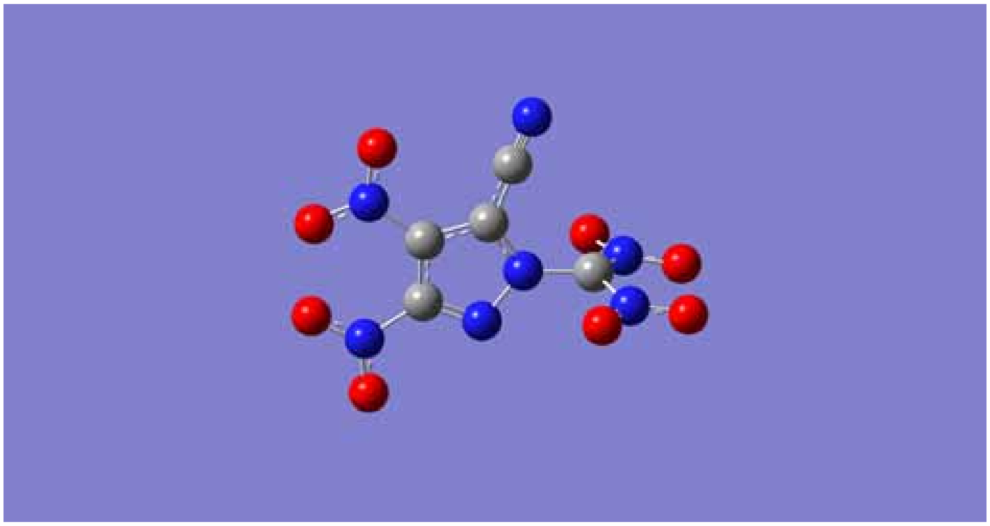

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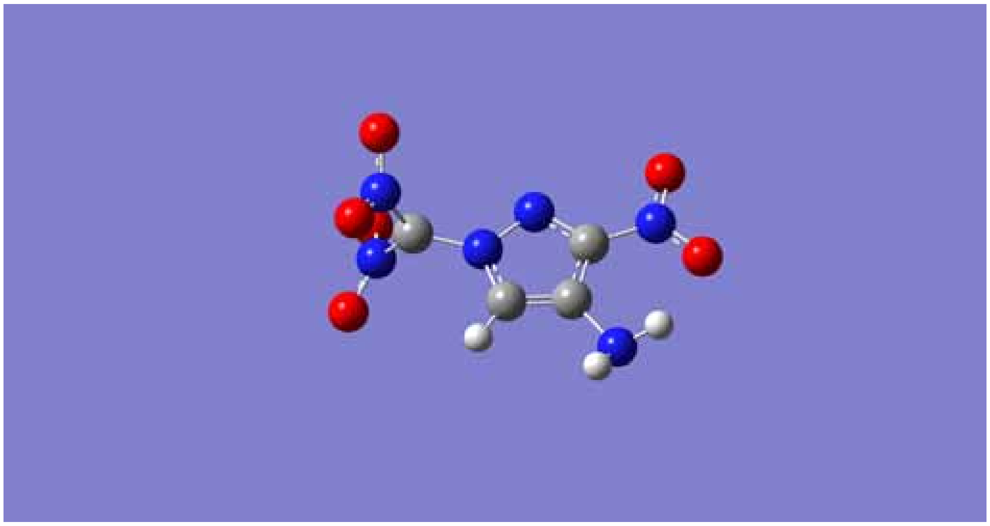

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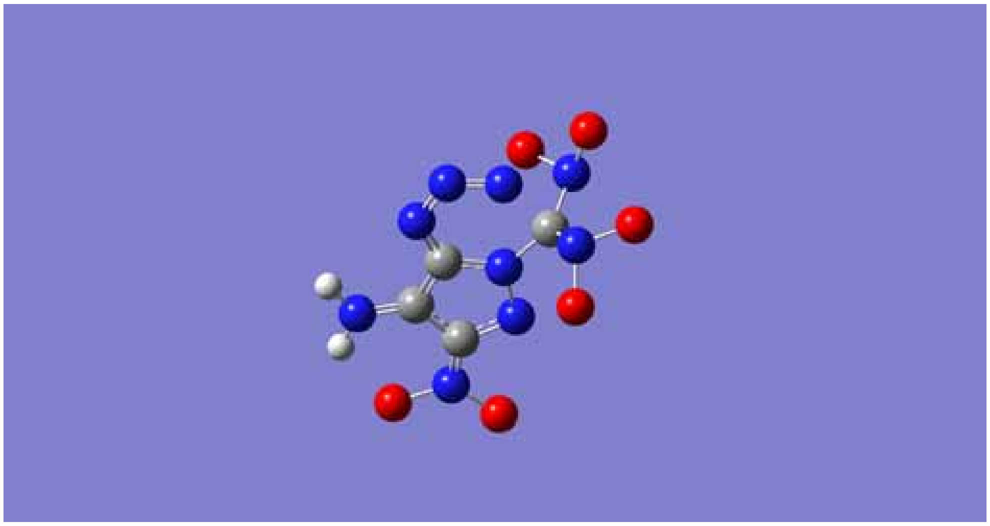

