

Theoretical studies on the stability of salts formed by 3-substituted 6-nitraminotetrazines with different cations

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Abstract A series of energetic salts based on the cations NH_4^+ , NH_3OH^+ , N_2H_5^+ and $\text{C}(\text{NH}_2)_3^+$ and the anions of 6-nitraminotetrazine and its 3-substituted derivatives of $-\text{NH}_2$, $-\text{N}_3$, $-\text{ONO}_2$, $-\text{NF}_2$ or $-\text{NO}_2$ was studied using dispersion-corrected density functional theory (DFT-D). In comparison with salts of unsubstituted 6-nitraminotetrazine, $-\text{NH}_2$ substitution strengthens the hydrogen bonding interaction and other intramolecular interactions (such as charge transfer, binding energy, second-order perturbation energy and dispersion energy), $-\text{N}_3$ has tiny effects on these interactions, and other groups weaken these interactions, with weakening decreasing in the order $-\text{NO}_2 > -\text{NF}_2 > -\text{ONO}_2$. The ability of the cations to produce strong intramolecular interactions decreases in the order $\text{NH}_3\text{OH}^+ > \text{N}_2\text{H}_5^+ > \text{NH}_4^+ > \text{C}(\text{NH}_2)_3^+$, which is contrary to the order of the basicity of bases. Stronger intramolecular interactions lead to more stable salts. All substituent groups improved the chemical stability except $-\text{ONO}_2$, while cations had no effect on chemical stability. All substituent groups were helpful in improving aromaticity, in the sequence $-\text{ONO}_2 > -\text{NF}_2 > -\text{NO}_2 > -\text{N}_3 > -\text{NH}_2$.

Keywords 6-Nitraminotetrazine derivatives · Cation · Intramolecular interactions · Stability · Density functional calculations

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Introduction

In recent years, substantial efforts have been devoted to developing new energetic compounds for various applications, e.g., propellants, explosives, and pyrotechnic fuels. As a unique class of energetic materials, energetic salts have received a lot of attention because of their advantages over non-ionic molecules in many aspects, such as their intrinsically low volatility, low vapor pressure, low handling hazard, high thermal stability, high density and energy, and simple synthesis route with low costs [1–6]. The anions in energetic salts are mainly those of HNO_3 , HClO_4 , $\text{HN}(\text{NO}_2)_2$ and $\text{HC}(\text{NO}_2)_3$ [7–10]. However, synthesized salts based on these acids have their respective shortcomings, for example, explosion products of the salts of HClO_4 pollute the environment [11]; ADN (ammonium dinitramide) is easily hygroscopic [12]; HNF (hydrazinium nitroformate) is sensitive to its purity and size [13].

Recently, the anion of 3-amino-6-nitraminotetrazine (ANAT) [14] has captured people's interest [15]. ANAT contains a 1,2,4,5-tetrazine heterocycle. Compounds with 1,2,4,5-tetrazine usually have positive heats of formation (HOFs) and high crystal densities, and can release a large amount of N_2 during detonation, which recommends them as energetic materials [15–18]. The nitramino group of ANAT is helpful for improving the oxygen balance (OB) and nitrogen content, which can lead to a high exothermicity in the combustion and detonation processes, and this group enables ANAT to form energetic salts as an acid. Several salts formed by ANAT have been synthesized with excellent yields and purities [15]. The detonation pressures and detonation velocities of these salts were estimated to be 20.90–28.96 GPa and 7.55–8.90 km/s, respectively [15]. Thermal gravimetric analysis (TGA) and differential scanning calorimetry (DSC) studies showed that the decomposition temperatures (T_d s) of these

salts were 147.7–248 °C, higher than the T_d s of the energetic salts ADN (140 °C) [16] and HNF (123 °C) [17]. Thus, salts formed by ANAT have better thermal stability.

The introduction of $-\text{NH}_2$, $-\text{N}_3$, $-\text{ONO}_2$, $-\text{NF}_2$ or $-\text{NO}_2$ groups to organic molecules has great effects on detonation properties, stabilities, and OBs [18, 19]. In order to search for new anions that can form energetic salts with good performance, the $-\text{NH}_2$ group of ANAT was replaced by $-\text{N}_3$, $-\text{ONO}_2$, $-\text{NF}_2$ and $-\text{NO}_2$ groups. For comparison, the unsubstituted 6-nitraminotetrazine was also considered. The anions of 6-nitraminotetrazine and its $-\text{NH}_2$, $-\text{N}_3$, $-\text{ONO}_2$, $-\text{NF}_2$ and $-\text{NO}_2$ substituted derivatives were numbered I–VI, respectively. The cations to pair with these anions came from the bases NH_3 , NH_2OH , N_2H_4 and $\text{C}(\text{NH})(\text{NH}_2)_2$, i.e., NH_4^+ (A), NH_3OH^+ (B), N_2H_5^+ (C), and $\text{C}(\text{NH}_2)_3^+$ (D). The salts were named based on their respective cation and anion, e.g., all representative salts with a cation of NH_3 contain A in their name, and with an anion of 3-amino-6-nitraminotetrazine contain II. The structures and names of all title salts are shown in Fig. 1. Our previous studies showed that intramolecular interactions affect the stability of the salt [20–22]. In order to evaluate the effects of different substituent groups and cations on stability, various intramolecular interactions were studied in this work.

Computational details

Calculations were conducted at the B97-D [23]/aug-cc-pvdz level of density functional theory with dispersion corrections (DFT-D). All structures were identified to be local minima without the presence of imaginary frequencies based on vibrational analysis. Natural bond orbital (NBO) [24] analyses were performed at the same level to estimate the second order perturbation energy. The DFT-D3 program was employed to evaluate the dispersion interaction energy between the cation and anion.

Quantum theory of atoms in molecule (QTAIM) analyses were performed using Multiwfn [25] with the input files (.wfn) generated from Gaussian [26]. The characteristics of the bond critical point (BCP) were obtained in terms of the

electron density (ρ_{BCP}) and its Laplacian ($\nabla^2\rho$) at the critical point, the total electron energy density (H_{BCP}), the electron potential energy density (V_{BCP}), and the Lagrangian kinetic energy (G_{BCP}). The relationships between these parameters are shown in Eqs. (1) and (2):

$$\frac{1}{4}\nabla^2\rho = 2G_{\text{BCP}} + V_{\text{BCP}} \quad (1)$$

$$H_{\text{BCP}} = G_{\text{BCP}} + V_{\text{BCP}} \quad (2)$$

The hydrogen bonding energy (in a.u.) was obtained using the following relationship proposed by Espinosa et al. [27]:

$$E_H = V_{\text{BCP}}/2 \quad (3)$$

ρ' , the density without interaction correction, was estimated as follows:

$$\rho' = \frac{M}{V_m} \quad (4)$$

$$V_m = pV_{\text{cation}} + qV_{\text{anion}} \quad (5)$$

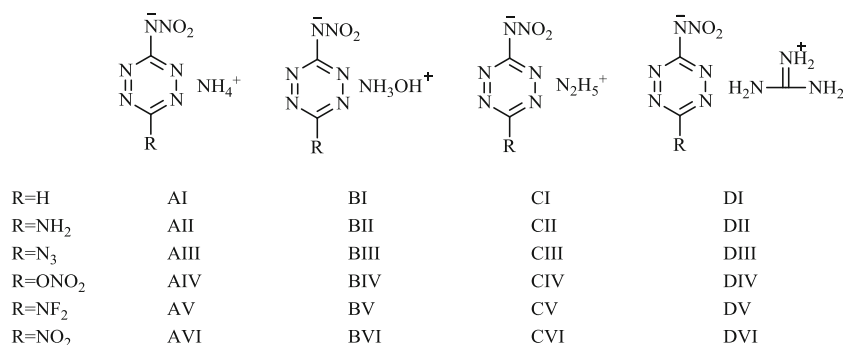
Where M is the molecular molar weight. V_{cation} and V_{anion} are the volumes of the cation and anion defined as that inside an electronic isodensity contour of 0.001 e/bohr³, respectively. p and q are the numbers of the cation (X) and anion (Y) in the salt X_pY_q , respectively.

