ORIGINAL PAPER

Theoretical studies on vicinal-tetrazine compounds: furoxano-1,2,3,4-tetrazine-1,3,5-trioxide (FTTO-α) and furoxano-1,2,3,4-tetrazine-1,3,7-trioxide (FTTO-β)

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Abstract The derivatives of 1,2,3,4-tetrazine may be promising candidates of high-energy density compounds and are receiving more and more attention. In this study, two 1,2,3,4-tetrazines, furoxano-1,2,3,4-tetrazine-1,3,5-trioxide (FTTO-α) and furoxano-1,2,3,4-tetrazine-1,3,7-trioxide (FTTO-β), were theoretically studied. The geometrical structures in gas phase were studied at the B3LYP/6-311++G(d,p) level of density functional theory (DFT). The gas phase enthalpies of formation were calculated by the homodesmotic reaction method. The enthalpies of sublimation and solid phase enthalpies of formation were predicted with corrections of electrostatic potential method at the B3PW91/6-31G(d,p) level. The detonation properties were estimated with the Kamlet-Jacobs equations based on the predicted densities and enthalpies of formation in solid state. The available free space in the lattice was calculated to evaluate their stability. Calculations of potential energy surface and structure interconversion thermodynamics under different temperatures were carried out to further confirm their stability. FTTOs have better performance than HMX and FTDO but are easy to decompose to 5,6-dinitroso-v-tetrazine 1,3-dioxide. A synthesis route for FTTO-β was proposed to provide a consideration for the further study. We believe FTTOs could be the key compounds to synthesize other v-tetrazines such as TTTO.

Keywords Detonation performance · DFT · Stability · 1,2,3,4-Tetrazine

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Introduction

The energetic heterocyclic compounds, for example, furazan, tetrazole, and tetrazine derivatives have been widely used for military and civilian applications, and the synthesis and theoretical study of them have attracted considerable interest due to their high formation enthalpy and thermal stability [1–6]. As a typical nitrogen-rich heterocyclic compound, 1,2,3,4-tetrazine, also called vicinal-tetrazine or v-tetrazine, inherits all the advantages while it has its own speciality. Four directly-linkaged nitrogens bring more inner energy but also instability [7]. Based on the "alternating positive negative charge" (APNC) theory (Fig. 1), dozens of v-tetrazine 1,3-dioxide compounds with acceptable thermal stability have been successfully synthesized in the last 20 years [8, 9].

5,6-(3,4-furazano)-1,2,3,4-tetrazine-1,3-dioxide (FTDO, 1), or [1,2,5]oxadiazolo[3,4-e][1,2,3,4]tetrazine 4,6-dioxide, was first described by Churakov et al. in 1995 [10]. The substance, with the density of 1.85 gcm^{-3} [11] and the enthalpy of formation of 160.9 kcal mol^{-1} [12], is of interest not only as a high-energy additive for increasing the specific momentum of rocket propellants but also as a component of energetic plasticizers of propellants [13]. Later, Zelenov and Lobanova et al. [14, 15] developed and studied new methods for the synthesis of FTDO from 4-(tert-butyl-NNO-azoxy)-N-nitro-1,2,5-oxadiazol-3-amine or its alkali metal salts and acid anhydrides (or chlorides) in the presence of strong acids, and discovered that the decomposition of FTDO in water proceeds with the formation of 5H-[1,2,3]triazolo[4,5-c][1,2,5]-oxadiazole and nitric acid (Scheme 1). Wang et al. [16] carried out a further study to the synthesis routine and obtained a series of high energy [1,2,3]triazolo[4,5-c][1,2,5]-oxadiazole salts.