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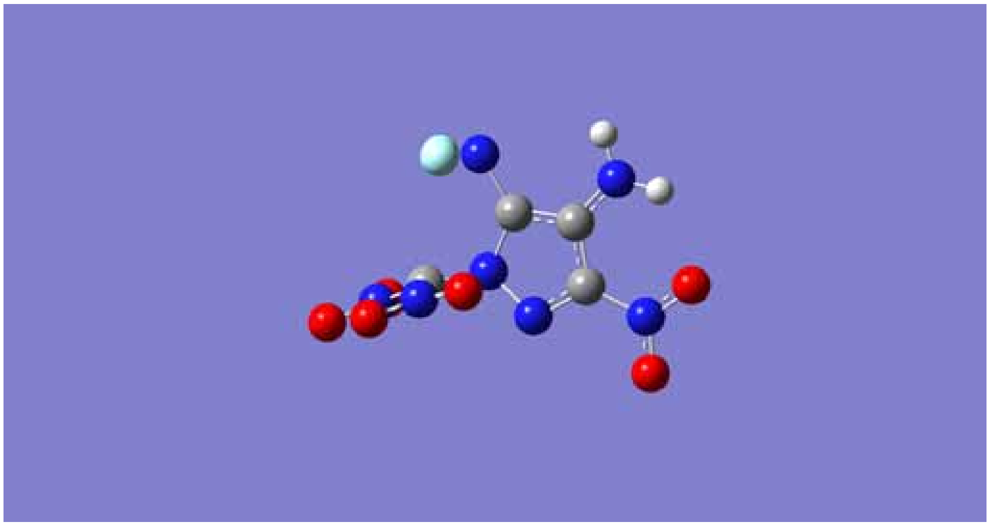

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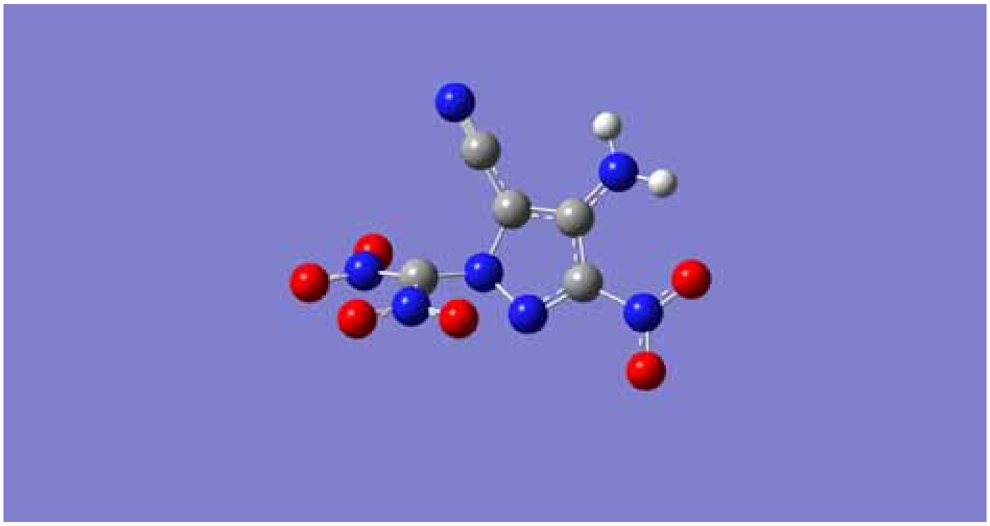