The electrostatic potential $V(r)$ created in the space around a molecule by its nuclei and electrons can be estimated by Eq. (6)

$$V(r) = \sum_A \frac{Z_A}{|R_A - r|} - \int \frac{\rho(r')dr'}{|r' - r|} \quad (6)$$

Z_A is the charge on the nucleus A, located at R_A , and $\rho(r)$ is the electronic density of the system. $V(r)$ is a physical observable, which can be determined computationally. The sign of

Fig. 1 Structures of the title salts



$V(r)$ in any region depends on whether the positive contribution of the nuclei or the negative one of the electrons dominates. When $V(r)$ is computed on a molecular surface, it is labelled as $V_S(r)$.

$$V_{S,ave}^+ = \frac{1}{m} \sum_{i=1}^m V_S^+(r_i) \tag{7}$$

$$V_{S,ave}^- = \frac{1}{n} \sum_{j=1}^n V_S^-(r_j) \tag{8}$$

$$\rho = \alpha_1 \rho' + \beta_1 \left(\frac{V_{S,ave}^+}{A_S^+} \right) + \gamma_1 \left(\frac{V_{S,ave}^-}{A_S^-} \right) + \delta_1 \tag{9}$$

Where i and j are indices, and m and n are the numbers of sampling points in positive and negative regions, respectively. A_S^+ indicates the surface area of a cation on which the electrostatic potential is positive and has an average of $V_{S,ave}^+$, A_S^- and $V_{S,ave}^-$ are the corresponding quantities for an anion. α_1 , β_1 , γ_1 and δ_1 came from reference [28].

The lattice energy H_L of the salt X_pY_q was obtained using Eq. (10):

$$H_L = U_{POT} + [(n_X/2-2)p + (n_Y/2-2)q] \times RT \\ = 2I \left[\alpha_2 V_m^{-1/3} + \beta_2 \right] + [(n_X/2-2)p + (n_Y/2-2)q] \times RT \tag{10}$$

$$V_m = \frac{M}{\rho N_A} \tag{11}$$

Where I is the ionic strength, which here equals 1 [29]. α_2 and β_2 were taken from reference [29]. n_X and n_Y both equal 6 for these title salts [30]. This method has been employed to predict H_L in many studies [22, 29]. V_m is the volume of a single molecule [29], ρ is the density obtained from Eq. (9).

The atomic charges were obtained from Mulliken population analysis. The net charge transfer was determined from the total number of donation and back donation electrons, i.e.,

$$q = CT(Y \rightarrow X) - CT(X \rightarrow Y) \tag{12}$$

Where $CT(Y \rightarrow X)$ is the charge transfer from anion to cation and $CT(X \rightarrow Y)$ is the charge transfer from cation to anion after considering the electron polarization effect [31]. It is calculated using Multiwfn by conducting extended charge decomposition analysis (ECDA) [31].

The binding energy (E_b) was obtained using the following equation:

$$E_b = E_{salt} - E_{cation} - E_{anion} + E_{bsse} \tag{13}$$

E_{salt} , E_{cation} and E_{anion} are the total energies of salt, cation and anion, respectively. E_{bsse} is the correction for basis set superposition error (BSSE).

Results and discussion

Intramolecular hydrogen bonding interactions

It is well known that hydrogen bonds formed in salts are beneficial to improving stability and density, which in turn enhances the explosive performance of energetic salts [32]. Structures of 24 salts with intramolecular hydrogen bonds are illustrated in Fig. 2. This figure shows that there are two intramolecular hydrogen bonds in the B–D series, while only one in the A series. So the numbers of intramolecular hydrogen bonds are affected only by cations, not anions or substituents. Inspection of Fig. 2 reveals that the N1–H2···N3 hydrogen bonding interaction exists in all these salts, which demonstrates that the nitramino group plays an important role in formation of intramolecular hydrogen bonds. The intramolecular hydrogen bond lengths in Table 1 show that the H2···N3 bond lengths are 1.580–1.690 Å for the A–C series while 1.842–1.931 Å for the D series. This implies that the N1–H2···N3 hydrogen bonding interactions of the D series are weaker than those of the A–C series. Another intramolecular hydrogen bonding interaction is O4–H5···O6 for the B series and N4–H5···O6 for the C and D series. The H5···O6 distances are 1.667–1.728 Å, 2.266–2.386 Å and 1.816–1.909 Å for series B, C, and D, respectively. The B series has two hydrogen bonds and the H5···O6 distances of the B series are shorter than those of the C and D series, so salts of the B series should possess the strongest hydrogen bonding interactions, and the C series should have the next strongest ones. Although the D series has one more hydrogen bond than the A series, two hydrogen bonds of the D series are obviously longer than those of the A series. So we conjecture that hydrogen bonding interactions of the A series should be stronger than those of the D series. In other words, the abilities of the cations to form intramolecular hydrogen bonds should decrease in the order $NH_3OH^+ > N_2H_5^+ > NH_4^+ > C(NH_2)_3^+$.

For the A–D series, the H2···N3 bond lengths have the order of II < I < III < IV < V < VI (but DIII < DI). Compared with series I, series II has shorter H2···N3, i.e., the $-NH_2$ group shortens the H2···N3 bond, while the $-ONO_2$, $-NF_2$ and $-NO_2$ groups elongate the H2···N3 bond, with elongations increasing in the order $-ONO_2 < -NF_2 < -NO_2$. The effects of

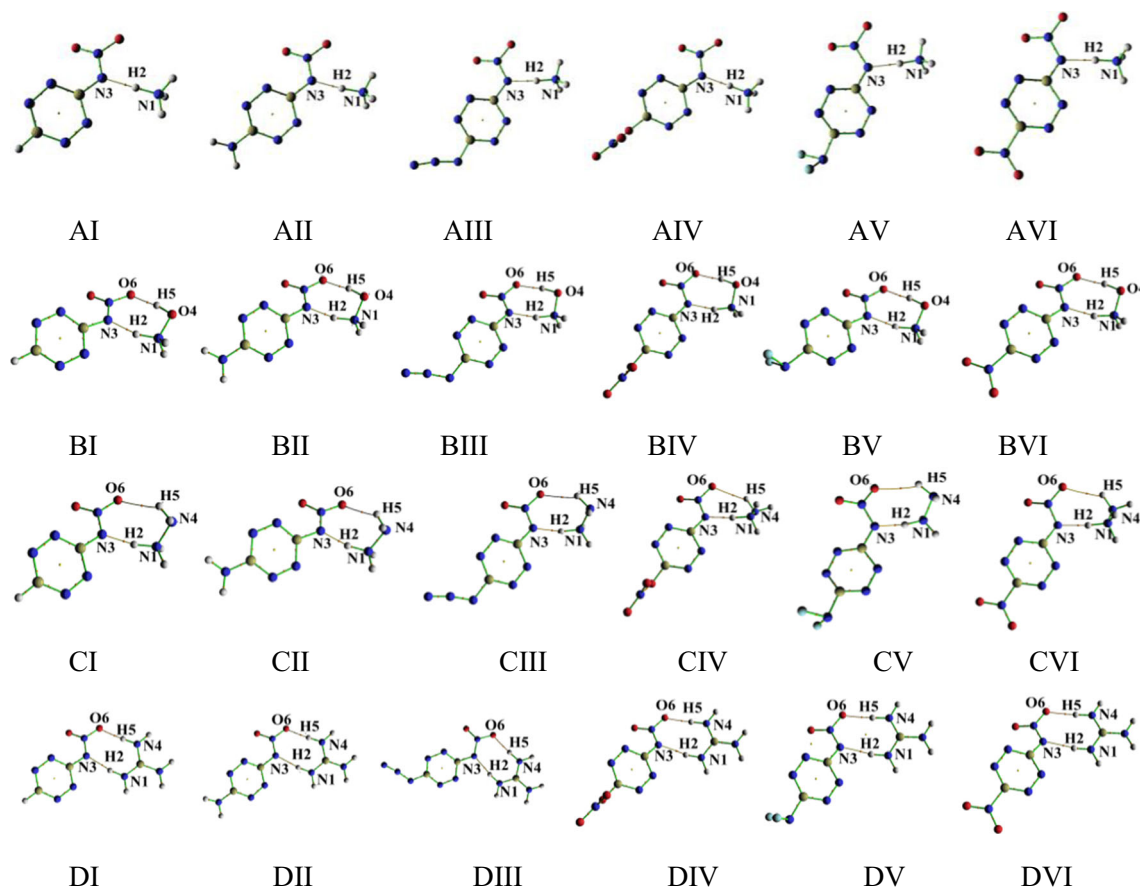


Fig. 2 Structures with intramolecular hydrogen bond paths

the $-N_3$ group on the $H_2 \cdots N_3$ bonds of various salts are tiny in comparison with those caused by other groups. For example, the absolute values of the differences between the $H_2 \cdots N_3$ bond lengths of AII–AVI and AI are AIII (0.007 \AA) < AII (0.035 \AA) < AIV (0.037 \AA) < AV (0.058 \AA) < AVI (0.066 \AA). For series B–D, the variations in $H_2 \cdots N_3$