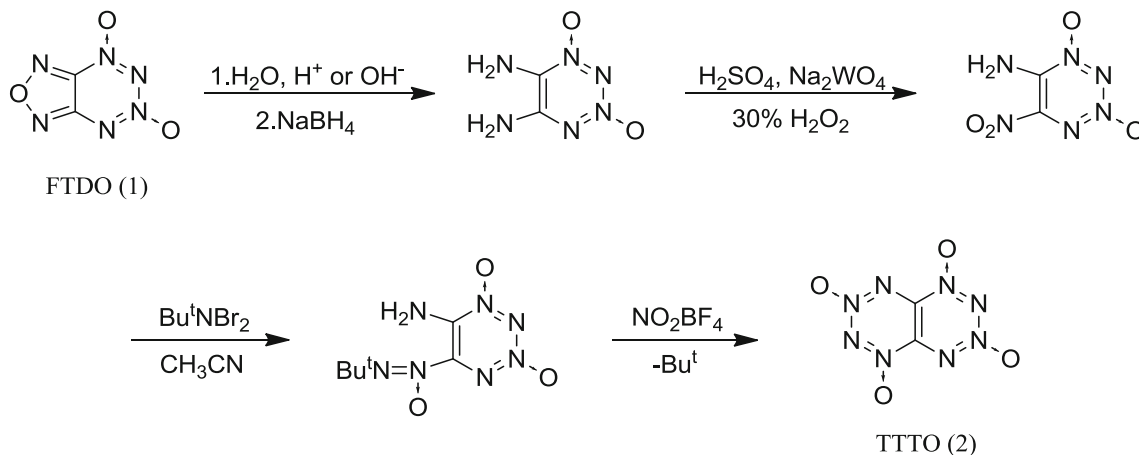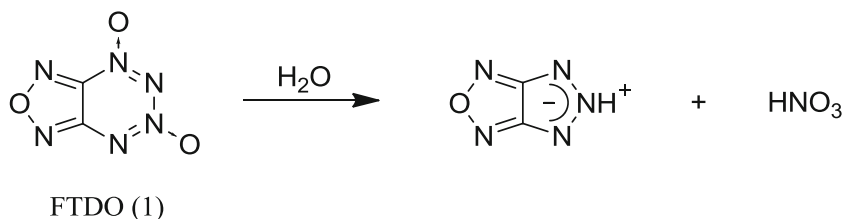**Fig. 1** Stabilized v-tetrazine systems described by the APNC theory
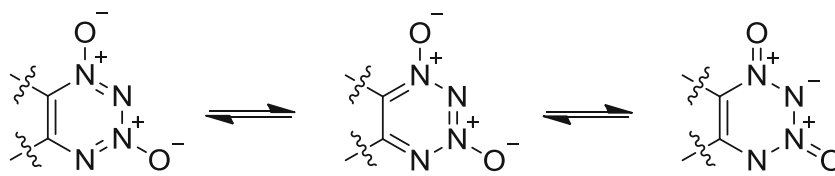
FTDO is of great interest not only as a promising high energetic density compound (HEDC), but also an assumed intermediate for the synthesis of TTTO (2) [17], another promising v-tetrazine HEDC whose synthesis has not been reported yet. The route shown in Scheme 2 was proposed by Russian scientists about ten years ago [18]. However, different from most of the v-tetrazines, FTDO seems to have a more vulnerable v-tetrazine ring which makes it melt and decompose near 110 °C and be highly sensitive to mechanical impacts [19]. Disturbance of aromaticity in the molecule of FTDO resulted from the conjugation of the v-tetrazine ring with the furazan ring makes it possible for both nucleophilic and electrophilic species to attack the nitrogen atoms in the v-tetrazine ring [15], and the furazan ring would hardly rupture before the v-tetrazine ring under most of the conditions.

As one of the highly anticipated v-tetrazine HEDCs, furoxano-1,2,3,4-tetrazine-trioxide (FTTO), which structurally has one more coordination oxygen atom
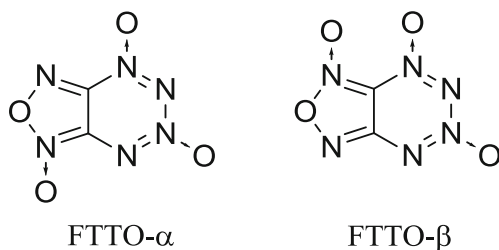
in furazan ring than FTDO, has been studied theoretically and experimentally few times since it was designed [17, 18, 20]. Compared to furazan, the furoxan brings higher enthalpy of formation and higher oxygen balance. By reduction with proper reducing agents, furoxan ring can be easily ruptured with the cleavage of the endocyclic N-O bond [21]. In the present study, two furoxano-1,2,3,4-tetrazine-trioxide isomers, furoxano-1,2,3,4-tetrazine-1,3,5-trioxide (FTTO-α) and furoxano-1,2,3,4-tetrazine-1,3,7-trioxide (FTTO-β) (Fig. 2), have been studied. Theoretical methods such as density functional theory (DFT) have been employed to predict their properties, such as molecular structures, enthalpies of formation, densities, detonation performance, and stability. A synthetic route was proposed. We believe FTTOs are key intermediates for further synthesis of other v-tetrazine HEDCs and our theoretical investigations on them will be helpful for further study.

Scheme 1 Decomposition of FTDO in water

FTDO (1)

Scheme 2 Proposed routine from FTDO to TTTO

Computational methods

Geometry optimization of the molecular structures were carried out at the B3LYP/6-311++G(d,p) level with the Gaussian program package [22]. The vibrational analysis was performed at the same level. The optimized structures were confirmed to be the local minimum without imaginary frequencies. According to the previous study, the calculated frequencies were scaled uniformly by 0.96 to approximately correct the systematic overestimation.

The enthalpies of formation were calculated from the designed homodesmotic reactions (1) and (2) [23].

$$\tag{1}$$

$$\tag{2}$$

$$\Delta H°_{298} = \Sigma \Delta_f H°_{298,P} - \Sigma \Delta_f H°_{298,R}$$
$$= \Delta E°_{298} + \Delta(pV) \tag{3}$$

where $\Delta H°_{298}$ is the standard enthalpy change at 298 K; $\Sigma \Delta_f H°_{298,P}$, $\Sigma \Delta_f H°_{298,R}$, $\Delta E°_{298}$, and $\Delta(pV)$ represent the sum of enthalpies of formation of products, the sum of enthalpies of formation of reactants, the change in the total energy at 298 K, and the change in the product of pressure p and volume V, respectively.

$$\Delta E°_{298} = \Delta E_0 + \Delta E_{ZPV} + \Delta H°_T \tag{4}$$

$$\Delta(pV) = (\Delta n)RT, \tag{5}$$

where ΔE_0, ΔE_{ZPV} and $\Delta H°_T$ denote the changes in the total energy at 0 K, in the zero-point vibrational energy, and in the temperature dependent enthalpy, respectively. Equation (5) assumes that substances in the reaction are all ideal gases.