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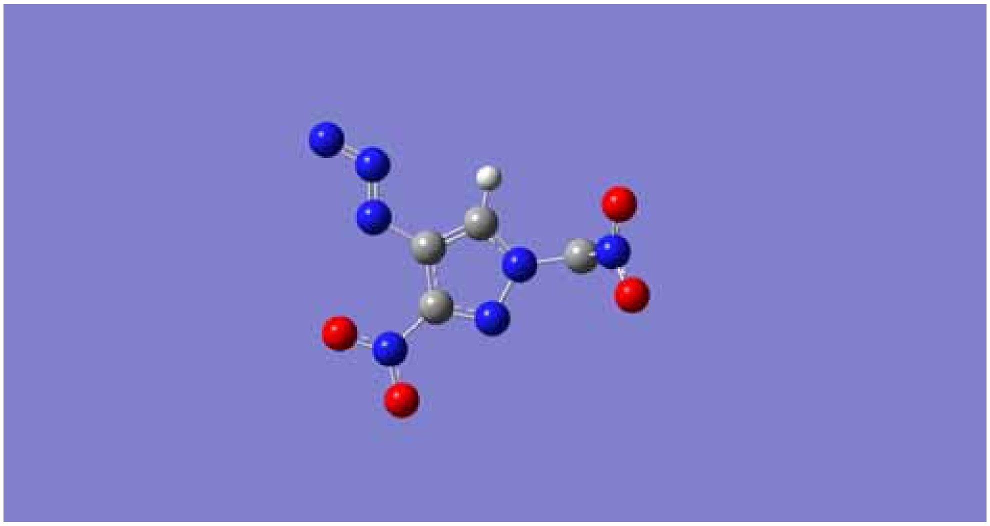

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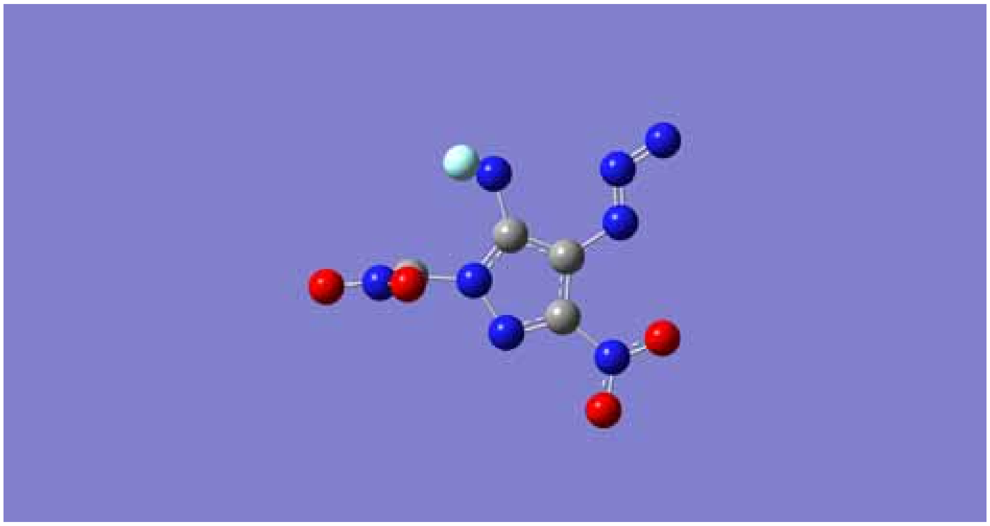

