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Computational Study of Azole Salts as High Energy Materials

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ABSTRACT: The crystal densities, heats of formation (HOFs), detonation properties, and impact sensitivity of a series of azole salts were investigated by the density functional theory and volume-based thermodynamics calculations. The HOFs of cations and anions, and lattice energies were obtained based on the Born-Haber energy cycles. The detonation parameters (Q , D and P) of 18 energetic salts have been calculated by the Kamlet-Jacobs equations with the calculated density and HOFs. The outcomes reflected that the hydroxylammonium cation has greater impact on the density and detonation properties of the azole salts than the hydrazine cation. Among all the series salts under investigation, 2-amino-3-nitroamino-4,5-dinitropyrazole and 3-nitroamino-4,5-dinitropyrazole anions have greater HOFs and better detonation performance than other anions. In summary, the incorporations of all the cations studied here with the 2-amino-3-nitroamino-4,5-dinitropyrazole or 3-nitroamino-4,5-dinitropyrazole anions can be considered as potential high-energy salts.

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

1. INTRODUCTION

There is a requirement for finding high performance energetic materials to replace those currently used. So the study of new energetic materials is a hot research

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field.¹ At present, we found that energetic salt is a vital part of energetic materials and a large amount of research results have been achieved.²⁻⁷ On the account of the lower VP (vapor pressures), higher densities, lower melting points, and higher CED (cohesive energy densities), the salt-based energetic materials have an advantage compared to nonionic energetic materials. According to the empirical equations, the packing density and detonation velocity of explosive has a direct relationship, and the packing density and the detonation pressure of the explosive has a quadratic relationship. This suggests that the density is the most important physical parameter for the detonation performances. The anions and cations in energetic salts may be modified independently, which will influence the property.⁸ In the normal state, the energetic salts are not volatile and have good stability, and their density is much larger than that of the corresponding neutral compounds. The coulomb electrostatic interaction in the energetic salts makes the anion and cation more closely together, thus weakening the rejection of different components in explosives. Through the well-design or the collocation of anions and cations, we could obtain high HOFs, high thermal stability, high oxygen balance, high density and friendly-environmental energetic ion salts. In general, when neutral molecules transform into energetic salts, thermal stability and sensitivity will be improved, and the detonation property of much energetic salts will be better than its precursor.

We paid much attention to the compounds with high nitrogen contents since they have high HOFs. The energy of traditional nitro compounds mainly come from burning carbon skeleton, but nitrogen-rich compounds derive their energy partly from the positive HOFs.⁸ New high energy density materials (HEDMs) of good performance have aroused people's attention due to their potential applications in national defense and civil economy.⁹ Klapötke and Shreeve¹⁰ had synthesized many HEDMs. However, systematic and comprehensive molecular design is still essential for the growth of high performance HEDMs.

In this work, we investigate diazole energetic salts with high energy and good stability by density functional theory (DFT)¹¹ and volume-based thermodynamics calculations. The incorporations of diazole anions containing different substituents

(-NO₂, -N₃, -NH₂) with simple amine cations (Figure 1) were made to establish some promising candidates with comprehensively good performances. Our main purpose is to discuss the properties of azole salts containing different diazole anions with basic amines cations. Finally, we will screen out potential high-energy salts with better detonation performance. The rest of this paper is listed in the following: Section 2 is a simple description of our computational method; Section 3 is the results and discussions; Section 4 is a summary of our conclusions.

2. COMPUTATIONAL METHODS

All calculations were computed using the Gaussian 09¹² software package at the B3LYP/6-311+G** level.^{13,14} When the optimization is processing, there are no constraints on the structure of molecules. Frequency analysis showed that all the optimized configuration are local minimum points on the potential energy surfaces without any imaginary frequencies. The molecular energies (proton affinities and ionization energies) were computed under the G2 level.¹⁵ One significant factor to change the properties of energetic material is the density. In order to predict the crystal density in the absence of the experimental crystal structure, several approaches have been developed.¹⁶⁻²⁰ These methods show that using single molecular volume is feasible to predict the crystal density. For an ionic crystal with formula unit MpXq, its volume is the sum of the volumes of its constituent ions, it is improved by the formula unit¹⁹:

