

## Theoretical studies on the stability of the salts formed by DTDO with HNO<sub>3</sub> and HN(NO<sub>2</sub>)<sub>2</sub>

XUELI ZHANG, JUNQING YANG and XUEDONG GONG\*

Department of Chemistry, Nanjing University of Science and Technology, Nanjing 210094 (P.R. China)  
e-mail: gongxd325@mail.njust.edu.cn

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**Abstract.** Three stable conformations of salts formed from 3,6-diguanidino-1,2,4,5-tetrazine-1,4-di-N-oxide (DTDO) and HNO<sub>3</sub> and HN(NO<sub>2</sub>)<sub>2</sub> were studied using the density functional theory. For two salts, free energies ( $G$ s) and total energies ( $E$ s) of the three conformations increase in the same order. Intramolecular interactions in the three conformations, such as the hydrogen bonding interaction ( $E_H$ ), the charge transfer ( $q$ ), the binding energy ( $E_b$ ), the dispersion energy ( $E_{dis}$ ) and the second-order perturbation energy ( $E_2$ ), decrease in completely opposite order to that of  $G$ s and  $E$ s. Different conformations have distinct effects on the chemical stabilities and UV stabilities of two salts. Aromaticities of tetrazine in different conformations are slightly different. Although stabilities of the three conformations are different, their values are comparable.

**Keywords.** Salts; conformations; stability; density functional theory, energetic materials.

### 1. Introduction

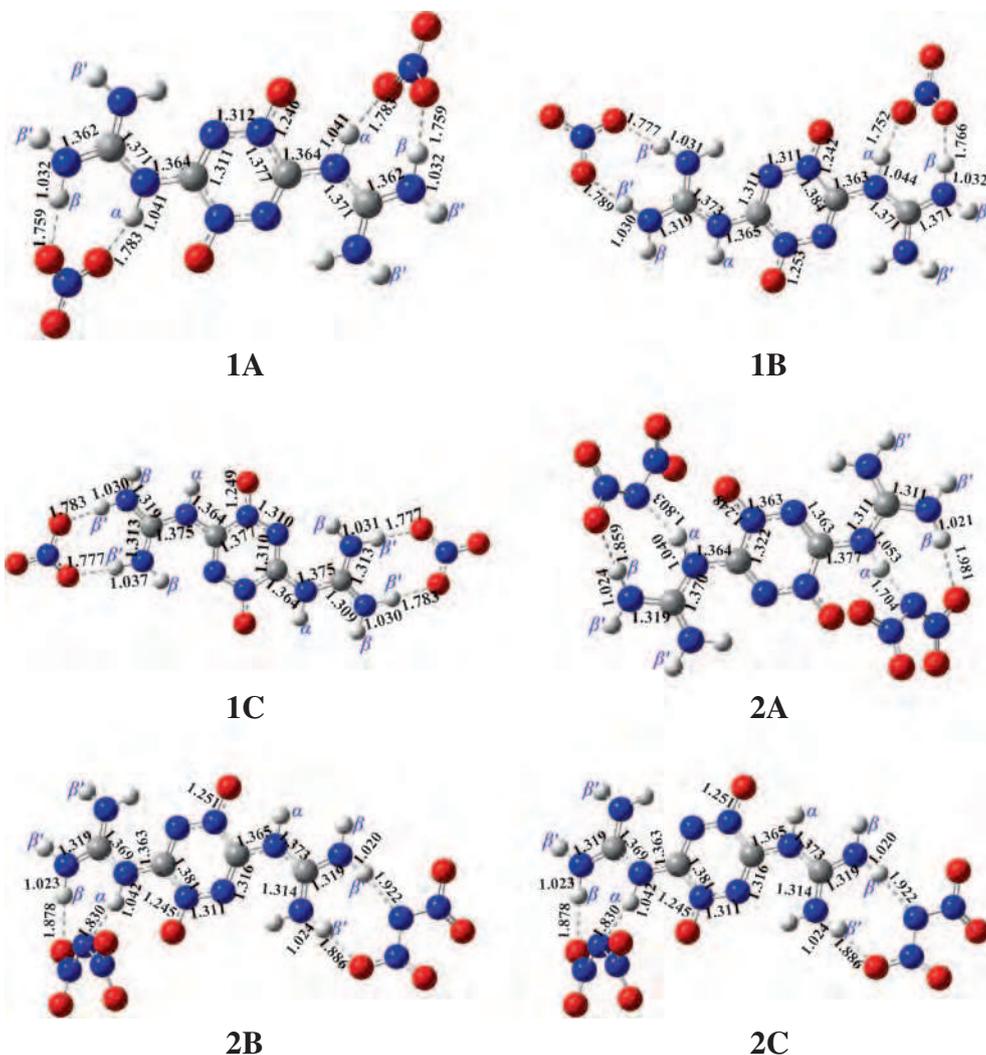
Recently, there has been considerable interest in tetrazine derivatives.<sup>1,2</sup> Syntheses and properties of various ionic salts based on 1,2,4,5-tetrazine such as 3,6-diguanidino-1,2,4,5-tetrazine, 3,6-diguanidino-1,2,4,5-tetrazine-1,4-di-N-oxide, and 3,6-dihydrazino-1,2,4,5-tetrazine, etc., have been reported.<sup>2–5</sup> These salts were conveniently prepared by reactions of the bases (tetrazines) with various acids. They have positive heats of formation (HOFs), high crystal densities, and acceptable oxygen balances (OBs) because of their high nitrogen content, low carbon and hydrogen contents, which make them good explosives.<sup>2,4</sup> Chavez *et al.* discovered<sup>2</sup> that these materials were surprisingly insensitive towards destructive stimuli such as impact, friction and electrostatic discharge. Therefore, they may be potential candidates for energetic materials with high stability and performance.