Equations (6) and (7) were used to calculate the enthalpies of formation in solid state from the enthalpies of formation in gas phase and the sublimation enthalpies of FTTOs [24], the surface properties for prediction of sublimation enthalpies were computed at the B3PW91/6-31G(d,p) level of DFT.

$$\Delta_f H°_{298}(s) = \Delta_f H°_{298}(g) + \Delta_{sub} H°_{298} \tag{6}$$

$$\Delta_{sub} H°_{298} = a_1 A_S^2 + a_2 \left(\nu \sigma_{tot}^2\right)^{0.5} + a_3 \tag{7}$$

where A_S is the molecular surface area, $\nu = \sigma_+^2 \sigma_-^2 / (\sigma_{tot}^2)^2$, $\sigma_{tot} = \sigma_+^2 + \sigma_-^2$, σ_+^2 and σ_-^2 are the mean variances of the positive and negative molecular electrostatic potential, respectively, α_1, α_2, and α_3 are the empirical parameters taken from [24].

The densities ρ (g cm^{-3}) of FTTOs in solid state were computed by the improved Eq. (8) proposed by Politzer et al. at the B3PW91/6-31G(d,p) level [25], where M and V represent molecular weight (g mol^{-1}) and volume of the 0.001 electrons bohr^{-3} contour of electronic density of the molecule (cm^3 per molecule), respectively. The coefficients β_1, β_2, and β_3 are 0.9183, 0.0028, and 0.0043, respectively.

$$\rho = \beta_1(M/V) + \beta_2\left(\nu \sigma_{tot}^2\right) + \beta_3 \tag{8}$$

The empirical Kamlet-Jacobs equations [26–28] were used to estimate two important parameters of energetic materials, i.e., the detonation velocity (D) and detonation pressure (P).

$$D = 1.01 \left(N \overline{M}^{1/2} Q^{1/2}\right)^{1/2} (1 + 1.30\rho) \tag{9}$$

$$P = 1.558 \rho^2 N \overline{M}^{1/2} Q^{1/2}, \tag{10}$$

FTTO-α   FTTO-β

Fig. 2 Molecular structures of FTTO-α and FTTO-β

where N is the moles of gaseous detonation products per gram of explosives, $\overline{M}$ is the mean molecular mass of the detonation products, and Q is the detonation energy (cal g^{-1}). N, $\overline{M}$ and Q are determined based on the most exothermic principle. The products are supposed to be only CO_2, H_2O, and N_2, so released energy in the decomposition reaction reaches its maximum.

To evaluate the stability of explosive molecules, some molecular structure related parameters, such as molecular electrostatic potential [29], Mulliken charge on nitro group [30], bond order [31], or bond dissociation energy of X-NO$_2$ (X=C, N, O) [32], have been employed to estimate the shock sensitivity of nitro-containing explosives or propellants [33–35]. However, sensitivity depends upon a number of factors and it is not clear which one(s) may be dominant in any particular case [36]. There is evidence that one of the factors related to sensitivity is the compressibility of the solid compound [37–41], and that sensitivity increases with the amount of free space available in the crystal lattice [42]. According to Politzer's suggestions [36, 42, 43], free space ΔV can be formulated as follows:

$$\Delta V = V_{\text{eff}} - V_{\text{int}} \tag{11}$$

$$V_{\text{eff}} = M/\rho, \tag{12}$$

where V_{eff} is the effective volume of the molecule that would correspond to 100 % packing of the unit cell, V_{int} is the space encompassed by the 0.003 au contour of the molecule's electronic density, M is the molecular mass and ρ is the crystal density.

Dissociation routes, dissociation energy barriers, and stability of FTTOs were predicted by scanning the pyrolysis potential energy surface. The enthalpy change ($\Delta_r H_m$) and Gibbs free energy change ($\Delta_r G_m$) under different temperatures (200-800 K) were calculated to further confirm their stability.

Results and discussion

Molecular structures and electrostatic potential surfaces

Geometric structure is the basic information that we can learn from a compound. The optimized molecular structure of FTDO, FTTO-α, and FTTO-β are shown in Fig. 3 for comparison.

All three molecules have planar structures. This planarity, as well as the endocyclic bond distances, indicates an extensive delocalization of the π electrons. The bond parameters of the tetrazine ring in FTTOs are close to those in FTDO. We can also notice the arresting length of 1.529 Å of the N5-O6 bond in FTTO-α. The value is far bigger than the normal length of N-O bond in furoxan, which probably means the furoxan ring in FTTO-α will be rather unstable and can easily decompose, or hardly exist. The O6-N7 bond length of 1.475 Å in FTTO-β is in the acceptable range. This may be from the electronegativity confliction between furoxan and 1,2,3,4-tetrazine 1,3-dioxide which was designed based on the APNC theory (Fig. 4). The positively charged N1 and N3, as well as the shortened N-O bond lengths, indicate the participation of the electrons on these oxygens in respective N-O bonds, which increases the stability of the compound by preventing the cleavage of the N-N single bond and the tetrazine ring. However, instead of N2-N3 bond (1.463 Å) in FTDO, O6-N7 (1.475 Å) is the longest bond in FTTO-β which may be the trigger bond.