bond lengths caused by the N_3 group are also very small (0.002 \AA , 0.005 \AA and -0.007 \AA for BIII, CIII and DIII, respectively). The $H_5 \cdots O_6$ bond lengths have the order of II < III < I < IV < V < VI. In a word, these substituent groups have similar effects on the $H_2 \cdots N_3$ and $H_5 \cdots O_6$ lengths, i.e., the $-NH_2$ group shortens these bonds, the $-ONO_2$, $-NF_2$ and $-NO_2$

Table 1 Bond length r (\AA) and hydrogen bond energy E_H (in kJ mol^{-1})

	I	II	III	IV	V	VI		I	II	III	IV	V	VI	
A	$r(H_2 \cdots N_3)$	1.623	1.588	1.63	1.66	1.681	1.689							
	$r(H_2-N_1)$	1.096	1.108	1.094	1.085	1.08	1.078							
	$E_H(N_1-H_2 \cdots N_3)$	-74.69	-86.16	-72.64	-64.34	-59.09	-57.25							
B	$r(N_3 \cdots H_2)$	1.624	1.586	1.626	1.651	1.666	1.678	$r(H_5 \cdots O_6)$	1.695	1.667	1.686	1.71	1.716	1.728
	$r(N_1-H_2)$	1.097	1.109	1.097	1.09	1.086	1.083	$r(O_4-H_5)$	1.007	1.012	1.009	1.005	1.004	1.003
	$E_H(N_1-H_2 \cdots N_3)$	-76.03	-88.7	-75.49	-68.57	-64.36	-61.59	$E_H(O_4-H_5 \cdots O_6)$	-48.94	-54.58	-50.62	-46.22	-45.05	-43.18
C	$r(N_3 \cdots H_2)$	1.632	1.597	1.637	1.645	1.645	1.673	$r(H_5 \cdots O_6)$	2.307	2.266	2.326	2.372	2.372	2.386
	$r(N_1-H_2)$	1.093	1.103	1.091	1.088	1.088	1.081	$r(N_4-H_5)$	1.028	1.029	1.028	1.025	1.025	1.025
	$E_H(N_1-H_2 \cdots N_3)$	-73.22	-84.24	-71.91	-69.01	-61.74	-60.58	$E_H(N_4-H_5 \cdots O_6)$	-12.51	-13.81	-12.19	-10.46	-10.17	-10.02
D	$r(N_3 \cdots H_2)$	1.882	1.842	1.875	1.906	1.917	1.931	$r(H_5 \cdots O_6)$	1.849	1.816	1.847	1.881	1.894	1.909
	$r(N_1-H_2)$	1.035	1.04	1.035	1.032	1.031	1.03	$r(N_4-H_5)$	1.032	1.036	1.032	1.029	1.028	1.026
	$E_H(N_1-H_2 \cdots N_3)$	-28.69	-32.88	-29.41	-26.58	-25.66	-24.57	$E_H(N_4-H_5 \cdots O_6)$	-29.88	-33.19	-29.91	-27.14	-26.11	-24.85

groups elongate these bonds in sequence, and the $-\text{N}_3$ group has tiny effects on these bonds.

BCPs and paths of intramolecular hydrogen bonds of all salts produced from QTAIM are shown in Fig. 2. The hydrogen bond energies ($E_{\text{H}}\text{s}$) of these salts are listed in Table 1. Parameters (ρ_{CB} , $\nabla^2\rho$, V_{BCP} , G_{BCP} and H_{BCP}) related to BCP are supplied in Table S1 as supporting information. The absolute values of ρ_{CB} , $\nabla^2\rho$, V_{BCP} , G_{BCP} and E_{H} increase with the decrease in hydrogen bond length. This implies that these parameters are sensitive to hydrogen bond length. Therefore, these parameters can be regarded as indicators of the strength of the hydrogen bond. According to the identification rule of hydrogen bond proposed by Rozas et al. [33] (i.e., $\nabla^2\rho > 0$ and $H_{\text{BCP}} > 0$ for weak hydrogen bonds, $\nabla^2\rho > 0$ and $H_{\text{BCP}} < 0$ for medium and strong hydrogen bonds, and $\nabla^2\rho < 0$ and $H_{\text{BCP}} < 0$ for very strong ones), the hydrogen bonds of A and B series salts are all strong, the salt of C series has one strong and one weak hydrogen bond, and the salt of D series has two weak hydrogen bonds. The total hydrogen bond energies $E_{\text{H,totS}}$ (Table 3) of the salts with the same anion follow the order of $\text{B} > \text{C} > \text{A} > \text{D}$. In light of the results of hydrogen bond strengths and $E_{\text{H,totS}}$ of salts with the same anion, we conclude that the ability to form hydrogen bonds of these cations is $\text{NH}_3\text{OH}^+ > \text{N}_2\text{H}_5^+ > \text{NH}_4^+ > \text{C}(\text{NH}_2)_3^+$. This order is the same as that obtained from the bond lengths and opposite to that of basicity ($\text{p}K_{\text{b}}$) of the corresponding bases [34]: $\text{D} (0.29) > \text{A} (4.79) > \text{C} (5.9) > \text{B} (8.03)$, i.e., the cation of the weaker base has a stronger ability to form hydrogen bonds. This is because the weaker base results in weaker attraction between the proton and base, which is helpful for the proton to form a hydrogen bond with the anion.

The absolute values of the $\text{H}2 \cdots \text{N}3$ hydrogen bond energy of salts with the same cation are in the order $\text{II} > \text{I} > \text{III} > \text{IV} > \text{V} > \text{VI}$ (but $\text{DIII} > \text{DI}$) which is totally contrary to the order of the $\text{H}2 \cdots \text{N}3$ bond lengths. The effects of all groups except $-\text{N}_3$ on the $\text{H}2 \cdots \text{N}3$ hydrogen bond energy are obvious. For the A series, the $-\text{NH}_2$ group improves this energy by 15 % ($= \frac{E_{\text{H}}(\text{AII}) - E_{\text{H}}(\text{AI})}{E_{\text{H}}(\text{AI})}$), while $-\text{ONO}_2$, $-\text{NF}_2$, $-\text{NO}_2$ and $-\text{N}_3$ decrease it by 14 %, 24 %, 30 % and 2 %, respectively. In comparison with AI, $-\text{NH}_2$, $-\text{N}_3$, $-\text{ONO}_2$, $-\text{NF}_2$ and $-\text{NO}_2$ groups change the $\text{H}2 \cdots \text{N}3$ length by only -2.16 %, 0.4 %, 2.27 %, 3.49 % and 3.93 %, respectively. So E_{H} is more sensitive to the substituent group than is the hydrogen bond length. For series B–D, the variations in the $\text{H}2 \cdots \text{N}3$ hydrogen bond energy caused by these groups are similar to those of the A series. For the $\text{H}5 \cdots \text{O}6$ hydrogen bond energies of series B–D, the $-\text{NH}_2$ group improves these energies by 10–12 %, the $-\text{ONO}_2$, $-\text{NF}_2$ and $-\text{NO}_2$ groups decrease these energies by 6–16 %, 8–19 % and 12–20 %, respectively. The $-\text{N}_3$ group changes this energy by only 3 %, -3 % and 0 for the B, D and D series, respectively. The absolute values of $E_{\text{H,totS}}$ of salts with the same cation are in the order $\text{II} > \text{I} > \text{III} > \text{IV} >$

$\text{V} > \text{VI}$ (but $\text{DIII} > \text{DI}$), i.e., the $-\text{NH}_2$ group improves $E_{\text{H,totS}}$ while the $-\text{ONO}_2$, $-\text{NF}_2$ and $-\text{NO}_2$ groups decrease $E_{\text{H,totS}}$ in sequence, and the $-\text{N}_3$ group has only a tiny effect on $E_{\text{H,totS}}$.