The experimental study<sup>2</sup> reported that the salt formed from 3,6-diguanidino-1,2,4,5-tetrazine-1,4-di-N-oxide (DTDO) and HClO<sub>4</sub> has a higher density (1.94 g/cm<sup>3</sup>) and a higher OB (-7%) than the salt formed from 3,6-diguanidino-1,2,4,5-tetrazine (DGT) and HClO<sub>4</sub> ( $\rho = 1.90$  g/cm<sup>3</sup>, OB = -16%). Although the decomposition temperature ( $T_d = 196^\circ\text{C}$ ) of the former is lower than that of the latter ( $T_d = 265^\circ\text{C}$ ), its thermal stability is still quite good.<sup>2</sup> Therefore, DTDO is the preferred base for producing energetic salts. Since the explosion

product (HCl) of the salt of HClO<sub>4</sub> pollutes environment, nitrate and dinitramide have been widely used as counter anions to synthesize energetic salts, such as ammonium nitrate<sup>6,7</sup> and ammonium dinitramide,<sup>8,9</sup> for which the detonation products are environment-friendly. The thermal stability of the salt (**1**) formed by DTDO with two HNO<sub>3</sub> is acceptable ( $T_d = 157^\circ\text{C}$ ). And according to our previous study,<sup>10</sup> many properties of ionic salts of NO<sub>3</sub> and N(NO<sub>2</sub>)<sub>2</sub> are comparable, so the thermal stability of the salt (**2**) formed from DTDO and HN(NO<sub>2</sub>)<sub>2</sub> should be acceptable too. Salts **1** and **2** may be potential candidates for energetic materials.

For salts **1** and **2**, the cation has a +2 charge (DTDO<sup>2+</sup>). DTDO<sup>2+</sup> and three types of hydrogen atoms ( $\alpha$ -H,  $\beta$ -H and  $\beta'$ -H) (cf. figure 1). These hydrogen atoms can form different intramolecular hydrogen bonds with the oxygen-rich anions and lead to different isomeric molecular structures (figure 1). It is well known that the molecular properties are determined by its structure. The different conformations certainly bring different stabilities of salts **1** and **2**. Our previous studies<sup>10,11</sup> have shown that the stability and density are tightly related to intramolecular interactions, which can be reflected by the hydrogen bonding interaction ( $E_H$ ), the charge transfer ( $q$ ), the binding energy ( $E_b$ ), and the second-order perturbation energy ( $E_2$ ), etc., between the cation and anion.<sup>11,12</sup> In this paper, these interactions in salts **1** and **2** were evaluated. The frontier molecular orbitals and UV spectra were also computed to estimate the effects of conformations on chemical and UV stabilities.

\*For correspondence



**Figure 1.** Optimized geometries of **1** and **2** at the M062X/6-311++G\*\* level.

## 2. Computational

Geometry optimizations and vibrational analyses were conducted at the M062X/6-311++G\*\* and B97-D/aug-cc-pvdz levels of the density functional theory with dispersion corrections (DFT-D) using the Gaussian03 package.<sup>13</sup> Previous studies showed that the performance of M062X and B97-D for non-covalently bound systems including van der Waals complexes were exceptionally good.<sup>14–17</sup> Natural bond orbital (NBO)<sup>18</sup> analyses were performed at the M062X/6-311++G\*\* level to estimate the second order perturbation energy ( $E_2$ ).

The proportions ( $p_i$ s) of isomers in the equilibrium state can be obtained by the Boltzmann distribution equation (1):

$$p_i = \frac{e^{-E_i/RT}}{\sum_j e^{-E_j/RT}} = \frac{Q_i}{Q} \quad (1)$$

$$e^{-E_i/RT} = e^{-(\Delta E_i + E_{\text{Ref}})/RT} \quad (2)$$

$E_i$  is the total energy of conformation  $i$ ,  $E_{\text{Ref}}$  is the total energy of the reference conformation,  $\Delta E_i$  is the difference between  $E_i$  and  $E_{\text{Ref}}$ .

The QTAIM analyses were performed using Multiwfn<sup>19</sup> with the input files (.wfn) generated from Gaussian. The electron potential energy densities ( $V_{\text{BCPs}}$ ) at the bond critical points (BCPs) were obtained and used to predict the hydrogen-bond energy ( $E_{\text{H}}$ ) from the following relationship:<sup>20</sup>

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

The net charge transfer, which is the difference between the total number of donation and back donation electrons was calculated using the following equation with the Multiwfn program by conducting the extended charge decomposition analysis (ECDA):<sup>21</sup>

$$q = \text{CT}(Y \rightarrow X) - \text{CT}(X \rightarrow Y) \quad (4)$$

Where  $CT(Y \rightarrow X)$  is the charge transfer from the anion to cation and  $CT(X \rightarrow Y)$  is the charge transfer from the cation to anion after considering the electron polarization effect.<sup>21</sup>

The binding energy ( $E_b$ ) was obtained using the equation (5):

$$E_b = E_{\text{salt}} - E_{\text{cation}} - 2 \times E_{\text{anion}} + E_{\text{bsse}} \quad (5)$$

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

The predicted  $E_H$ , dispersion energy ( $E_{\text{dis}}$ ) and  $E_b$  were negative. Herein, these quantities were defined as their absolute values for clear depiction.