Fig. 3 Molecular geometrical parameters of FTDO, FTTO-α, and FTTO-β

FTDO   FTTO-α   FTTO-β
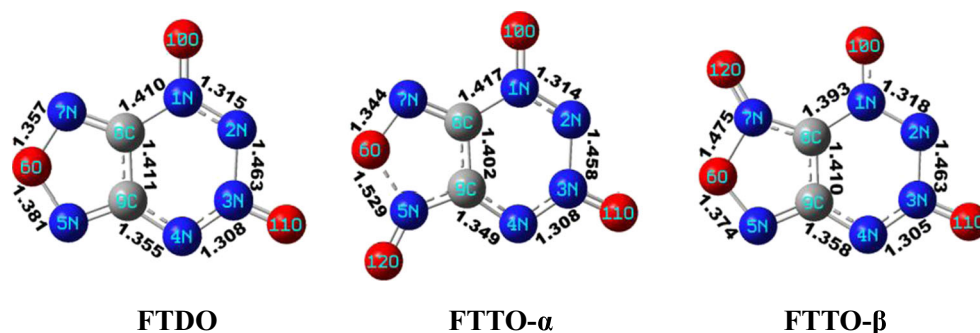
Fig. 4 APNC systems in FTTO-α and FTTO-β

FTTO-α   **FTTO-β**
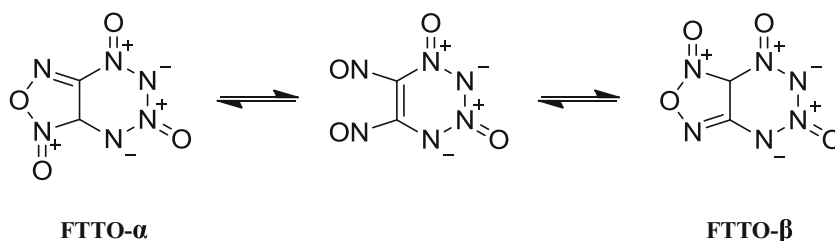
The surface potentials of FTDO, FTTO-α, and FTTO-β are presented in Fig. 5. Positive values are strongly around the central portions of the molecules, as is characteristic of energetic compounds [44, 45], and the negatives around the peripheries. The negative surface potentials are due to the oxygens and the unsubstituted ring nitrogens. The surface potentials are positive around all nitrogens, and are more obvious for the ones bearing oxygens. The unsubstituted nitrogens have less regions of positive surface potentials than the substituted ones. It is fair to say that the unsubstituted nitrogens have more negative (or less positive) potentials than the substituted ones, which is consistent with the APNC systems in FTTO-α and FTTO-β.

Enthalpy of formation

The enthalpy of formation is the key property for energetic materials, by which we can estimate their energy output performance. Many methods have been used to predict the enthalpy of formation, such as semiempirical molecular orbital methods, atomization reaction method and isodesmic reaction method. Here the homodesmotic reactions (1) and (2), in which the chemical environments of the reactants and products are similar, were used to calculate the enthalpy of formation of FTTO-α and FTTO-β.

Table 1 lists the calculated total energies at 0 K (E_0) for five compounds in reactions (1) and (2), with some of their enthalpies of formation ($\Delta_f H°_S$). Additional

calculations have been carried out using the G3 theory to get the accurate $\Delta_f H°_S$ of furoxan and 1,2,3,4-tetrazine 1,3-dioxide through the atomization reaction $C_a H_b O_c N_d(g) \rightarrow aC(g) + bH(g) + cO(g) + dN(g)$, because their experimental $\Delta_f H°_S$ are unavailable. The zero-point vibration energy (E_{ZPV}), the temperature dependent thermal enthalpy change ($\Delta H°_T$), and the calculated enthalpies of formation in both gas and solid phases of two FTTO isomers are listed in Table 2.

Detonation parameters

The calculated detonation heats, velocities and pressures according to Eqs. (8), (9), and (10) are shown in Table 3. The detonation parameters of FTDO and typical explosives (HMX and CL-20) are also provided for comparison. We can find that FTTOs are more powerful than the commonly used explosive HMX and less powerful than CL-20. The detonation properties of FTTOs are also slightly better than those of FTDO.

Sensitivity

In the molecule of 1,2,3,4-tetrazine, the single N-N bond is the weakest chemical bond, which is usually considered as the key factor that determines the stability of 1,2,3,4-tetrazine compounds. According to our calculations, the bond dissociation activation energy (BDAE) of the central N-N single bond is about 250 to 280 kJ mol^{-1} while that of two N=N double bonds is around

Fig. 5 Computed electrostatic potential on the 0.001 au molecular surface at B3LYP/6-311++G(d,p) level, with values −0.025 to +0.025 a.u.. Color coding: red, negative; yellow, slightly negative; green, neutral; light blue, slightly positive; dark blue, positive