$$V = pV_{M^+} + qV_{X^-} \quad (1)$$

where M denotes the cation and X denotes the anion. On the consideration that we used the DFT procedure to estimate the volumes of individual ions, we took Eq. (1) to calculate formula unit volumes of ionic crystals. Due to the lack of correction for the interaction between ions, the traditional method $\rho = M/V$ to calculate crystal density might result in some calculation error. The crystal density of ionic crystals may be improved by:

$$\rho = \alpha(M/V) + \beta(V_S^+/A_S^+) + \gamma(V_S^-/A_S^-) + \delta \quad (2)$$

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

isolated gas molecule. A_S^+ is positive surface area. V_S^+ is positive average value. A_S^- and V_S^- are the analogous quantities for an anion. α , β , γ , and δ are taken from the Ref [21].

Based on a Born-Haber energy cycle (Scheme 1), the HOF of a salt is simplified by the formula:

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

where ΔH_L is the lattice energy to form the ionic salts. The formula presented by Jenkins²² et al. 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 are up to the own nature of the ions M^{p+} and X^{q-} , respectively. For monatomic ions, both of them are equal to 3, 5 for linear polyatomic ions, and 6 for nonlinear polyatomic ions. The lattice energy U_{POT} ($\text{kJ}\cdot\text{mol}^{-1}$) can be expressed as follows:

$$U_{\text{POT}}/\text{kJ}\cdot\text{mol}^{-1} = \gamma(\rho_m/M_m)^{1/3} + \delta \quad (5)$$

where ρ_m ($\text{g}\cdot\text{cm}^{-3}$) is density, M_m is the chemical formula mass of the ionic material, and the coefficients $\gamma/\text{kJ}\cdot\text{mol}^{-1}\cdot\text{cm}$ and $\delta/\text{kJ}\cdot\text{mol}^{-1}$ are values taken from the literature.

²² We designed the isodemic reactions (Scheme 2) to calculate the HOFs of azole anions. We calculated the HOFs of small ions by the G2 method if their experimental HOFs are not feasible. The detonation properties of high energy compounds can be estimated by the Kamlet–Jacobs empirical equation²³:

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

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

Where D stands for the detonation velocity in $\text{km}\cdot\text{s}^{-1}$; P the detonation pressure in GPa; N the moles of detonation gases produced by per gram explosive; M the average molecular weight of these gases in $\text{g}\cdot\text{mol}^{-1}$; Q the heat of detonation in $\text{cal}\cdot\text{g}^{-1}$; and ρ the loaded density of explosives in $\text{g}\cdot\text{cm}^{-3}$. If the detonation heat and density of the known explosive have been achieved through the experiment, their D and P can be calculated by Eq. (6) and (7). However, the Q and ρ cannot be obtained for all compounds from the experiment, so we need rely on theoretical calculation. Hence, to

116 get their D and P , we need to calculate the Q and ρ firstly.

117 The sensitivity must be considered as the key factor for projecting the high-energy
118 compounds. Experimentally, to calculate impact sensitivity, we will do a drop weight
119 test. Impact drop height (h_{50} , cm, where 1 cm = 0.245 J (Nm) with 2.5 kg dropping
120 mass.) is the height that causes its 50% explosion height measurement. Recently,
121 Keshavarz²⁴ suggested a simple method to estimate the h_{50} (cm) of energetic
122 compounds.

$$123 \quad (\log h_{50})_{\text{core}} = -0.584 + 61.62a + 21.53b + 27.96c$$

$$124 \quad (\log h_{50}) = (\log h_{50})_{\text{core}} + 84.47F^+/\text{MW} - 147.1F^-/\text{MW}$$

125 where $(\log h_{50})_{\text{core}}$ is the core function for prediction of impact sensitivity according to
126 the composition of element; a , b , and c are the number of carbon, hydrogen, and
127 nitrogen atoms divided by molecular mass of the energetic compound, respectively;
128 MW is the molecular mass of the explosion compound. The data of F^+ and F^- are
129 taken from the literature.²⁴

130

131 3. RESULTS AND DISCUSSIONS

132 3.1 Crystal Density.