### 3. Results and Discussion

#### 3.1 Structures and thermal stability

Possible conformations of the salts formed from DTDO and  $\text{HNO}_3$  (**1A-1C**) and  $\text{HN}(\text{NO}_2)_2$  (**2A-2C**) with intramolecular hydrogen bonds which are helpful for stabilizing salts are shown in figure 1. Isomers differ from each other in positions of two anions: In conformation **A**, each anion connects with one  $\alpha$ -H and one  $\beta$ -H of the cation; In **B**, one anion connects with one  $\alpha$ -H and one  $\beta$ -H of the cation and another anion connects with two  $\beta'$ -Hs of the cation; While in **C**, each anion connects with two  $\beta'$ -Hs of the cation (cf. figure 1).

Each conformation has four intramolecular hydrogen bonds. The hydrogen bond lengths between hydrogen atom and the acceptor atoms (H...O and N...H) in different conformations are obviously different, which is because the different hydrogen atoms ( $\alpha$ -H,  $\beta$ -H and  $\beta'$ -H) lead to the different hydrogen bond strengths and different hydrogen bond lengths. For example, the hydrogen bond lengths are 1.759 Å, 1.783 Å, 1.752 Å and 1.783 Å in **1A**, 1.789 Å, 1.777 Å, 1.752 Å and 1.766 Å in **1B**, and 1.783 Å, 1.777 Å, 1.778 Å and 1.783 Å in **1C**. The average hydrogen bond lengths gradually elongate from **A** to **C** (for example, 1.769 Å, 1.771 Å and 1.780 Å for **1A-1C**, respectively), this suggests that the intramolecular hydrogen bonding interactions gradually weaken from **A** to **C**. In addition to these hydrogen bonds, the other bond lengths of **AC** are close to each other. The symmetries of the conformations **A** and **C** are obviously higher than that of **B**, and high symmetry is helpful for improving the stability.

For the isomers, free energies ( $G_s$ ) and total energies ( $E_s$ ) can be used as indicators of their relative stability. The computed  $G_s$  and  $E_s$  are listed in table 1. In order to conveniently figure out the energetically

favoured structure, the relative free energies ( $\Delta G_s$ ) and the relative total energies ( $\Delta E_s$ ) are also shown in table 1.

Due to the same compositions of conformations **A-C**, their  $G_s$  and  $E_s$  are comparable. For salts **1** and **2**,  $\Delta E_s$  and  $\Delta G_s$  have the same variation trend of **A** < **B** < **C**. Therefore, conformations **1A** and **2A** are most energetically favoured while **1C** and **2C** are least favoured. Synthesis of **A** should be more possible than that of **B** and **C**. Due to the smaller  $G_s$  of **A** in comparison with that of **B** and **C**, the latter conformations can spontaneously convert into conformation **A**. It is worth noting, although  $G_s$  and  $E_s$  of **B** and **C** are higher than those of **A**, the differences are not significant. The ratios of these isomers in the equilibrium state were predicted and the detailed results are also tabulated in table 1. The percentages of three conformations decrease in the order of **A** > **B** > **C** for salts **1** and **2**. This order is completely contrary to that of  $E$ , i.e., the percentage of the conformation with the higher  $E$  is lower. Although the contents of **1C** and **2C** are the lowest, their values are still higher than 20%. So the conformation **C** can also be observed in the mixture, in other words, conformations **A-C** exist simultaneously in the equilibrium state.

#### 3.2 Intra-molecular interactions

Various intramolecular interactions exist between  $\text{DTDO}^{2+}$  and anions affect density and stability of salt.<sup>10-12</sup> In order to comprehensively reveal the effects of conformations on intramolecular interactions and stability, various intramolecular interactions were predicted and results are tabulated in table 2, the variation trends of these parameters are plotted in figure 2.

It is well known that hydrogen bond is beneficial to improving density and stability.<sup>22</sup> The calculated results of  $V_H$  of each hydrogen bond listed in table S1 show that the strengths of hydrogen bonds decrease in the order of  $\alpha\text{-H}\dots\text{O} > \beta 1\text{-H}\dots\text{O} > \beta 2\text{-H}\dots\text{O}$  and  $\alpha\text{-H}\dots\text{N} > \beta 2\text{-H}\dots\text{N}$ . Figure 1 shows that the conformation **A** has two  $\alpha\text{-H}\dots\text{O}$  (N) and two  $\beta 1\text{-H}\dots\text{O}$  hydrogen bonds, **B** has one  $\alpha\text{-H}\dots\text{O}$  (N) hydrogen bond, one  $\beta 1\text{-H}\dots\text{O}$  hydrogen bond and two  $\beta 2\text{-H}\dots\text{O}$  (N) hydrogen bonds, **C** has four  $\beta 2\text{-H}\dots\text{O}$  (two  $\beta 2\text{-H}\dots\text{O}$  and two  $\beta 2\text{-H}\dots\text{N}$  in **2C**) hydrogen bonds. Therefore, the total  $V_H$  of each conformation ( $V_{H,t}$ ) listed in table 2 has the order of **A** < **B** < **C** and  $E_{H,t}$ , the sum of the hydrogen bond energy ( $E_H$ ) of a conformation, decreases in the order of **A** > **B** > **C**.