FTDO   **FTTO-α**   **FTTO-β**
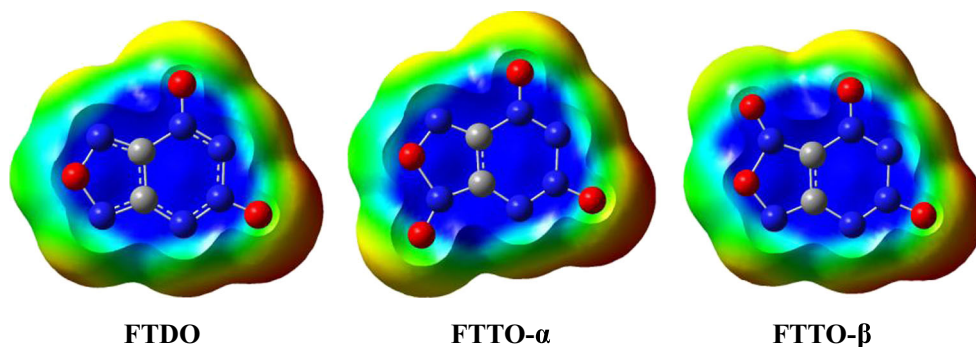
Table 1 Enthalpies of formation and calculated total energies at 0 K of the compounds in reactions (1) and (2)

	$\Delta_f H°$ / kJ mol^{-1}	E_0 / a.u.
FTTO-α	–	−705.41133
FTTO-β	–	−705.41048
ethene	52.40[a]	−78.61554
furoxan	210.11[b]	−337.30435
1,2,3,4-tetrazine 1,3-dioxide	462.03[b]	−446.77959

[a] Ref. [46]

[b] Calculated at the G3 level from the atomization reaction

290 kJ mol^{-1} for some 1,2,3,4-tetrazine compounds [49]. The BDAEs of the central N-N single bond of FTDO and FTTOs are 252.05 kJ mol^{-1} and 246.79 kJ mol^{-1}, respectively. However, for FTTOs, the trigger linkage to explosion may be different because the O-N bond in the furoxan near the coordinated oxygen atom is the longest chemical bond and a rather fragile one.

Calculations of potential energy surface and structure interconversion thermodynamics under different temperatures were carried out to further confirm their stability. Figure 6 demonstrates that in the ring-opening reaction, the cleavage of the furoxan ring in FTTO-α needs only 45.8 kJ while FTTO-β must cross a transition state with an activation barrier of 60.1 kJ to become 5,6-dinitroso-v-tetrazine 1,3-dioxide. Both energies are far less than that needed for the cleavage of their v-tetrazine rings. Relatively, FTTO-β is more stable than FTTO-α. Figure 7 shows the thermodynamic parameters of two reactions from FTTO-α and FTTO-β to 5,6-dinitroso-v-tetrazine 1,3-dioxide at different temperatures (T=200-800 K).

For both reactions, $\Delta_r G_m$ decreases continuously while $\Delta_r H_m$ increases slowly with the increasing temperature. The reactions are exothermic and $\Delta_r G_m$s are always negative in 200–800 K and are more negative at higher temperatures, therefore, high temperatures are more preferred for the two ring-opening reactions.
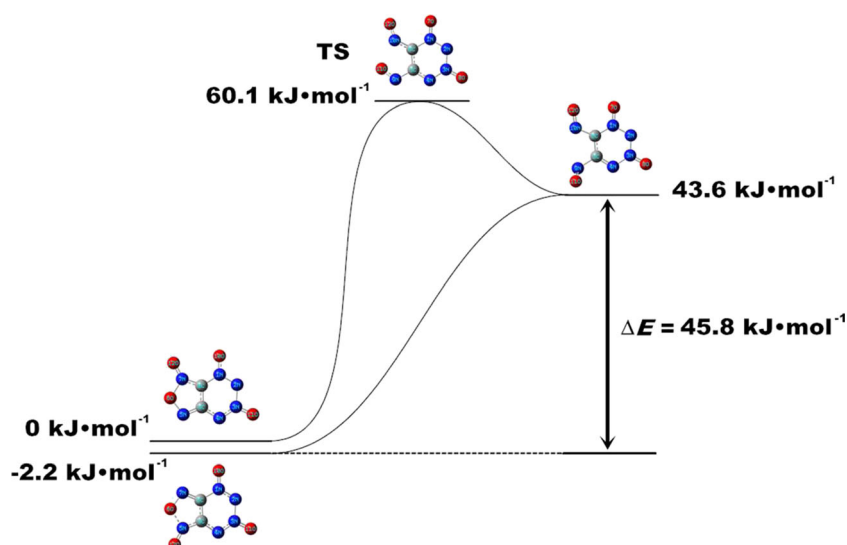
Sometimes, the BDAE or the bond dissociation energy (BDE) of ring-shaped or net-shaped molecules is hard to be accurately figured out [35] because of the presence of ring strains or conjugation. Politzer and co-workers [42] have shown that there is a rough relationship between the available free space in the lattice (ΔV) and the experimental impact sensitivity (H_{50}), and the sensitivity tends to increase as ΔV becomes large. This relationship has been applied to estimate the impact sensitivities of many promising energy compounds.

The ΔVs of FTDO, FTTO-α, FTTO-β, and several typical explosives are shown in Table 4 with the available experimental impact sensitivity for comparison. It is seen that FTTO-α and FTTO-β have ΔV value close to FTDO, which has the mechanical sensitivity close to lead azide [19]. According to the values of ΔV, FTTOs are less sensitive than HMX. However, FTTOs and HMX are two different species, the formers are heterocyclic compounds and the latter is a nitramine compound, and the free space gives only a rough estimate of the sensitivity, basically, the sensitivities of FTTOs, FTDO, and HMX are at the same level.