It is well known that hydrogen bonds are helpful in improving the stability of salts, and previous investigations have shown that stronger hydrogen bond interactions are tightly correlated to higher stability of the salt [32, 22]. According to the above conclusions, the order of the ability to improve the stability of the salts is $\text{NH}_3\text{OH}^+ > \text{N}_2\text{H}_5^+ > \text{NH}_4^+ > \text{C}(\text{NH}_2)_3^+$ for cations and $-\text{NH}_2 > -\text{H} > -\text{N}_3 > -\text{ONO}_2 > -\text{NF}_2 > -\text{NO}_2$ for substituents.

Other intramolecular interactions

The second-order perturbation energy (E_2) from orbital interactions is usually called the stabilization energy. In this paper, $E_{2\text{s}}$ between the lone pairs $\text{LP}(\text{N}3)$, $\text{LP}(\text{N}6)$ or $\text{LP}(\text{O}6)$ of anions and the $\sigma^*(\text{N}1-\text{H}2)$ or $\sigma^*(\text{N}4-\text{H}5)$ of cations were evaluated and the results are listed in Table 2. $E_{2\text{s}}$ from the different orbital interactions of the salts with the same cation generally have the order of $\text{II} > \text{I} > \text{III} > \text{IV} > \text{V} > \text{VI}$. Just like the effects on $E_{\text{H}}\text{s}$, $E_{2\text{s}}$ are improved by the $-\text{NH}_2$ group, while successively decreased by the $-\text{ONO}_2$, $-\text{NF}_2$ and $-\text{NO}_2$ groups. The effect of the $-\text{N}_3$ group is slight; the largest deviation caused by the $-\text{N}_3$ group is only $1.29 \text{ kcal mol}^{-1}$.

$E_{2\text{s}}$ of $\text{LP}(\text{N}3) \rightarrow \sigma^*(\text{N}1-\text{H}2)$ of series A–C salts with the same anion are comparable (the largest deviation is about $2.9 \text{ kcal mol}^{-1}$) and are obviously larger than the corresponding values of the D series (the least deviation between the D series and series A–C is $23.59 \text{ kcal mol}^{-1}$). This phenomenon should be related to the fact that the $\text{H}2 \cdots \text{N}3$ bond lengths of series A–C salts with the same anion are close to each other and are distinctly smaller than those of the D series (for example, the $\text{H}2 \cdots \text{N}3$ bond lengths are 1.623 \AA , 1.624 \AA , 1.632 \AA and 1.882 \AA for AI–DI, respectively). The $E_{2\text{s}}$ of $\text{LP}(\text{N}6) \rightarrow \sigma^*(\text{O}4-\text{H}5)$ of C series salts are obviously smaller than the corresponding values of series B and D, which is consistent with the fact that the $\text{H}5 \cdots \text{N}6$ bond lengths of the C series are obviously larger than those of the B and D series. In light of these conclusions, E_2 should be tightly related with the hydrogen bond length. Therefore, the relationships between the $\text{H} \cdots \text{N}$ or $\text{H} \cdots \text{O}$ length and the corresponding $E_{2\text{s}}$ were fitted, and the quadratic relationships found. The results are shown in Fig. 3. This figure clearly shows that $E_{2\text{s}}$ gradually decreases with elongation of the hydrogen bond.

The total second-order perturbation energies ($E_{2,\text{totS}}$) of all salts are listed in Table 3. $E_{2,\text{totS}}$ of the salts with the same cation have the order $\text{II} > \text{I} > \text{III} > \text{IV} > \text{V} > \text{VI}$, and $E_{2,\text{totS}}$ of the salts with the same anion decrease in the order $\text{B} > \text{C} > \text{A} > \text{D}$. A previous study reported that a larger $E_{2,\text{tot}}$ between the ions results in more stable compounds [22]. Therefore, it can be concluded that the abilities of groups to improve the stability of salts have the order of $-\text{NH}_2 > -\text{H} > -\text{N}_3 > -\text{ONO}_2 > -\text{NF}_2 > -$

Table 2 Orbital interactions and second-order perturbation energy (E_2 , in kcal mol⁻¹)

$E_2(\text{LP}(\text{N}3) \rightarrow \sigma^*(\text{N}1\text{-H}2))$	AI	AII	AIII	AIV	AV	AVI
	50.91	57.53	49.62	44.49	41.15	39.85
$E_2(\text{LP}(\text{N}3) \rightarrow \sigma^*(\text{N}1\text{-H}2))$	BI	BII	BIII	BIV	BV	BVI
	49.86	56.64	49.21	45.09	42.55	40.84
$E_2(\text{LP}(\text{O}6) \rightarrow \sigma^*(\text{O}4\text{-H}5))$	CI	CII	CIII	CIV	CV	CVI
	25.75	28.97	26.64	23.97	23.23	22.14
$E_2(\text{LP}(\text{N}3) \rightarrow \sigma^*(\text{N}1\text{-H}2))$	DI	DII	DIII	DIV	DV	DVI
	49.55	55.29	48.60	47.39	40.99	42.67
$E_2(\text{LP}(\text{N}6) \rightarrow \sigma^*(\text{O}4\text{-H}5))$	DI	DII	DIII	DIV	DV	DVI
	2.54	3.02	2.29	1.23	1.06	1.17
$E_2(\text{LP}(\text{N}3) \rightarrow \sigma^*(\text{N}1\text{-H}2))$	DI	DII	DIII	DIV	DV	DVI
	19.62	22.49	20.14	17.90	17.15	16.26
$E_2(\text{LP}(\text{N}6) \rightarrow \sigma^*(\text{O}4\text{-H}5))$	DI	DII	DIII	DIV	DV	DVI
	16.25	18.89	16.17	14.36	13.47	12.21

NO_2 , and the contributions of cations to the second-order perturbation energies decrease in the order of $\text{NH}_3\text{OH}^+ > \text{N}_2\text{H}_5^+ > \text{NH}_4^+ > \text{C}(\text{NH}_2)_3^+$.

In order to comprehensively elucidate the influences of different substituent groups and different cations on the intramolecular interactions between the cation and anion, the charge transfer, binding energy, dispersion energy and lattice energy were estimated. The energies of the frontier orbitals are also listed in Table 3. The variations of these parameters are plotted in Fig. 4.

The energies released upon formations of salts by the isolated ions are reflected in the E_b s values. A larger E_b means greater stabilization of the ions after formation of the salt. When the cation is the same, anions with the $-\text{NH}_2$ group give the largest E_b s, and anions with $-\text{N}_3$ and $-\text{H}$ lead to very similar E_b s. The E_b s of salts with $-\text{ONO}_2$, $-\text{NF}_2$ and $-\text{NO}_2$ groups are smaller than those of the salts in I series. In other words, the stabilization of anions with different substituents follows the order $-\text{NH}_2 > -\text{H} > -\text{N}_3 > -\text{ONO}_2 > -\text{NF}_2 > -\text{NO}_2$, when they form salts with the same cation, and stabilization of cations follows the order $\text{NH}_3\text{OH}^+ > \text{N}_2\text{H}_5^+ > \text{NH}_4^+ > \text{C}(\text{NH}_2)_3^+$ when they form salts with the same anion.

The values of q and E_{dis} of salts with the same cation have similar variation trends: $\text{II} > \text{I} \approx \text{III} > \text{IV} > \text{V} > \text{VI}$, i.e., these interactions are strengthened by the $-\text{NH}_2$ group, while weakened by the $-\text{ONO}_2$, $-\text{NF}_2$ and $-\text{NO}_2$ groups in sequence. The $-\text{N}_3$ group has hardly any obvious effect on these interactions.