$E_2$  is derived from the electron transfer between the lone pair of O or N (LP(O/N)) of the anion and the  $\sigma^*(\text{N-H})$  of the cation and is helpful for stabilizing

**Table 1.** Predicted  $G$ s and  $E$ s of three conformations at the M062X/6-311++G\*\* and B97D/aug-cc-pvdz levels\*.

	$G$ (M062X) (a.u.)	$\Delta G$ (M062X) (kJ/mol)	$E$ (B97D) (a.u.)	$\Delta E$ (B97D) (kJ/mol)	$P_i$ (%)
<b>1A</b>	-1416.65055	0.00	-1416.37155	0.00	0.389
<b>1B</b>	-1416.64996	1.55	-1416.37135	0.54	0.313
<b>1C</b>	-1416.64983	1.89	-1416.37130	0.66	0.298
<b>2A</b>	-1785.81768	0.00	-1785.45929	0.00	0.504
<b>2B</b>	-1785.81489	7.33	-1785.45875	1.44	0.282
<b>2C</b>	-1785.81388	9.98	-1785.45848	2.13	0.214

\*  $\Delta G$  and  $\Delta E$  are the values relative to those of **1A** and **2A**, respectively.

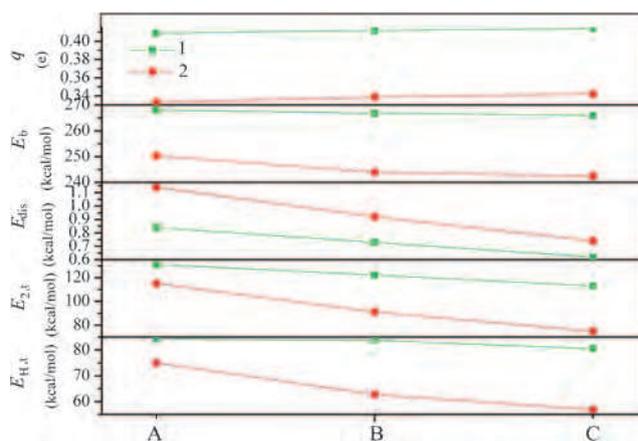
**Table 2.** Predicted  $V_{H,t}$ ,  $E_{H,t}$ ,  $E_{2,t}$ ,  $q$ ,  $E_b$  and  $E_{dis}$ .

	$V_{H,t}$ (a.u.)	$E_{H,t}$ (kcal/mol)	$E_{2,t}$ (kcal/mol)	$E_b$ (kcal/mol)	$E_{dis}$ (kcal/mol)	$q$ (e)
<b>1A</b>	-0.13425	84.24	130.90	268.06	0.84	0.409
<b>1B</b>	-0.13344	83.73	122.26	266.88	0.73	0.412
<b>1C</b>	-0.12828	80.50	113.08	265.96	0.62	0.414
<b>2A</b>	-0.11955	75.02	115.16	250.34	1.14	0.333
<b>2B</b>	-0.09996	62.72	91.22	243.96	0.92	0.339
<b>2C</b>	-0.09062	56.86	74.82	242.46	0.74	0.342

molecule. According to our previous studies,<sup>10–12</sup>  $E_2$  is tightly related with  $E_H$ . In this study, the variation trend of  $E_{2,t}$  (sum of  $E_2$ ) is same to that of  $E_{H,t}$ , i.e., **A** > **B** > **C**. So  $E_{H,t}$  and  $E_{2,t}$  of the conformation **A** are the largest, while those of **C** are the smallest. This means that **A** should be the most stable conformation, and **C** should be the most unstable conformation, which agrees with the conclusion obtained from  $\Delta G$ s and  $\Delta E$ s

The energies released in the formation of salts by the isolated ions can be reflected by  $E_b$ . The larger  $E_b$  corresponds to the bigger stabilization of the cation and anion and can result in the more stable salt. Inspections of figure 2 and table 2 reveal that  $E_b$ s of conformation **A** are the largest in comparison to that of conformations **B** and **C** that is, **A** is the most favourable conformation for stabilizing ions.

The transferred electrons from the anion to cation ( $q$ ) has the order of **A** < **B** < **C**, which indicates that the ability of DTDO<sup>2+</sup> to withdraw electrons in the conformation **C** is the strongest, while in the conformation **A** is the weakest. The more electron transfers result in the smaller absolute values of the ionic charges which lead to decrements in the strengths of ionic interactions. So the larger  $q$  corresponds to the weaker ionic interactions and the more unstable conformation. The ionic interactions in salts **1** and **2** decrease in the order of **A** > **B** > **C**. The order of  $E_{dis}$  is **A** > **B** > **C**, too. Hence the conformation **A** possesses the strongest intramolecular interactions and is most energetically favoured, while the conformation **C** has the weakest intramolecular interactions and is least energetically favoured. In

**Figure 2.** Variation trends of  $E_{H,t}$ ,  $E_{2,t}$ ,  $E_{dis}$ ,  $E_b$  and  $q$  in various conformations.

light of the above discussion, the stabilities of three conformations should decrease in the order of **A** > **B** > **C**. However, since the effects of different conformations on all intramolecular interactions but  $E_{2,t}$  are not significant, especially for the salt **1**, the stabilities of different conformations should not be obviously diverse.