Possible synthetic route

V-tetrazine 1,3-dioxides are generally synthesized from aromatic amines with an ortho amino tert-butyl-NNO structure in which the tert-butyl group is the leaving group. Method of nitrating (e.g., with N_2O_5, NO_2BF_4),

Table 2 Enthalpies of formation and sublimation of FTTO-α and FTTO-β

	E_{ZPV} / a.u.	$\Delta H°_T$ / kJ mol^{-1}	$\Delta_f H°_{298}$(g) / kJ mol^{-1}	$\Delta_{sub} H°_{298}$ / kJ mol^{-1}	$\Delta_f H°_{298}$(s) / kJ mol^{-1}
FTTO-α	0.05468	25.87	764.50	70.96	693.54
FTTO-β	0.05482	25.69	766.92	72.89	694.03

Table 3 Detonation parameters of FTTOs and other explosives

Explosive	OB / %	ρ / g cm^{-3}	Q / cal g^{-1}	D / m s^{-1}	P / GPa
FTTO-α	0	1.84	2057	9525	41
FTTO-β	0	1.85	2057	9563	41
FTDO [47]	−10	1.86	1935	9493	41
HMX [48]	−22	1.91	1619	9320	39
CL-20 [48]	−11	2.04	1659	10,065	48

Fig. 6 Gas-phase relative energies of FTTO-α and FTTO-β to 5,6-dinitroso-v-tetrazine 1,3-dioxide
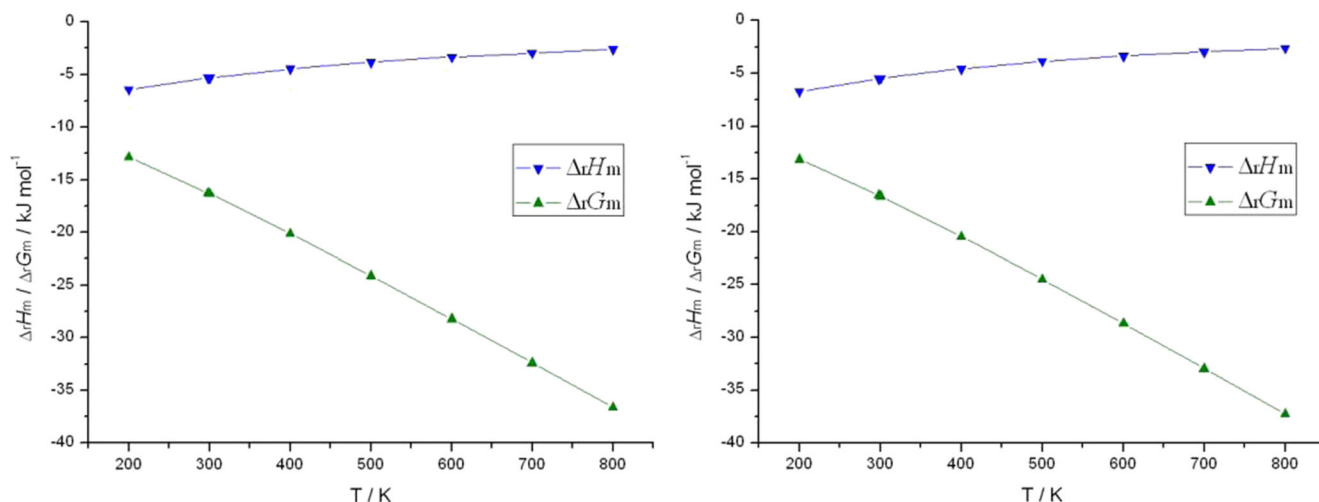

phosphorylating (e.g., with P_4O_{10}, PCl_5), sulfonating (with SO_3), and acylating (with $AcCl/AlCl_3$, Ac_2O/H_2SO_4 etc.) were successfully used to prepare v-tetrazine 1,3-dioxides of the aromatic series [14, 50–55]. Amino-(tert-butyl-NNO-azoxy) furoxan is unknown until last year [56], when Churakov and his colleagues experimentally confirmed the feasibility of the routine (Scheme 3). However, FTTOs were not mentioned in the work.

Although the yield of 4-aminofuroxan is only 1 % for the last step, we suggest using it as the starting material for the synthesis of FTTO-β because of the relatively higher stability of FTTO-β. The proposed synthesis route is shown in Scheme 4. In consideration of the possibility of isomerization or ring-opening, we believe it is better to deal with 4-aminofuroxan with

softer cyclization reaction conditions such as HNO_3-H_2SO_4-Ac_2O system under 20 °C. We presume that 4-aminofuroxan (3) will be first nitrated to 4-nitroaminofuroxan (4), then attacked by ionic systems Ac_2O-H_2SO_4 at the N-nitroamine fragment to yield the intermediate oxodiazonium ion (5) which undergoes a cyclization to FTTO-β via the elimination of tert-butyl (Scheme 5). Reaction (13) is the key step which determines whether the cyclization is practical. To estimate the thermodynamic possibility of the last step from (4) to the target product, the changes in thermodynamic functions of this reaction in the solvent of Ac_2O at different temperatures (T=200-800 K) were calculated. The results are presented in Fig. 8.