Briefly, the intramolecular interactions of salts with the same cation and the same anion follow the order $\text{II} > \text{I} \approx \text{III} > \text{IV} > \text{V} > \text{VI}$ and $\text{B} > \text{C} > \text{A} > \text{D}$, respectively. In addition, the values of q obtained from NBO analysis (listed in Table S2) exhibit the same variation trends as that from Mulliken analysis.

Figure 4 shows that the variation trends of q , $E_{2,\text{tot}}$, E_b , E_{dis} and $E_{\text{H,tot}}$ of salts with the same cation are similar, which may imply that relationships exist between these parameters. Therefore, the relationships between q and $E_{2,\text{tot}}$, E_b , E_{dis} and $E_{\text{H,tot}}$ were fitted. Herein, only the fitted results of the B series are shown (Fig. 5) since they are similar for series A–D. As seen in Fig. 5, linear relationships exist between q and $E_{2,\text{tot}}$, E_b , E_{dis} and $E_{\text{H,tot}}$, and in fact a linear relationship exists between any two of them. This means that these intramolecular interactions are tightly related to each other. It is well known that the larger E_2 and E_{H} may lead to a more stable salt [22]. According to the above discussion, the larger E_2 and E_{H} also correspond to stronger intramolecular interactions, which may in turn result in a more stable salt. Therefore, the stabilities of salts with the same cation and the same anion have the order of $\text{II} > \text{I} \approx \text{III} > \text{IV} > \text{V} > \text{VI}$ and $\text{B} > \text{C} > \text{A} > \text{D}$, respectively.

For salts with the same cation, H_L s values follow the order $\text{I} > \text{II} > \text{VI} > \text{V} > \text{III} > \text{IV}$, i.e., all substituents decrease H_L . H_L s of salts with the same anion have the order of $\text{A} > \text{B} > \text{C} > \text{D}$. According to Eq. (10), H_L is determined mainly by the volume and type of salt. All title salts are of the XY type, i.e., the ratio of the number of cations to anions is 1:1. So the cationic and

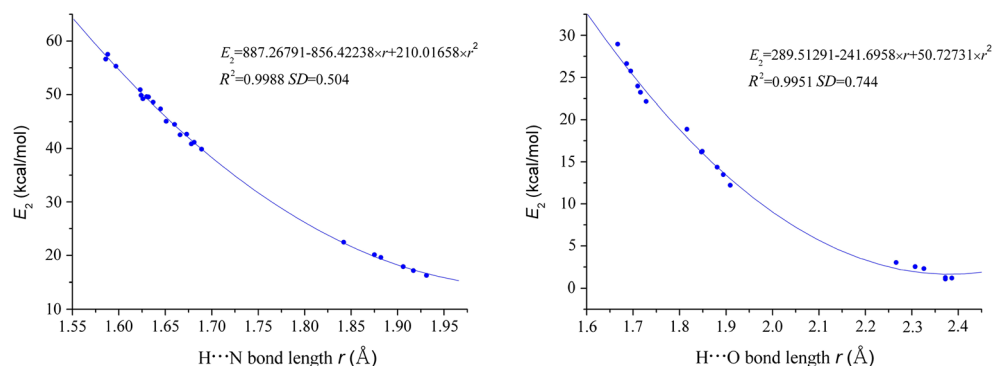
Fig. 3 Relationship between the distances of $\text{H} \cdots \text{N}$ and $\text{H} \cdots \text{O}$ hydrogen bonds and second-order perturbation energy (E_2 , in kcal mol⁻¹)

Table 3 Predicted total second-order perturbation energies ($E_{2,tot}$), lattice energy (H_L), binding energy (E_b), dispersion energy (E_{dis}), total hydrogen bond energies ($E_{H,tot}$), energy of the highest occupied

molecular orbitals (E_{HOMO}), energy of the lowest unoccupied molecular orbitals (E_{LUMO}), chemical stability (E_g) and net charge transfer (q) of all salts under investigation

Compound	q (e)	$E_{2,tot}$ (kcal mol ⁻¹)	E_b (kcal mol ⁻¹)	E_{dis} (kcal mol ⁻¹)	$E_{H,tot}$ (kcal mol ⁻¹)	H_L (kcal mol ⁻¹)	E_{HOMO} (eV)	E_{LUMO} (eV)	E_g (eV)
AI	0.251	50.91	-113.96	-3.86	-74.69	126.94	-4.96	-3.19	1.77
AII	0.275	57.53	-120.78	-3.90	-86.16	123.93	-4.83	-2.94	1.89
AIII	0.250	49.62	-111.17	-3.85	-72.64	121.11	-5.21	-3.39	1.82
AIV	0.234	44.49	-105.17	-3.76	-64.34	119.25	-5.17	-3.67	1.51
AV	0.225	41.15	-102.65	-3.69	-59.09	121.63	-5.45	-3.60	1.85
AVI	0.221	39.85	-99.91	-3.70	-57.25	121.91	-5.59	-3.69	1.90
BI	0.345	75.61	-132.21	-5.31	-124.97	124.84	-5.31	-3.56	1.75
BII	0.371	85.61	-140.46	-5.35	-143.28	121.90	-5.17	-3.28	1.89
BIII	0.345	75.85	-129.68	-5.29	-126.11	119.30	-5.55	-3.75	1.80
BIV	0.329	69.06	-123.77	-5.26	-114.79	117.57	-5.48	-3.94	1.55
BV	0.318	65.78	-120.75	-5.20	-109.41	119.78	-5.82	-4.02	1.80
BVI	0.311	62.98	-117.52	-5.18	-104.77	120.04	-5.91	-4.06	1.85
CI	0.279	52.09	-117.08	-5.09	-85.73	123.84	-5.05	-3.28	1.77
CII	0.303	58.31	-124.25	-5.20	-98.05	121.01	-4.94	-3.05	1.89
CIII	0.275	50.89	-114.30	-5.13	-84.1	118.50	-5.31	-3.50	1.81
CIV	0.264	48.62	-107.72	-4.91	-79.47	116.83	-5.17	-3.67	1.50
CV	0.247	42.05	-105.42	-4.85	-71.91	118.96	-5.55	-3.71	1.84
CVI	0.248	43.84	-101.98	-4.76	-70.6	119.21	-5.58	-3.70	1.88
DI	0.259	35.87	-99.12	-5.13	-58.57	119.16	-4.64	-2.87	1.77
DII	0.278	41.38	-105.13	-5.22	-66.07	116.82	-4.55	-2.66	1.89
DIII	0.259	36.31	-97.03	-5.15	-59.32	114.70	-4.93	-3.12	1.81
DIV	0.244	32.26	-91.78	-5.07	-53.72	113.28	-4.86	-3.43	1.43
DV	0.237	30.62	-89.92	-5.00	-51.77	115.10	-5.16	-3.32	1.84
DVI	0.230	28.47	-87.31	-4.93	-49.42	115.30	-5.25	-3.42	1.83

anionic volumes are the only influence factors. The substituent groups naturally increase the volumes of anions, and the larger anionic volume certainly results in the smaller H_L , so the lattice energies of series II–VI salts are all smaller than those of the I series. The order of cationic volumes is $NH_4^+ <$

$NH_3OH^+ < N_2H_5^+ < C(NH_2)_3^+$, which naturally results in the opposite order of H_L s for salts with the same anion.