Figure 2 shows that the variation trends of  $E_{H,t}$ ,  $E_{2,t}$ ,  $E_b$ ,  $E_{dis}$  and  $q$  are similar. Their similar variation trends imply that some relationships exist between these parameters, as shown in figure 3. Linear relationships between  $q$  and  $E_{H,t}$ ,  $E_{2,t}$ ,  $E_b$  and  $E_{dis}$  reveal that the more electrons transfers correspond to the weaker intramolecular interactions. In fact, linear relationships exist between any two of them, that is, these intramolecular interactions are tightly correlated. Therefore,

any one of these parameters can be used to indicate the relative strength of intra-molecular interactions of isomers.

### 3.3 Chemical and UV stabilities

Frontier molecular orbital energies ( $E_{\text{HOMOS}}$  and  $E_{\text{LUMOS}}$ ) and the energy gaps between the frontier orbitals ( $E_{\text{g}}$ s) were estimated and are listed in table 3.  $E_{\text{LUMO}}$  and  $E_{\text{g}}$  obviously decrease from **A** to **C**. This means that the stability in chemical or photochemical processes with electron transfer decreases from **A** to **C**. In comparison with the effects of different conformations on the intra-molecular interactions, the effect on the chemical stability is more obvious.

Figure 4 presents the 3D pictures of HOMOs and LUMOs of all conformations. HOMOs are derived from two  $\text{NO}_3^-$  for **1A** and **1C**, while from one  $\text{NO}_3^-$  or  $\text{N}(\text{NO}_2)_2^-$  for **1B** or **2A-2C**. LUMOs of **1A-1C** and **2A-2C** are all contributed by the cation and have the similar shapes and compositions which are mainly the  $\pi^*(\text{N-N})$  and  $p(\text{O})$ . So diverse conformations have little effect on the distributions of LUMOs, they obviously affect HOMOs.

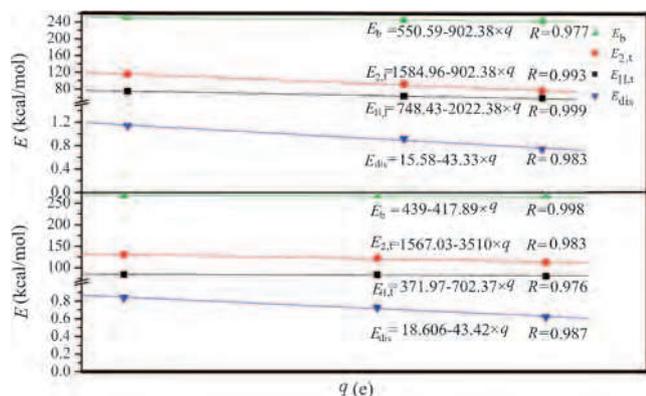
Previous studies have shown that orbital interaction diagrams can reflect the relationships between the orbitals of salts and the isolated ions.<sup>10-12</sup> The orbital

interaction diagrams of all conformations were analyzed. Results show that the orbital interaction diagrams of **1B** and **2A2C** are very similar, only that of **1A** and **1C** are different. So only the orbital interaction diagrams of **1A** and **1B** are shown in figure 5.

Figure 5 clearly shows the contributions from the orbitals of the isolated anion and cation to the orbitals of salts. 100% of the LUMO of **1A** and 99% of the LUMO of **1B** are contributed by the LUMO of  $\text{DTDO}^{2+}$ , so LUMOs of **1A** and **1B** are basically derived from that of  $\text{DTDO}^{2+}$ . The contribution of one  $\text{NO}_3^-$  to the HOMO of **1B** is about 94%, while to the HOMO of **1A** is about 47%. This means that the HOMO of **1B** is mainly derived from the HOMO of one  $\text{NO}_3^-$  while the HOMO of **1A** is mainly from the HOMOs of two  $\text{NO}_3^-$ . These orbital interaction diagrams of **1A** and **1B** explain why the LUMOs of **1A** and **1B** mainly are located at the cation, and why the HOMO of **1A** are located on two  $\text{NO}_3^-$  and that of **1B** on one  $\text{NO}_3^-$ . Due to similar orbital interaction diagrams of **1A** and **1C**, and **1B** and **2A-2C**, their frontier orbital distributions should be similar. It is worth mentioning that the occupied and vacant orbitals of the individual ions correspond to the occupied and vacant orbitals of salts, which means that the symmetries of the orbitals are conserved when the ions form salts according to the Woodward-Hoffman rule.<sup>23</sup>

UV stability is widely investigated for applications in bio-based and biodegradable polymers, food and medicines.<sup>24-29</sup> This is because absorption of UV light can lead to photolysis reactions, photo-oxidation, cleavage of bonds and excited states which imply a higher energy and lower stability.<sup>24</sup> The UV absorption is mainly resulted from the electron excitation in the double bond, tertiary hydrogen, tertiary chlorine, and functional groups containing oxygen, etc. Salts **1** and **2** both have unsaturated bonds and functional groups with oxygen, so UV may affect their stabilities, applications and storages. And the ultraviolet spectrum raised from the transition of the valence electron can provide useful information, such as quantitative or qualitative analysis and simple structure analysis. Therefore, the ultraviolet spectra of **1A-1C** and **2A-2C** in water were computed using the conductor-like polarizable continuum model (CPCM)<sup>30</sup> at the TD-M062X/6-311++G\*\* level and results are plotted in figure 6. The vertical excitation energies ( $E$ s) and the oscillator strengths ( $f$ s) of the first three excited states are tabulated in table 4.