133 Energetic materials are required to have relatively high density, because the
134 higher the density is, the more energy per unit volume contains. We studied the
135 impacts of different diazoles anions with different substituents ($-\text{NO}_2$, $-\text{N}_3$, $-\text{NH}_2$)
136 with basic amines cations on the densities of the salts. The densities and other
137 corresponding data of azole salts were listed in Table 1. Figure 2 exhibits the
138 influences of different diazoles anions and the simple amine cations on the densities
139 of azole salts.

140 In Table 1, we can see that all the azole salts have densities ranging from 1.70 to
141 2.00 $\text{g}\cdot\text{cm}^{-3}$. **B6** is the anion that guarantees the largest crystal density for the azole
142 salts with the same series of cations. This suggests that the anion **B6** is better than the
143 other anions for increasing the densities of the azole salts. In all the **A1~A3** series
144 salts, the crystal densities are the maximum ones when the cations incorporate with
145 anion **B6**, and when the anion is **B4**, the crystal densities are the minimum.

Figure 2 exhibits the trends of the crystal densities of **A1~A3** series azole salts. Evidently, the change trends of **A1~A3** series azole salts are unanimous. In all the cations, the **A1** (ammonia) was the best cation for increasing the densities of the salts, while the **A2** (hydroxylammonium) was not beneficial for promoting the densities of the salts. For the anions **B1** versus **B2**, the substituent position is the same, but the substituent group is different, the density of the salts containing **B1** anion are larger than the salts containing **B2** anion. For the anions **B3** versus **B5**, the density of aminating azole salts is greater than the unaminating azole salts. When the substituents are $-\text{NO}_2$, $-\text{N}_3$ and $-\text{NH}_2$, the crystal density of azole salts are larger than the corresponding unsubstituted salts. It can be found that the azole ring and substituent group could form a π conjugation, and it may be the reason that result in the consequence above. As is known to all, the existence of π bond not only helps to enhance the stability of the energetic compound, but also significantly improves the crystal density.

3.2 Heats of Formation

The heats of formation play great role in the properties of ionic salts.²⁶ The heats of formation of the salts can be influenced by the functional groups. The azido or amino group usually increases the heats of formation. For example, the amino group bonded to nitrogen usually contributes more positively than when bonded to carbon. The heats of formation of reference molecules and ions were listed in Table 2 for deriving the HOFs of the azole salts. Figure 3 exhibits the effects of different diazoles anions with some amine cations on the heats of formation of azole salts.

From Table 3, we see that **B5** anion has the highest HOFs among all the series salts with the same cations. This means that the anion **B5** has greater impact on the HOFs of the azole salts than the other anions.

The variation of HOFs of **A1~A3** series azole salts is unanimous (Figure 3). In all the cations, the cation **A2** has the greatest impact on the HOFs of azole salts. Due to the symmetric structure of hydrazinium and the high nitrogen content of diazole anions, the HOFs of these energetic salts are larger than the other salts. The higher energy is due to the existence of N-N bond. On the other hand, the anions **B3** and **B5**

are favorable for advancing the HOFs of the azole salts. Hence, the salts containing the cation **A2** and the anions **B3** or **B5** may have high HOFs and larger detonation heats. The substituent is a major factor to influence the HOFs of azole salts. Compared to the unsubstituted salts, the HOFs of all substituted azole salts are larger.

3.3 Detonation Property and Sensitivity

Based on the predicted HOFs and densities of the title salts, we get detonation velocity and detonation pressure (Table 4) in light of Kamlet-Jacobs (K-J) equation. For comparison, the experimental values of HMX and RDX from the literature³³ were also listed in Table 4. In Table 4, for the same series cations, the azole salts containing **B3** and **B5** anions have relatively better detonation performances.