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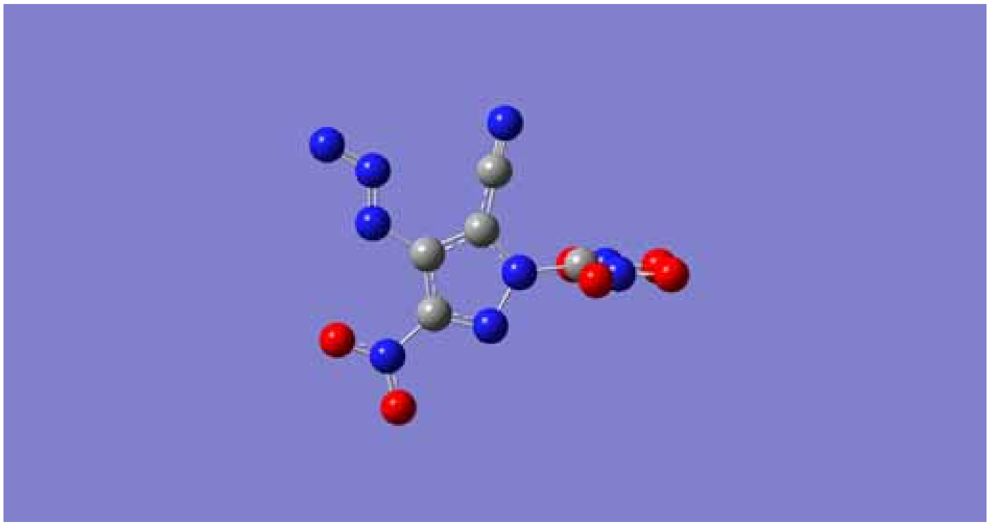
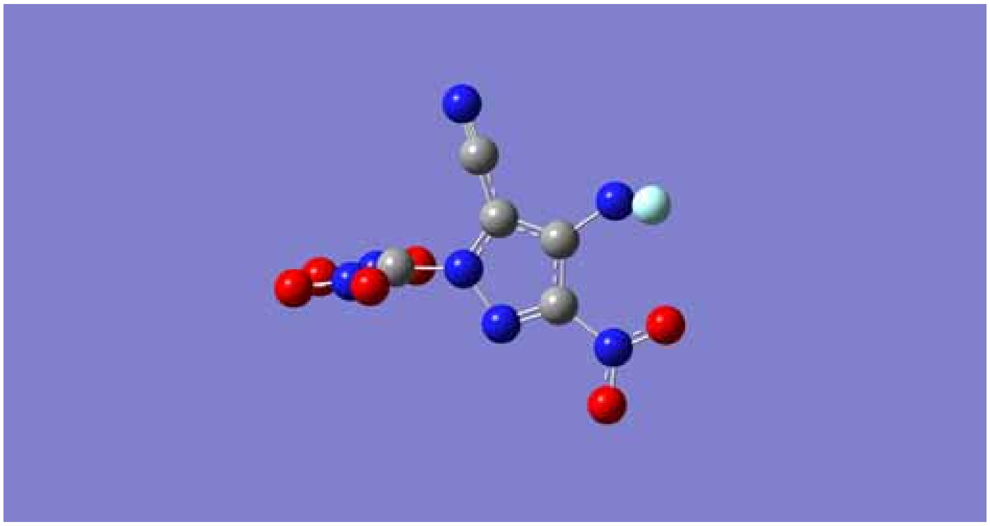
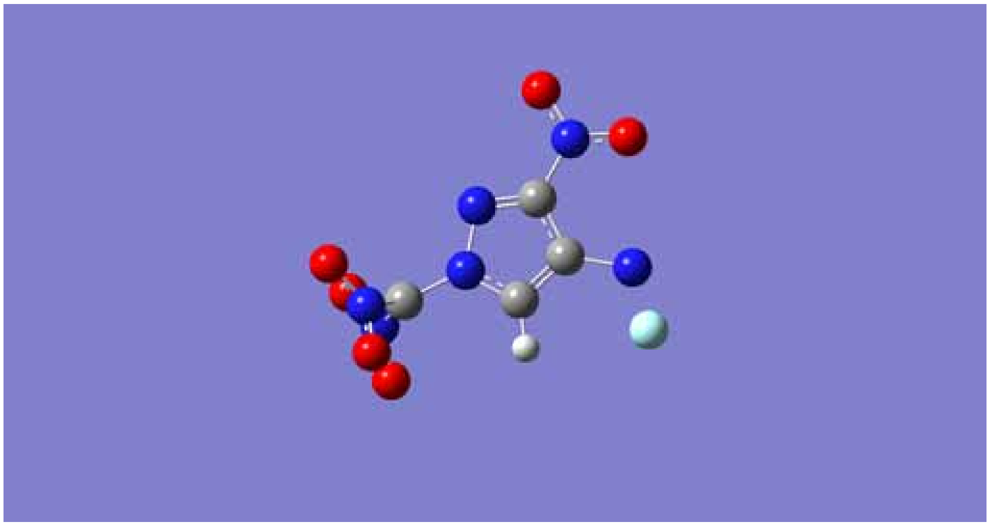


B14



B15



B16