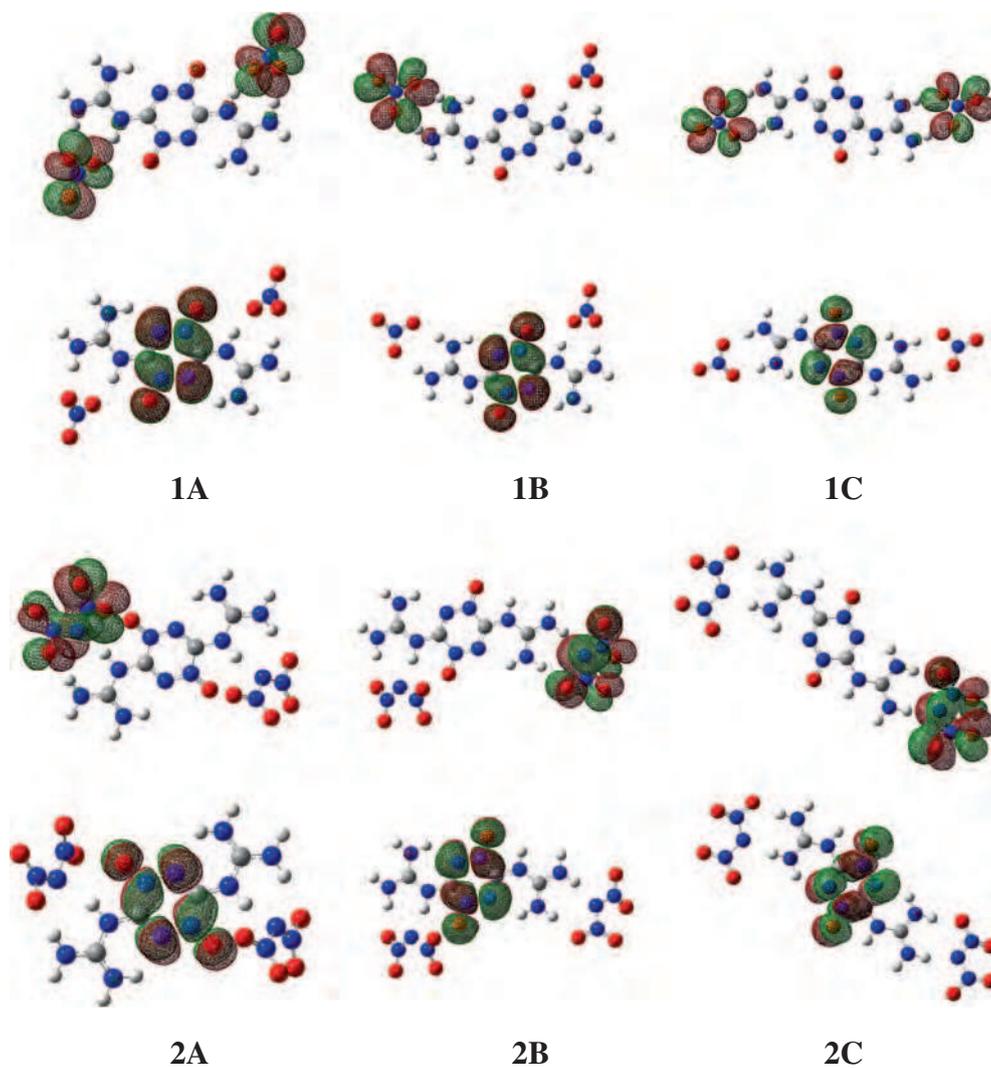
Figure 6 presents that UVs of **1A-1C** have three absorption peaks. The strongest peak correspond to the second excited state (cf. Table 4).  $f$ s and  $E$ s of the excited state **2** increase from **A** to **C**, the increments in  $f$ s are obvious, while that in  $E$ s are tiny. This reflects that different conformations absorb UV with very close



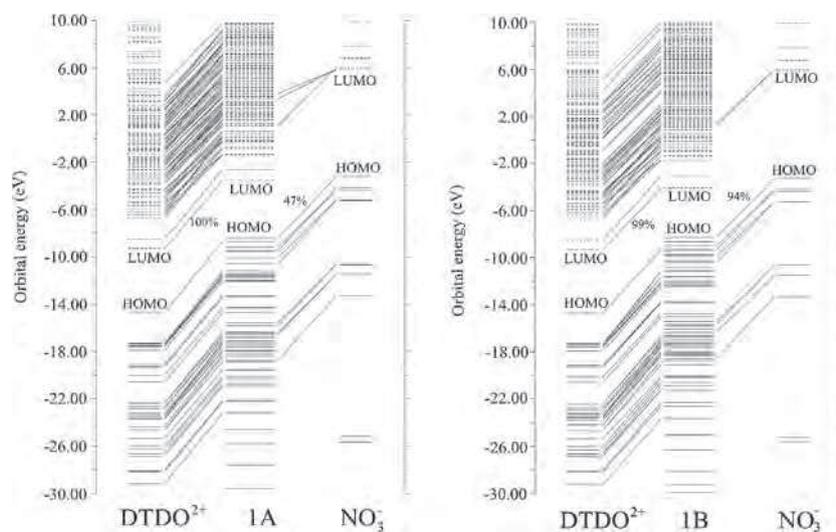
**Figure 3.** Relationships between  $q$  and  $E_{\text{H,t}}$ ,  $E_{2,t}$ ,  $E_{\text{b}}$  and  $E_{\text{dis}}$  of **1** (top) and **2** (bottom).