Inspection of Table 3 reveals that the energies of the highest occupied molecular orbitals (E_{HOMO} s) and the lowest unoccupied molecular orbitals (E_{LUMO} s) of series II–VI salts with the

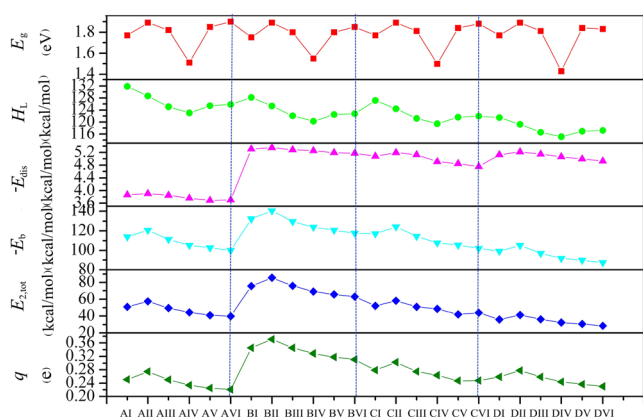


Fig. 4 Variations in net charge transfer (q), total second-order perturbation energies ($E_{2,tot}$), binding energy (E_b), dispersion energy (E_{dis}), lattice energy (H_L) and chemical stability (E_g)

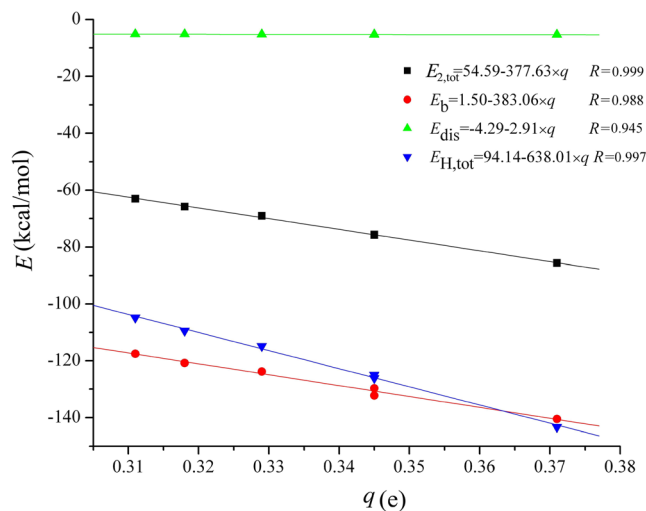


Fig. 5 Relationships between q and $E_{2,tot}$, E_b , E_{dis} and $E_{H,tot}$

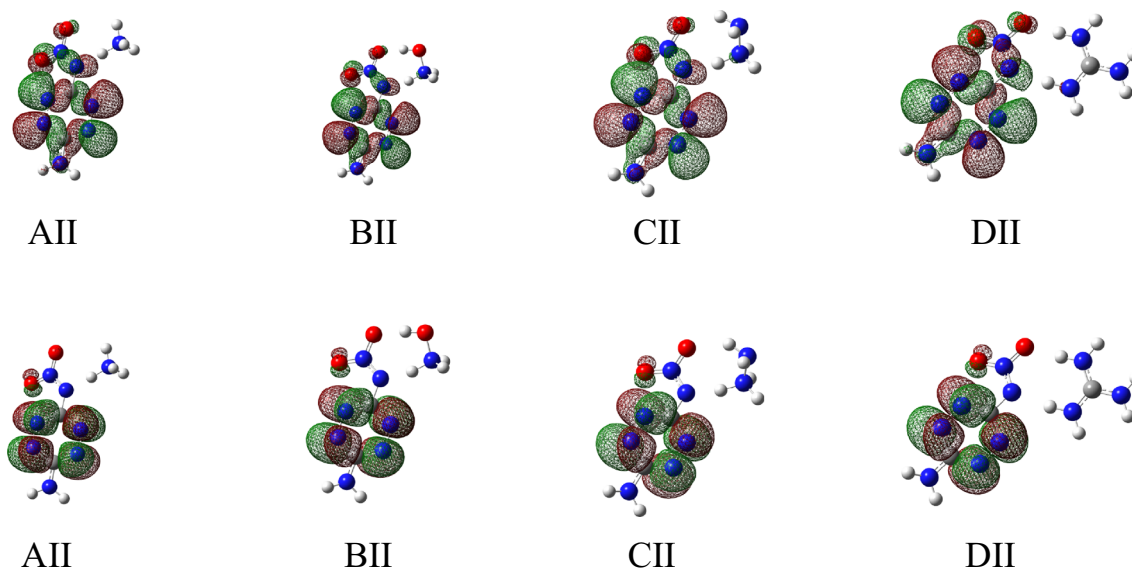


Fig. 6 Highest occupied molecular orbitals (HOMOs, top) and lowest unoccupied molecular orbitals (LUMOs, bottom) of series II

same cation are obviously different from those of the I series. This implies that these groups have distinct effects on HOMOs and LUMOs. The order of E_g generally is II>VI>V>III>I>IV, i.e., all substituent groups except $-\text{ONO}_2$ are helpful for

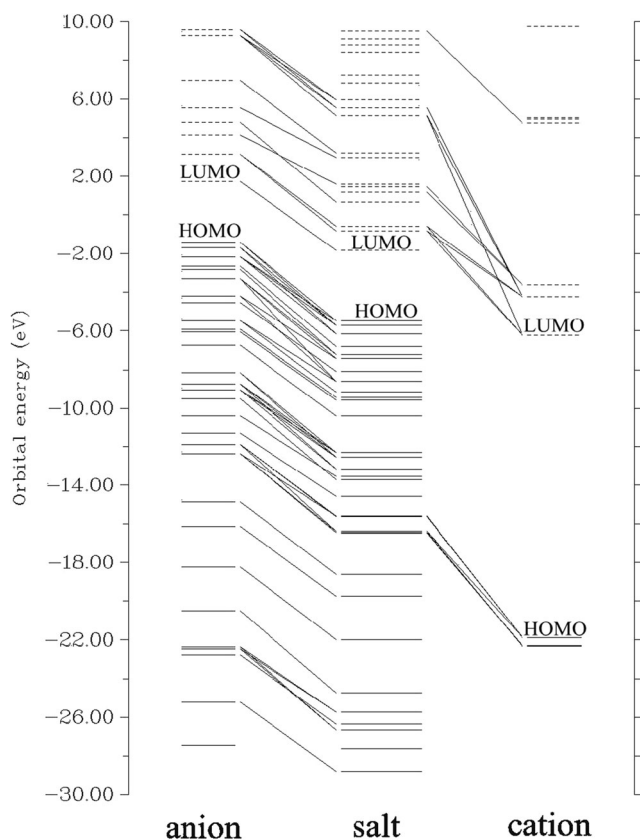


Fig. 7 Orbital interaction diagram of AI. *Solid lines* Occupied orbitals, *dashed lines* virtual orbitals

improving E_g , i.e., chemical stability. It is worth noting that salts with the same anion have very close E_g s (for example, the E_g s of AIII–DIII are 1.82 eV, 1.80 eV, 1.81 eV and 1.81 eV, respectively), so the effects of different cations on E_g are negligible. In view of the fact that E_g is determined mainly by the anion, HOMO and LUMO should be contributed from that anion. This is verified by the 3D frontier orbital distributions shown in Fig. 6. Since all salts have similar frontier orbital distributions, only those of series II are shown. Obviously, HOMOs and LUMOs are derived from completely anions, cations make hardly any contribution to these frontier orbitals. In addition, the shapes of HOMOs and LUMOs of the salts with the same anion are almost the same, with different cations having hardly any effects.

The contributions of the orbitals of isolated ions to the frontier orbitals of the salts can be seen clearly in orbital interaction diagrams. Since all the salts here have similar orbital interaction diagrams, only that of AI is shown (Fig. 7). The orbital interaction diagram shows that the HOMO (the highest solid line) and LUMO (the lowest dashed line) of the salt are both contributed from the HOMO and LUMO of the anion in the isolated state. The frontier orbitals of the isolated cation make no contribution. The occupied and vacant orbitals of the individual anion correspond to the corresponding occupied and vacant orbitals of the salts, which means that the symmetries of the orbitals are conserved when the individual ions form salts according to the Woodward-Hoffman rule [35].