Figure 4 exhibits the trends of detonation properties of **A1~A3** series azole salts. The **A1**, **A2** and **A3** series have little influence on the Q, D and P, while the anions have more important role in affecting the detonation performance especially for the **B3** and **B5** anions. Therefore, the anion is the more important factor that greatly affects the detonation performance of azole salts. As the analysis previous, the HOFs of the **B5** and **B3** anions were larger, thereby the Q, D and P of the azole salts containing the **B5** or **B3** anions were larger. The density is the main factor, and the HOF influences less on the detonation heat, so the possible reason why **B3** and **B5** having higher detonation performance is that the density and HOF together influence the detonation performance. Consequently, the HOFs and the detonation performance of the **A1~A3** series azole salts with different anions follow same trends. Furthermore, **A1** was the best cation for increasing the detonation properties of the **A1~A3** series azole salts, that may be caused by that **A1** cation has the largest density among all the cations. Amine group has a remarkable effect on the detonation properties of the azole salts. The reason why the designed compounds have highlighted detonation properties is that they have high heats of detonation and densities. In all the salts, the detonation velocity and pressure of the salt including the **B5** anion and the **A1** cation were the largest. The salts composed of the **A1~A3** cations and the **B3** or **B5** anions exhibit good energetic properties that are near or better than those of RDX or HMX, indicating that these compounds can be used as potential high-energy salts.

For judging the response to the external stimuli, we choose to use impact sensitivity. The impact sensitivity is generally reported as the height in cm, designated h_{50} .³⁵ The higher the h_{50} is, the less sensitive of the explosive. A comparison of the effects of different diazoles anions containing different substituents (-NO₂, -N₃, -NH₂) in combination with amine cations on the h_{50} is presented in Figure 5.

From Figure 5, when the anions were same, the impact sensitivity of the **A2** series salts was the lowest, but the impact sensitivity of the **A3** series salts was the highest. The cation **A2** was favorable for reducing the impact sensitivity of the salts. Additional, the **B4** was the best anion for decreasing the impact sensitivity of the salts, while the **B6** was not helpful for reducing the impact sensitivity of the salts. The results showed that the order of impact sensitivity of these salts with **B4** and **B6** anions is not in agreement with the densities of the corresponding compounds. B4 salts are highly sensitive because the B4 anion has the -N₃ group. B3 and B5 anions have more -NO₂ group, so their densities are higher and at the same time their detonation performance are better. The introduction of the nitro group increases the nitrogen content and HOF, and simultaneously increases the number of intramolecular hydrogen bonding, the thermal stability and the density, which make the detonation performance of energetic ion salt better. The impact sensitivity of -NH₂ substituted azole ionic salts is lower than the corresponding unsubstituted salts, indicating that -NH₂ group lower the impact sensitivity of azole salts. So, the impact sensitivities of hydroxyl ammonium series cationic salts are higher than that of the other cationic salts. The impact sensitivities of **A1** and **A2** series salts were near or below the impact sensitivity of RDX or HMX, especially the salts containing **B4** or **B5** anions. Comparing the impact sensitivity with the detonation performance, it was also found that the two are opposite, the better the performance of the detonation is, the larger the sensitivity.

232

233 4. CONCLUSIONS

234 We performed the DFT-B3LYP study on the densities, HOFs, detonation
235 properties, and the impact sensitivity for the salts composed of diazole anions and

amine cations. The results showed that the hydroxylammonium cation has greater impact on the densities and detonation performances of the azole salts than the hydrazine cation, although the hydrazine cation is better than the hydroxylammonium cation to advance the HOFs of the azole salts. 3-nitroamino-1,2,4-trinitroimidazole was the best anion for enhancing the densities of the salts, while the 1-amino-2-azido-3-nitroamino-imidazole anion was not useful for advancing the densities of the salts. Increasing the number of the $-\text{NO}_2$ or $-\text{NH}_2$ substituents is helpful for increasing the densities of the salts. The 2-amino-3-nitroamino-4,5-dinitropyrazole and 3-nitroamino-4,5-dinitropyrazole anions have the advantage of enhancing the HOFs and the detonation performances of the A1~A3 series azole salts. A combination of different energetic cations and anions is helpful for the energy and density of the salts. The incorporation of all the cations studied with the 2-amino-3-nitroamino-4,5-dinitropyrazole and 3-nitroamino-4,5-dinitropyrazole anions can be used as potential high-energy salts. Compared to RDX or HMX, the new energetic salts are less sensitive or comparable, which indicates that they are good choice for future applications. What's more, they are environmentally friendly materials with high nitrogen contents.