**Table 3.** Predicted  $E_{\text{HOMO}}$ ,  $E_{\text{LUMO}}$  and  $E_{\text{g}}$ .

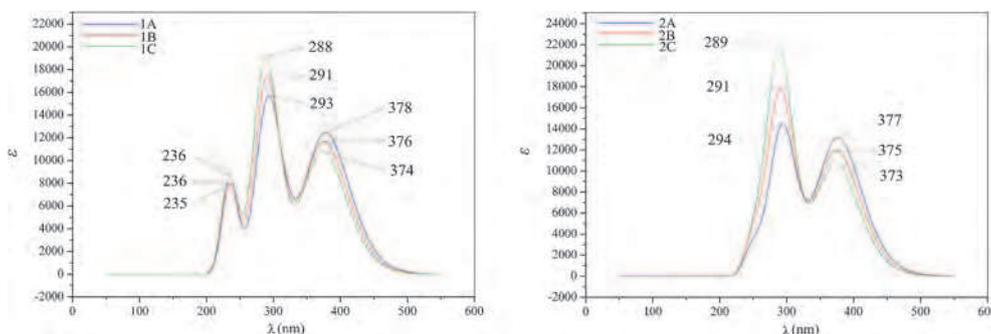
	$E_{\text{HOMO}}$ (eV)	$E_{\text{LUMO}}$ (eV)	$E_{\text{g}}$ (eV)
<b>1A</b>	-8.44	-3.53	4.91
<b>1B</b>	-8.26	-4.04	4.22
<b>1C</b>	-8.53	-4.63	3.90
<b>2A</b>	-8.75	-3.53	5.22
<b>2B</b>	-8.92	-4.22	4.70
<b>2C</b>	-9.20	-4.81	4.39



**Figure 4.** Occupied (HOMO, top) and unoccupied (LUMO, bottom) frontier orbitals.



**Figure 5.** Orbital interaction diagrams of 1A and 1B. The occupied and virtual orbitals are represented by the solid and dashed bars, respectively.



**Figure 6.** Simulated UV spectra in aqueous solution.

**Table 4.** Electron transitions in the first three excited states of **1** and **2**.

	Excited State	$E$ (eV)	$\lambda$ (nm)	$f$	Major contribution
<b>1A</b>	1	3.28	378	0.3065	H→L(91%) H→L+1(8%)
	2	4.23	293	0.3706	H→L+1(86%) H→L(8%)
	3	5.28	235	0.1830	H-9→L(35%) H-5→L(28%) H-3→L(27%)
<b>1B</b>	1	3.30	376	0.2867	H→L(91%) H→L+1(7%)
	2	4.27	291	0.4220	H→L+1(88%) H→L(7%)
	3	5.27	236	0.1840	H-9→L(45%) H-6→L(22%) H-3→L(12%)
<b>1C</b>	1	3.31	374	0.2665	H→L(92%) H→L+1(7%)
	2	4.30	288	0.4716	H→L+1(90%) H→L(7%)
	3	5.27	236	0.1872	H-9→L(61%) H-3→L(14%) H-1→L(16%)
<b>2A</b>	1	3.29	377	0.3233	H→L(90%) H→L+1(8%)
	2	4.22	294	0.2533	H→L+1(60%)
	3	4.90	253	0.0487	H-15→L+3(19%) H-6→L+3(26%) H-1→L+3(20%)
<b>2B</b>	1	3.31	375	0.2939	H→L(91%) H→L+1(7%)
	2	4.26	291	0.3971	H→L+1(86%) H→L(8%)
	3	4.88	254	0.0595	H-15→L+2(28%) H-6→L+2(27%) H-1→L+2(25%)
<b>2C</b>	1	3.32	373	0.2620	H→L(91%) H→L+1(7%)
	2	4.29	289	0.4812	H→L+1(89%) H→L(7%)
	3	4.88	254	0.0585	H-14→L+2(19%) H-7→L+2(29%) H-1→L+2(24%)

wavelengths (288–293 nm), while the absorption intensity significantly increases in the order of **A** < **B** < **C**.  $E$ s of the first and the third excited states of **1A–1C** are very close, namely, the UV wavelengths are comparable. UVs of **2A–2C** have two strong absorptions, the strongest one corresponds to the excited state 2. The third absorption is obviously weaker, so it does not appear in UV spectra.  $E$ s of the first two strong absorptions of different conformations are close to each other (377–373 nm and 294–289 nm forexcited states 1 and 2, respectively).  $f$  of state 2 increases from **2A** to **2C**.

In a word, for salts **1** and **2**, different conformations slightly affect the wavelengths of UV absorption, while distinctly change the strength of the strongest absorption, i.e.,  $f$  of state 2. The larger  $f$  is more likely to lead to the excited state with a higher energy, breaking of bonds, and photolysis reactions, i.e., lower stability. Therefore, we can conclude that the UV stabilities of three conformations obviously decrease in the order of **A** < **B** < **C**.