Aromaticity

Aromaticity is an important concept in physical organic chemistry [36, 37]. It is useful in the rationalization of structure,

Table 4 Values of nucleus-independent chemical shifts (NICS)(1)_{ZZS} (in ppm) of all salts

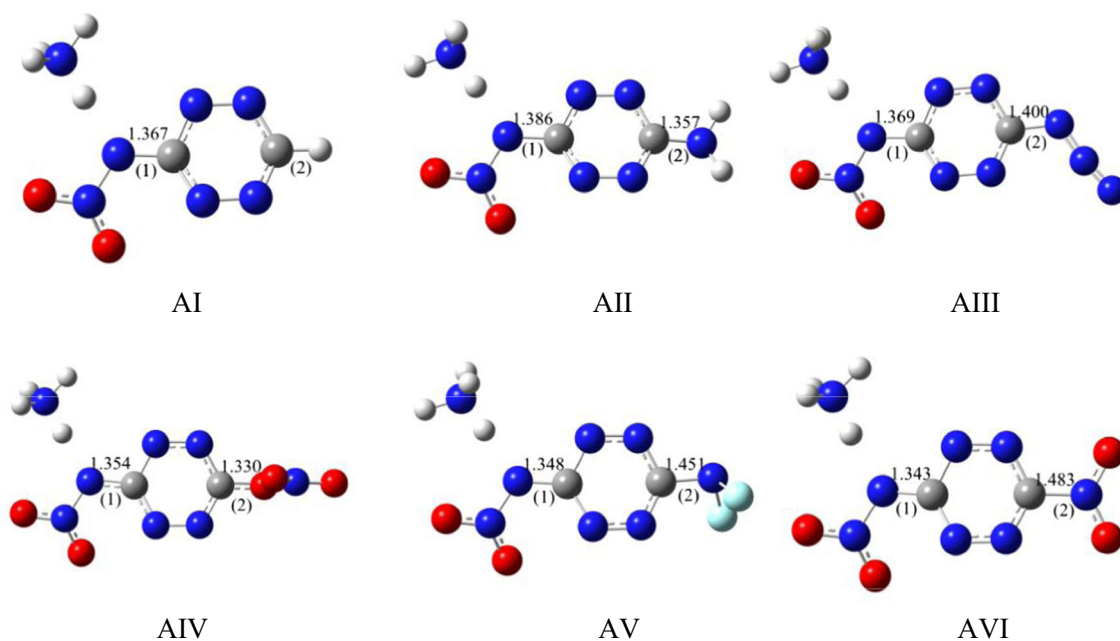
	I	II	III	IV	V	VI
A	-10.0230	-13.5312	-20.0748	-21.3985	-20.4782	-20.2531
B	-5.2529	-7.4579	-18.8560	-26.1249	-21.3279	-20.5292
C	-5.3284	-7.8117	-19.8001	-24.7078	-19.6265	-18.8899
D	-2.4981	-8.1969	-9.5252	-25.8049	-12.1491	-11.6217

stability, and reactivity of molecules. However, because of its multiple manifestations, as yet there is no generally accepted quantitative definition of aromaticity. Among the many indexes of aromaticity, a magnetic criterion, nucleus-independent chemical shifts (NICS) [38] is most widely used due to its simplicity and efficiency. An earlier study [39] showed that NICS(1)_{ZZ}, i.e., the NICS calculated at the point 1 Å above (or below) the ring center, is a better index than the original definition of NICS, known as NICS(0). Here, the NICS(1)_{ZZS} of these salts were estimated at the B3LYP/6-31+G*/B97D/aug-cc-pvdz level. The definition of the ring center was highly arbitrary, with the geometry or mass center being used first. Use of the ring critical point (RCP) of AIM (atoms in molecule) theory as the ring center has also been recommended [40]. In this paper, the RCPs were estimated using Multiwfn and used as the ring centers. Multiwfn was also employed to calculate NICS(1)_{ZZS}.

The calculated NICS(1)_{ZZS} (Table 4) of these salts are all negative, i.e., they are all aromatic [38]. Previous studies [38, 41] revealed that the more negative the NICS(1)_{ZZ}, the stronger the aromaticity of the compound. The aromaticities of A–D series salts follow the order of IV>V>VI>III>II>I, which means that these groups are helpful in improving aromaticity.

The ability to improve aromaticity is strongest for the –ONO₂ group, and for other groups it decreases gradually in the order –NF₂>–NO₂>–N₃>–NH₂. The effects of cations on aromaticity are not coincident. Generally speaking, salts with NH₄⁺ have the strongest aromaticity, and those of the salts with NH₃OH⁺ and N₂H₅⁺ are comparable.

The atoms of substituents that connect directly with the tetrazine ring and participate in delocalization may improve the aromaticity of the ring. Figure 8 shows the delocalized bonds between the ring and the substituents of AI–AVI. The delocalized bonds of a salt are numbered as bond (1) and bond (2) (see Fig. 8). The lengths of bond (1) of AI–AVI are 1.367, 1.386, 1.369, 1.354, 1.348 and 1.343 Å, respectively. The C–N and C=N bond lengths of CH₃NH₂ and CH₂NH are 1.476 and 1.280 Å at the same level, respectively. So the lengths of bond (1) of the A series are between those of the C–N and C=N bonds, i.e., this bond is delocalized. And the delocalization degree has the order of AVI>AV>AIV>AI>AIII>AII. The order is generally in agreement with the order of the ability of electron-withdrawing of the substituent groups [42], which means that the stronger electron-withdrawing ability of the substituent group leads to the more delocalized bond (1). The lengths of bond (1) of AI and AIII are very similar, i.e., the –

**Fig. 8** Structures of AI–AVI with delocalized bonds

N_3 group has little effect on this bond. Bond (2) is the C–N bond for AII, AIII, AV and AVI and the C–O bond for AIV. The lengths are 1.357, 1.400, 1.451 and 1.483 Å in AII, AIII, AV and AVI, respectively, so the delocalization gradually weakens and in AVI it is actually localized. The delocalization of the C–N bonds in AII and AIII is much more obvious, so their aromaticities are stronger than that of AI. The length of bond (2) of AIV is 1.330 Å, which is smaller than that (1.437 Å) of CH_3OH and larger than that (1.214 Å) of CH_2O . So the delocalization of bond (2) in AIV is large, which is very helpful in improving the aromaticity of AIV and leads to the aromaticity of AIV being stronger than that of AV and AVI.

Conclusions

The ability of substituent groups to improve hydrogen bonding interactions decreases in the order $-NH_2 > -H \approx -N_3 > -ONO_2 > -NF_2 > -NO_2$. The abilities of cations to form hydrogen bonds follow the order $NH_3OH^+ > N_2H_5^+ > NH_4^+ > C(NH_2)_3^+$. The effects of substituent groups and cations on the other intramolecular interactions are same as on the hydrogen bonding interactions. Linear relationships exist between q , $E_{2,tot}$, E_b , E_{dis} and $E_{H,tot}$. Stronger intramolecular interactions lead to more stable salts. The stabilities of salts with the same cation and the same anion are in the order $II > I \approx III > IV > V > VI$ and $B > C > A > D$, respectively.

All substituents except $-ONO_2$ improve E_g , and cations have no effect on frontier orbital distribution and E_g . All substituents improve aromaticity, following the order $-ONO_2 > -NF_2 > -NO_2 > -N_3 > -NH_2$.