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Figure 1. Frameworks of cations and diazole anions.

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Figure 2. Comparison of the densities of the azole salts.

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Figure 3. Comparison of the HOFs of the azole salts.

Figure 4. Heats of detonation, detonation velocities, and detonation pressures of the azole salts.

Figure 5. Comparison of the impact sensitivity of the azole salts.

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

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Scheme 2. Isodesmic reactions for the anions.

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Table 1. Volumes ($\text{cm}^3 \cdot \text{mol}^{-1}$) and densities ($\text{g} \cdot \text{cm}^{-3}$) of the azole salts

Cation	Anion	B3 LYP/6-311G**						B3PW91/6-31G(d,p)					
		V	A_s^+	V_s^+	A_s^-	V_s^-	ρ	V	A_s^+	V_s^+	A_s^-	V_s^-	ρ
A1	B1	161.19	48.42	170.29	235.91	-74.45	1.95	153.53	47.43	171.78	227.39	-77.43	2.29
A1	B2	147.11	48.42	170.29	213.85	-78.48	1.93	142.62	47.43	171.78	213.85	-78.48	2.26
A1	B3	139.69	48.42	170.29	204.32	-79.71	1.91	133.71	47.43	171.78	196.11	-83.02	2.28
A1	B4	141.85	48.42	170.29	210.55	-79.26	1.86	136.75	47.43	171.78	202.11	-81.69	2.19
A1	B5	147.54	48.42	170.29	217.26	-77.93	1.93	141.90	47.43	171.78	209.11	-81.12	2.27
A1	B6	158.75	48.42	170.29	232.07	-75.78	1.99	164.27	47.43	171.78	224.34	-78.76	2.31
A2	B1	171.74	68.19	145.41	235.91	-74.45	1.86	163.79	66.46	146.85	227.39	-77.43	2.33
A2	B2	157.66	68.19	145.41	213.85	-78.48	1.84	152.89	66.46	146.85	213.85	-78.48	2.31
A2	B3	150.23	68.19	145.41	204.32	-79.71	1.82	143.98	66.46	146.85	196.11	-83.02	2.34
A2	B4	152.40	68.19	145.41	210.55	-79.26	1.77	147.01	66.46	146.85	202.11	-81.69	2.25
A2	B5	158.08	68.19	145.41	217.26	-77.93	1.84	152.17	66.46	146.85	209.11	-81.12	2.32
A2	B6	169.29	68.19	145.41	232.07	-75.78	1.91	160.52	66.46	146.85	224.34	-78.76	2.35
A3	B1	169.36	62.52	151.54	235.91	-74.45	1.90	160.05	60.61	153.44	227.39	-77.43	2.36
A3	B2	155.27	62.52	151.54	213.85	-78.48	1.89	149.14	60.61	153.44	213.85	-78.48	2.33
A3	B3	147.85	62.52	151.54	204.32	-79.71	1.87	140.24	60.61	153.44	196.11	-83.02	2.37
A3	B4	150.02	62.52	151.54	210.55	-79.26	1.82	143.27	60.61	153.44	202.11	-81.69	2.28
A3	B5	155.70	62.52	151.54	217.26	-77.93	1.89	148.42	60.61	153.44	209.11	-81.12	2.35
A3	B6	166.91	62.52	151.54	232.07	-75.78	1.95	135.62	60.61	153.44	224.34	-78.76	2.38

475 ^a The values are taken from Ref [25].