In addition to  $E$  and  $f$  of UV, the contributions of different electron transition to the excited states were further studied. Since the excited state 3 of all conformations are substantially weaker than the first two states, only the contributions to state 1 and state 2 are discussed. For **1A–1C**, the states 1 are mainly raised by the electron transition from HOMO to LUMO (H→L, 91–92%), and H→L+1 (7–8%) does a little contribution too. The states 2 are mainly contributed by the transitions of H→L+1 (86–90%) and H→L (7–8%). Different conformations hardly generate obvious effects on the contributions of electron transitions to the first two excited states of the salt **1**. For **2A–2C**, the states 1 are mainly from the transitions of H→L (90–91%) and H→L+1(7–8%), which is almost the same to that of the salt **1**. The states **2** are mainly derived from the transition of H→L+1, but the contribution of this transition to **2A** (60%) is far smaller than that to **2B** (86%) and **2C** (89%).

**Table 5.** NICSs at different points (in ppm) of all conformations.

Point	1A	1B	1C	2A	2B	2C
Ring centre	-11.04	-10.98	-10.50	-10.55	-10.81	-10.45
0.5 (Å)	-0.94	-0.81	-0.12	-0.44	-0.47	0.09
1.0 (Å)	9.02	9.13	9.91	9.18	9.50	10.02
1.5 (Å)	9.38	9.70	10.37	9.55	9.92	10.35
2.0 (Å)	7.15	7.53	8.02	7.31	7.55	7.96

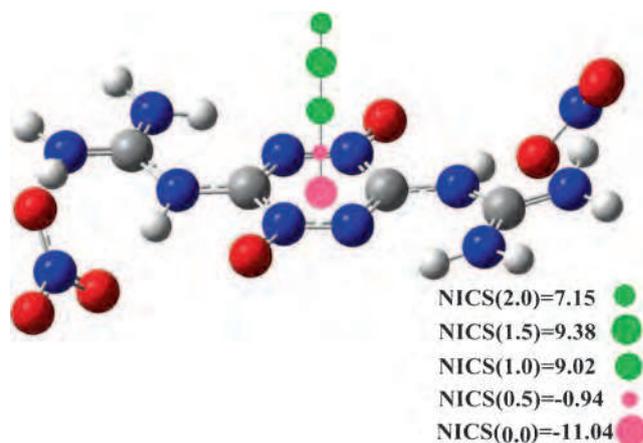
### 3.4 Aromaticity

Aromaticity is an important concept in physical organic chemistry<sup>31,32</sup> and is a useful quantity for rationalizing the structure, the reactivity, and especially the stability of molecules. It is well known that the strong aromaticity is helpful for improving stability.<sup>33,34</sup> The nucleus-independent chemical shifts (NICS)<sup>35</sup> is most widely used to estimate aromaticity due to its simplicity and efficiency. The NICSs obtained at the points locating at the ring centre and at 0.5, 1.0, 1.5, and 2 Å above the ring centre are listed in table 5.

Since the variation trends of NICSs at different points of all conformations are the same, only those of **1A** are plotted in figure 7. The NICSs at the ring centre and at the point 0.5 Å above the ring are negative, i.e., these regions are aromatic.<sup>35</sup> NICSs at the points 1.0, 1.5 and 2 Å above the ring centre are positive, which means that these points are anti-aromatic.<sup>35</sup> The value of NICS at the ring centre is most negative, this reveals that the aromaticity at the ring centre is the strongest.<sup>35,36</sup> So the NICS at the ring centre (NICS(0)) is the most suitable indicator of aromaticity. NICS(0) increases in the order of **1A** < **1B** < **1C**, implying that the aromaticity of **1A** is the strongest, and that of **1C** is the weakest. For the salt **2**, this order is **2B** < **2A** < **2C**, so **2B** has the strongest aromaticity, while that of **2C** is the weakest. Since the differences between the NICS(0)s of diverse conformations are tiny, the aromaticity of the tetrazine ring is hardly significantly affected by different conformations.

## 4. Conclusion

For salts **1** and **2**, *G*s and *E*s of conformations **A-C** increase in the order as **A** < **B** < **C**. **A** should be the most energetically favoured conformation and **C**, the least. Chemical and UV stabilities both decrease in the order of **A** > **B** > **C**. So **A** should be the most stable conformation, while **C**, the most unstable. Aromaticities of the tetrazine ring of these conformations are the strongest at the ring centre. Different conformations hardly generate obvious effects on aromaticity.



**Figure 7.** NICS grid plot of **1A** at the B3LYP/6-31+G\* level. The pink and green dots denote the aromatic and antiaromatic points, respectively.

To conclude, different conformations affect the chemical stability, UV stability and percentages in the equilibrium state, while slightly affect the intra-molecular interactions which are tightly related with thermal stability. The differences between the intra-molecular interactions in the salts **1** and **2** are not significant, i.e., their stabilities should be comparable. Since the salt **1** has been synthesized, salt **2** with comparable stability can be synthesized too.

### Supplementary Information

Predicted  $V_H$  of each hydrogen bond, Table S1, is available at [www.ias.ac.in/chemsci](http://www.ias.ac.in/chemsci).

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