Δ_rG_m decreases continuously and while Δ_rH_m increases slowly with the increasing temperature. Δ_rG_m is about
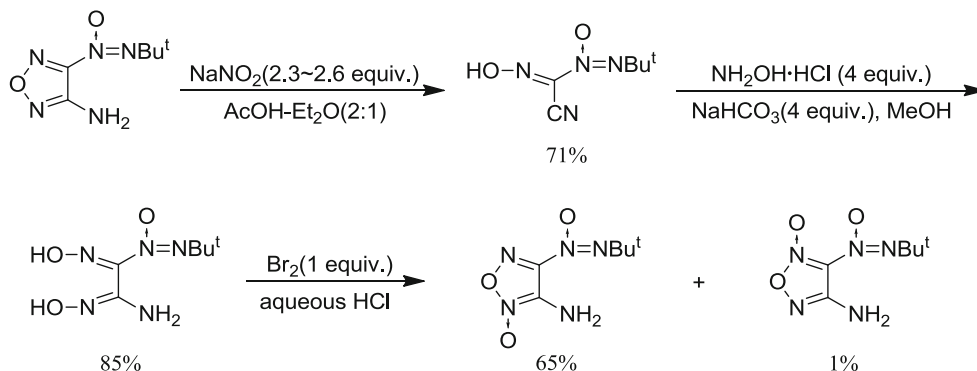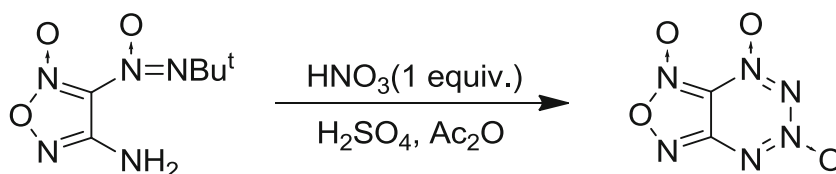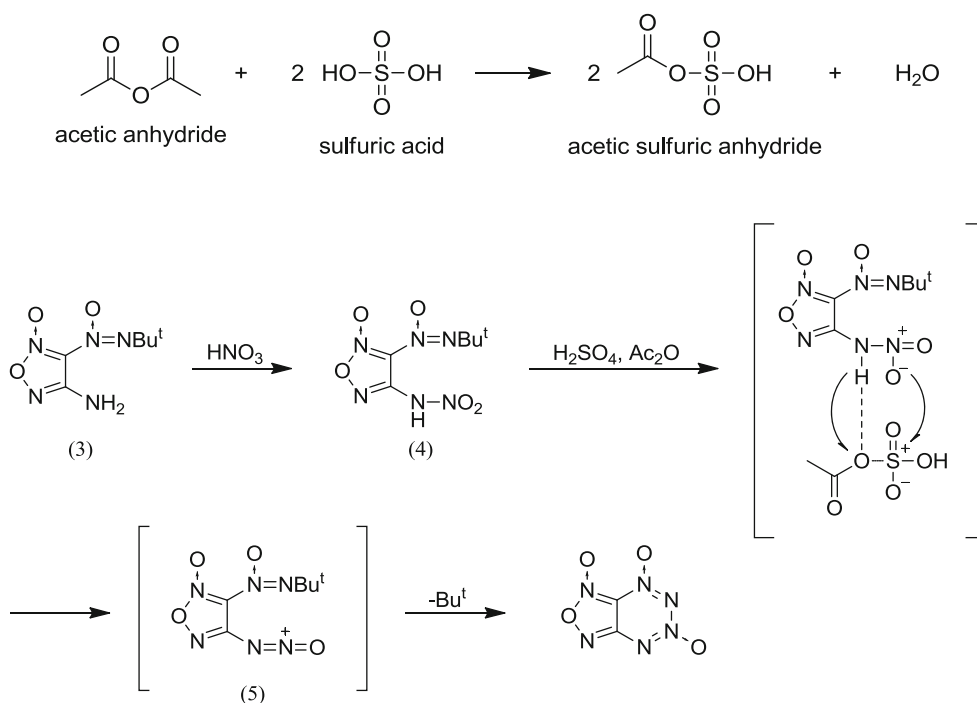

Fig. 7 Δ_rH_m and Δ_rG_m at different temperatures for ring-opening reactions of FTTO-α (left) and FTTO-β (right)

Table 4 ΔV and H_{50} of FTTOs and several other explosives

Explosive	ΔV / Å³	H_{50} / cm
FTTO-α	40.84	–
FTTO-β	40.59	–
FTDO	39.87	–
HMX [45]	49.20	29
TNAZ [45]	35.22	30
FOX-7 [45]	23.17	126

−60 kJ mol⁻¹ at 293.15 K. The reaction is endothermic at low temperature and exothermic above 250 K and will release a small amount of heat at room temperature. In conclusion, the proposed reaction is quite possible at ambient temperature. However, according to the changes in free energy we can only learn the thermodynamic possibility of the reactions, it is more practical to use activation energies to predict the feasibility of the reac-