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

Molecules	ΔH_f° (Expt.)	Molecules / ions	ΔH_f° (Expt.)
NH ₃	-46.1 ^b	CH ₃ NH ₂	-22.5 ^f
CH ₄	-74.4 ^b	CH ₃ NNO ₂ ⁻	1347.5 ^g
NH ₂ NO ₂	-3.9 ^c	NH ₃ OH ⁺	678.8 ^h
NH ₂ NH ₂	95.4 ^d	H ⁺	1536.2 ^b
NH ₂ OH	-45.0 ^d	pyrazole	183.01
CH ₃ NO ₂	-80.8 ^b	imidazole	135.50
CH ₃ N ₃	296.5 ^e		

^a The values in this work were calculated at the G2 level. ^{b-d} The experimental data are taken from Refs [27-29]. ^{e-g} The calculated data are taken from Refs [30-32]. ^h The values were calculated by protonation reactions $\text{NH}_2\text{OH} + \text{H}^+ \rightarrow \text{NH}_3\text{OH}^+$.

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Table 3. Heats of formation ($\text{kJ}\cdot\text{mol}^{-1}$) for the azole anions, amine cations, and their azole salts and lattice energies of these salts

Cation	Anion	ΔH_f (cation)	ΔH_f (anion)	Lattice energy	ΔH_f (salt)
A1	B1	630.51	-14.13	488.72	127.65 (125.84) ^a
A1	B2	630.51	-333.13	500.43	-203.06 (-208.64) ^a
A1	B3	630.51	1077.29	507.31	1200.48 (1018.24) ^a
A1	B4	630.51	-73.85	505.74	50.92
A1	B5	630.51	1342.18	500.11	1472.57
A1	B6	630.51	-396.28	490.27	-256.05
A2	B1	760.37	-14.13	476.27	269.97
A2	B2	760.37	-333.13	486.82	-59.59
A2	B3	760.37	1077.29	492.96	1344.70
A2	B4	760.37	-73.85	491.43	195.10
A2	B5	760.37	1342.18	486.53	1616.02
A2	B6	760.37	-396.28	477.79	-113.70
A3	B1	668.58	-14.13	478.83	175.62
A3	B2	668.58	-333.13	489.61	-154.16
A3	B3	668.58	1077.29	495.89	1249.98
A3	B4	668.58	-73.85	494.34	100.40
A3	B5	668.58	1342.18	489.31	1521.45
A3	B6	668.58	-396.28	480.36	-208.06

^a The values are taken from Ref [25].

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

Cation	Anion	<i>Q</i> (cal·g ⁻¹)	<i>D</i> (km·s ⁻¹)	<i>P</i> (GPa)	<i>h</i> ₅₀ (cm)
A1	B1	1210.90	8.84 (9.17) ^a	36.30 (40.94) ^a	20.57
A1	B2	1063.78	8.54 (8.65) ^a	33.68 (33.7) ^a	28.78
A1	B3	2536.18	10.48 (9.24) ^a	50.46 (43.27) ^a	23.93
A1	B4	983.58	8.02	29.05	35.10
A1	B5	2665.68	10.72	53.06	28.78
A1	B6	1201.98	9.06	38.72	9.91
A2	B1	1283.88	8.72	34.34	24.29
A2	B2	1153.29	8.46	32.17	33.90
A2	B3	2543.43	10.19	46.40	28.78
A2	B4	1085.58	8.00	28.10	41.36
A2	B5	2664.50	10.41	48.67	33.90
A2	B6	1274.45	8.93	36.57	12.12
A3	B1	1344.86	8.98	36.94	16.19
A3	B2	1220.51	8.75	34.93	21.69
A3	B3	2608.99	10.46	49.69	17.94
A3	B4	1158.12	8.29	30.73	25.55
A3	B5	2726.04	10.68	51.96	21.69
A3	B6	1334.63	9.19	39.29	8.14
RDX		1597.4	8.9 (8.8) ^b	34.8 (34.7) ^b	29.17 (26-33) ^b
HMX		1633.9	9.3 (9.1) ^b	39.2 (39.0) ^b	31.28 (29-36) ^b

^a The values are taken from Ref [25]. ^b The values are taken from Refs [24, 33-34].