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References

- Huang Y, Gao H, Twamley B, Shreeve JM (2008) Nitroamino triazoles: nitrogen-rich precursors of stable energetic salts. *Eur J Inorg Chem* 2008(16):2560–2568
- Ji NN, Shi ZQ, Zhao RG, Zheng ZB, Li ZF (2010) Synthesis, crystal structure and quantum chemistry of a novel schiff base N-(2,4-dinitro-phenyl)-N'-(1-phenyl-ethylidene)-hydrazine. *Bull Korean Chem Soc* 31:881–886
- Klapötke TM, Mayer P, Miró Sabaté C, Welch JM, Wiegand N (2008) Simple, nitrogen-rich, energetic salts of 5-nitrotetrazole. *Inorg Chem* 47(13):6014–6027
- Xue H, Arritt SW, Twamley B, Shreeve JM (2004) Energetic salts from N-aminoazoles. *Inorg Chem* 43(25):7972–7977
- MacFarlane D, Forsyth S, Golding J, Deacon G (2002) Ionic liquids based on imidazolium, ammonium and pyrrolidinium salts of the dicyanamide anion. *Green Chem* 4(5):444–448
- Hiskey MA, Goldman N, Stine JR (1998) High-nitrogen energetic materials derived from azotetrazolate. *J Energy Mater* 16(2–3):119–127
- Singh RP, Verma RD, Meshri DT, Shreeve JM (2006) Energetic nitrogen-rich salts and ionic liquids. *Angew Chem Int Ed* 45(22):3584–3601
- Venkatachalam S, Santhosh G, Ninan Ninan K (2004) An overview on the synthetic routes and properties of ammonium dinitramide (ADN) and other dinitramide salts. *Propell Explos Pyrotechnics* 29(3):178–187
- Boldyrev V (2006) Thermal decomposition of ammonium perchlorate. *Thermochim Acta* 443(1):1–36
- Lu LM, Sun XM, Li JX, Ma YH (2009) Determination of hydrazinium nitroformate content by UV-spectrophotometry. *Chin J Explos Propell* 32(2):84–86
- Talawar M, Sivabalan R, Mukundan T, Muthurajan H, Sikder A, Gandhe B, Rao AS (2009) Environmentally compatible next generation green energetic materials (GEMs). *J Hazard Mater* 161(2):589–607
- Cui JH, Han JY, Wang JG, Huang R (2010) Study on the crystal structure and hygroscopicity of ammonium dinitramide. *J Chem Eng Data* 55(9):3229–3234
- Dendage P, Sarwade D, Asthana S, Singh H (2001) Hydrazinium nitroformate (HNF) and HNF based propellants: a review. *J Energy Mater* 19(1):41–78
- Chavez DE, Hiskey MA (1999) 1,2,4,5-Tetrazine based energetic materials. *J Energy Mater* 17:357–377
- Gao H, Wang R, Twamley B, Hiskey MA, Jean'ne MS (2006) 3-Amino-6-nitroamino-tetrazine (ANAT)-based energetic salts. *Chem Commun* 38:4007–4009
- Bottaro JC, Penwell PE, Ross DS, Schmitt RJ (1993) Dinitramide salts and method of making same. US Patent No. 5254324
- Williams GK, Brill TB (1995) Thermal decomposition of energetic materials 67. Hydrazinium nitroformate (HNF) rates and pathways under combustionlike conditions. *Combust Flame* 102(3):418–426
- Liu H, Wang F, Wang GX, Gong XD (2012) Theoretical investigations on structure, density, detonation properties, and sensitivity of the derivatives of PYX. *J Comput Chem* 33(22):1790–1796
- Wang GX, Gong XD, Liu Y, Du HC, Xu XJ, Xiao HM (2011) Looking for high energy density compounds applicable for propellant among the derivatives of DPO with N_3 , ONO_2 , and NNO_2 groups. *J Comput Chem* 32(5):943–952
- Zhang XL, Liu Y, Wang F, Gong XD (2014) A theoretical study on the structure, intramolecular interactions, and detonation performance of hydrazinium dinitramide. *Chem Asian J* 9(1):229–236
- Zhang XL, Gong XD (2014) Screening nitrogen-rich bases and oxygen-rich acids for forming highly stable salts by theoretical calculations. *Chem Phys Chem* 15:2281–2287
- Wang F, Du HC, Liu H, Gong XD (2012) Hydrogen-bonding interactions and properties of energetic nitroamino [1,3,5]triazine-based guanidinium salts: DFT-D and QTAIM studies. *Chem Asian J* 7:2577–2591
- Grimme S (2006) Semiempirical GGA-type density functional constructed with a long-range dispersion correction. *J Comput Chem* 27(15):1787–1799
- Glendening E, Badenhoop J, Reed A, Carpenter J, Bohmann J, Morales C, Weinhold F (2001) NBO, Version 5.0. Theoretical Chemistry Institute, University of Wisconsin, Madison
- Lu T, Chen F (2012) Multiwfn: A multifunctional wavefunction analyzer. *J Comput Chem* 33(5):580–592
- Frisch MJ, Trucks GW, Schlegel HB, Scuseria GE, Robb MA, Cheeseman JR, Montgomery JA, Vreven T, Kudin KN, Burant JC, Millam JM, Iyengar SS, Tomasi J, Barone V, Mennucci B, Cossi M, Scalmani G, Rega N, Petersson GA, Nakatsuji H, Hada M, Ehara M, Toyota K, Fukuda R, Hasegawa J, Ishida M, Nakajima T, Honda Y, Kitao O, Nakai H, Klene M, Li X, Knox JE, Hratchian HP, Cross

- JB, Bakken V, Adamo C, Jaramillo J, Gomperts R, Stratmann RE, Yazyev O, Austin AJ, Cammi R, Pomelli C, Ochterski JW, Ayala PY, Morokuma K, Voth GA, Salvador P, Dannenberg JJ, Zakrzewski VG, Dapprich S, Daniels AD, Strain MC, Farkas O, Malick DK, Rabuck AD, Raghavachari K, Foresman JB, Ortiz JV, Cui Q, Baboul AG, Clifford S, Cioslowski J, Stefanov BB, Liu G, Liashenko A, Piskorz P, Komaromi I, Martin RL, Fox DJ, Keith T, Al-Laham MA, Peng CY, Nanayakkara A, Challacombe M, Gill PMW, Johnson B, Chen W, Wong MW, Gonzalez C, Pople JA (2004) Gaussian 03, Revision C02. Gaussian, Inc, Wallingford
27. Espinosa E, Molins E, Lecomte C (1998) Hydrogen bond strengths revealed by topological analyses of experimentally observed electron densities. *Chem Phys Lett* 285(3):170–173
28. Politzer P, Martinez J, Murray JS, Concha MC (2010) An electrostatic correction for improved crystal density predictions of energetic ionic compounds. *Mol Phys* 108(10):1391–1396
29. Jenkins HDB, Tudela D, Glasser L (2002) Lattice potential energy estimation for complex ionic salts from density measurements. *Inorg Chem* 41(9):2364–2367
30. Gao H, Ye C, Piekarski CM, Shreeve JM (2007) Computational characterization of energetic salts. *J Phys Chem C* 111(28):10718–10731
31. Gorelsky SI, Ghosh S, Solomon EI (2006) Mechanism of N₂O reduction by the μ_4 -S tetranuclear Cu₂ cluster of nitrous oxide reductase. *J Am Chem Soc* 128(1):278–290
32. Klapötke TM, Sabaté CM, Stierstorfer J (2008) Hydrogen-bonding stabilization in energetic perchlorate salts: 5-Amino-1H-tetrazolium perchlorate and its adduct with 5-amino-1H-tetrazole. *Z Anorg Allg Chem* 634(11):1867–1874
33. Rozas I, Alkorta I, Elguero J (2000) Behaviour of ylides containing N, O and C atoms as hydrogen bond acceptors. *J Am Chem Soc* 122: 11154–11161
34. Williams R, Jencks W, Westheimer F (2004) pKa data compiled by R Williams. http://research.chem.psu.edu/brpgrp/pKa_compilation.pdf
35. Hoffmann R (1969) Symmetry requirements for the stabilization of one class of diradicals. *J Chem Soc Chem Commun* 5: 240–241
36. von Ragué SP, Manoharan M, Wang ZX, Kiran B, Jiao H, Puchta R, van Eikema Hommes NJ (2001) Dissected nucleus-independent chemical shift analysis of π -aromaticity and antiaromaticity. *Org Lett* 3(16):2465–2468
37. Krygowski TM, Cyranski MK (2001) Structural aspects of aromaticity. *Chem Rev* 101(5):1385–1420
38. Schleyer PR, Maerker C, Dransfeld A, Jiao H, Hommes NJE (1996) Nucleus-independent chemical shifts: a simple and efficient aromaticity probe. *J Am Chem Soc* 118(26):6317–6318
39. Fallah-Bagher-Shaidaei H, Wannere CS, Corminboeuf C, Puchta R, Schleyer PR (2006) Which NICS aromaticity index for planar π rings is best? *Org Lett* 8(5):863–866
40. Howard S, Krygowski T (1997) Benzenoid hydrocarbon aromaticity in terms of charge density descriptors. *Can J Chem* 75(9):1174–1181
41. Chen Z, Wannere CS, Corminboeuf C, Puchta R, Schleyer PR (2005) Nucleus-independent chemical shifts (NICS) as an aromaticity criterion. *Chem Rev* 105(10):3842–3888
42. Nie C (2000) Calculation of group electronegativity. *J Wuhan Univ* 46:176–180