Scheme 3 Synthesis route for amino-(tert-butyl-NNO-azoxy) furoxan

Scheme 4 Proposed synthesis route for FTTO-β


Scheme 5 Cyclization mechanism for FTTO-β

(13)
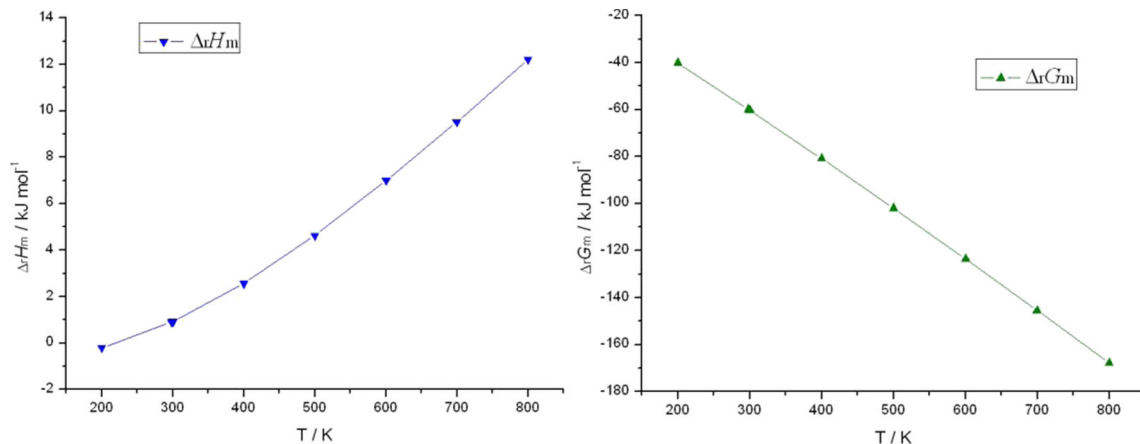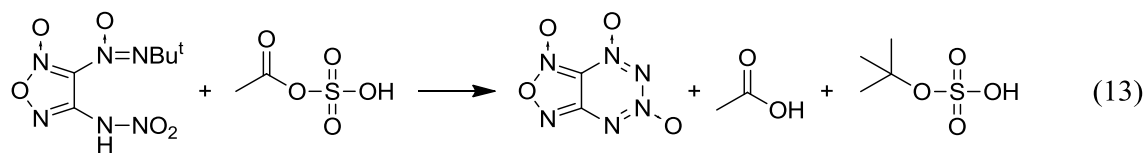
Fig. 8 $\Delta_r H_m$ and $\Delta_r G_m$ at different temperatures for cyclization reaction of FTTO-β in Ac$_2$O solvent

tions, this will be considered in our future synthetic and theoretical research works.

Conclusions

1. With the help of DFT calculations, the properties of FTTOs were predicted. It was confirmed that FTTO-α and FTTO-β are interesting materials with the density >1.90 g cm^{-3}, the detonation velocity >9000 m s^{-1} and detonation pressure >40 GPa. They show better performance than HMX and FTDO.
2. FTTOs may be very sensitive. FTTO-α is less stable than FTTO-β. Although the BDAE of

cleavage of v-tetrazine ring is about 246 kJ mol^{-1}, the cleavage of furoxan ring needs only 45.8 kJ mol^{-1} for FTTO-α and 60.1 kJ mol^{-1} for FTTO-β. The results of ΔV also confirmed that FTTOs are less stable and have higher impact sensitivity than FTDO.

3. According to the characteristics of FTTOs, we believe, FTTOs, if prepared successfully, could be the key material to synthesize monocyclic v-tetrazine dinitro-v-tetrazine 1,3-dioxide (DNTDO) and other v-tetrazine HEDCs such as TTTO (Scheme 6). We suggest choosing the relatively more stable FTTO-β as the research target and the thermodynamic possibility of the proposed synthesis route has been proved theoretically.
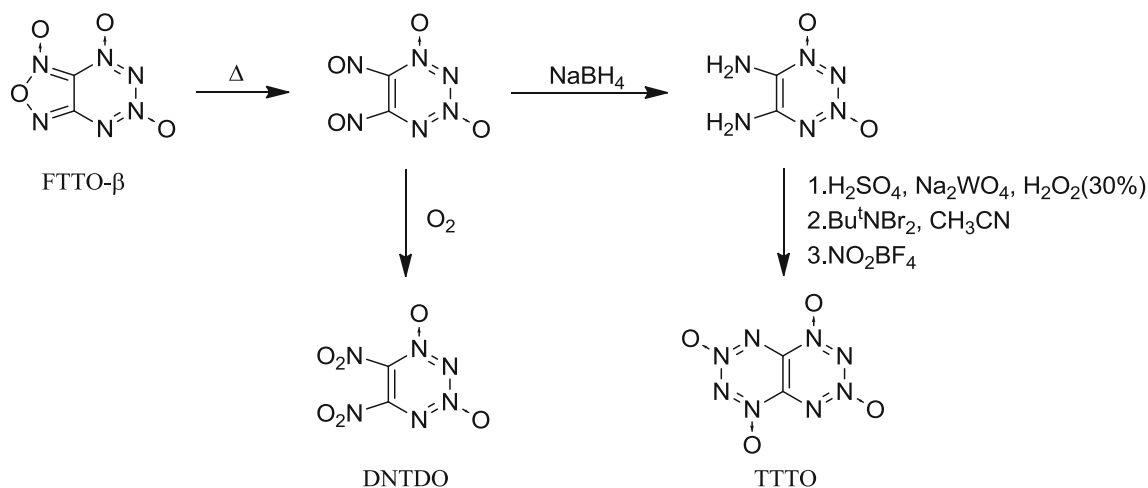
Scheme 6 A possible route for preparing TTTO from FTTO-β

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