In-silico design of a new energetic material—1-Amino-5-nitrotetrazole with high energy and density

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ABSTRACT

Ideal energetic materials should first possess high energy and high crystal density for their practical applications. In this study, a new energetic material—1-amino-5-nitrotetrazole (ANTz) has been molecularly designed. ANTz has been demonstrated to possess highest gas-phase heat of formation (HOF) based on our theoretical calculations of 14 derivatives of tetrazole. Its high density value equally demonstrated its excellent performance. However, computational impact sensitivity (h_{50}) has a great derivative with experimental BAM test impact sensitivity value for recently synthesized 2-amino-5-nitrotetrazole, which is ANTz's isomer. That makes us doubt the QSPR model of predicting impact sensitivity for tetrazole derivatives. Although we cannot precisely predict its impact sensitivity for the lack of suitable theoretical methods and incomplete database, ANTz is expected to be a good candidate as energetic material from the perspective of energy and density. The pyrolysis pathways of ANTz were also systematically analyzed, which demonstrated that ANTz is prone to decompose by direct ring rupture from a reaction kinetic perspective. And its preferable final products are HNO_2, N_2 and CN_3H.

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1. Introduction

Energetic materials have attracted worldwide attentions over the last century for both civil and military applications [1,2]. In order to meet their future requirements, screening new energetic materials with desirable properties, such as high energy density and low sensitivity is urgent, while it is challenging [3–5]. Chemicals with nitrogen-containing five-member heterocyclic rings, which are defined as azole rings, are one of the best candidates for energetic materials due to their high energy-density [3,5–11]. Among such chemicals with azole rings, tetrazole (Tz), which include four N atoms in each azole ring, has the highest nitrogen content. It suggests that Tz possesses higher positive heats of formation (HOFs) than others with azole rings. Furthermore, Tz molecules can be synthesized with well developed method. Therefore, Tz molecule is a promising building block for the design of energetic materials with high energy-density [8,10,11].

To improve detonation properties of Tz, its azole ring needs to be modified using energy-rich functional groups [12]. Generally, the introduction of a nitro group (–NO_2) can improve the oxygen balance and density of energetic compounds, and thus the detonation properties [13–15]. However, highly nitrated azole-based compounds usually suffer from several drawbacks, such as high sensitivity. Therefore, an amino group (–NH_2) is often introduced by modifying the azole ring to enhance the stability and lower the sensitivity of energetic materials [16,17]. Moreover, the amino group can undergo further functionalization. If a nitro group is introduced in an adjacent position of amino, both the intra- and/ or inter-molecular hydrogen bonds can form which can further improve the stability and density of Tz chemicals. Consequently, new energetic materials can be designed by modifying azole rings of Tz chemicals with amino and nitro [17–20]. Indeed, a new energetic material, 2-amino-5-nitrotetrazole, has been synthesised by the amination of the parent anion with O-tosylhydroxylamine, which has been used as a novel energetic material with high explosive performance in the range of hexogen and octogen [17]. This result further stimulates our interest to design new energetic materials based on the modification of Tz.

In the past decades, in-silico design of novel energetic materials has been demonstrated as a useful research tool, thereby avoiding expensive and dangerous experimental tests [12,20–28]. This strategy can also provide theoretic insights to help the understanding of the structure-performance relationships of designed materials. For example, Ravi et al. successfully theoretically predicted the

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relationship between Tz and its derivatives structures and their energetic properties heat of explosion, detonation velocity and detonation pressure, density and stability [19]. We carried out very similar compounds but used quite different methods and focused on different targets.

Each azole ring of Tz has two hydrogen atoms associated with N and C atoms, respectively, which can be substituted by nitro and/or amino groups. Considering that there are two isomers of Tz, we studied 14 configurations by the substitution of H atoms in the azole ring of Tz with nitro or/and amino. Different high-level computational methods have been employed to calculate heats of formation (HOFs) of 14 Tz derivatives. We found that 1-amino-5-nitrotetrazole (ANTz) has the largest HOFs, which suggests that it contains the highest energy. We calculated the density and impact sensitivity of ANTz and its derivatives using Politzer' structure-property relationship (QSPR) models [29,30] and compared these theoretical value with other known computational or experimental value of energetic materials. We aim at verifying if ANTz is the most excellent candidate among its derivatives. Although some computational h_{50} values of traditional compounds are very consistent with experimental value, the computational h_{50} value of ANTz' isomer 2-amino-5-nitrotetrazole (compound 14) differs far from experimental value [31]. That makes us doubt the QSPR model [30] of predicting impact sensitivity for tetrazole derivatives. Finally we gave up predicting impact sensitivity temporarily for lack of other suitable theoretical methods. From the perspective of energy and density, ANTz also can be a good candidate as energetic material among its derivatives. Herein, the pyrolysis mechanisms of ANTz have also been systematically analyzed on the basis of *intrinsic reaction coordinate* (IRC) calculations.

2. Computational details

All computations were performed with Gaussian 09 program package to analyze the geometries of Tz derivatives, their gas-phase HOFs, volumes, and the pyrolysis pathways of ANTz [32].

The B3LYP hybrid functional with two different basis sets: 6-311++g(d,p) and cc-pVTZ, and two highly accurate composite procedures, G3 [33,34] and W1 [35] methods, were employed to calculate the gas-phase HOFs of 14 derivatives of Tz and compare these four methods' accuracy. Two approaches, one based on atomization reaction [34] and another based on isodesmic reaction [36], were also used to understand the effects of different approaches on HOFs. The details of these two approaches are given in ESI.

A B3LYP/6-311++g(d,p) method was used to optimize each of the stationary points (Tz and its reference derivatives, reactants, transition states, intermediates and final products). All the stationary points was fully optimized and characterized by vibration analysis as either energy minima (zero imaginary frequencies) or first-order saddle points (one imaginary frequency). Symmetries or geometrical constraints were not allowed during the energy minimization with default convergence criteria throughout. On the basis of optimized structures by B3LYP/6-311++g(d,p), we recalculated the energies of each stationary points and saddle points by B3LYP/cc-pVTZ.

To understand the stability and sensitivity of ANTz and its derivative, we calculated its crystal density and impact sensitivity (h_{50}) values based on Politzer' developed quantitative structure-property relationship (QSPR) models [29,30,37,38]. Crystal densities of molecules were once predicted by Politzer [29] using Eq. (1) which reflects the features of molecular surface electrostatic potentials in order to better account for intermolecular interactions in crystal:

$$\rho_{cry} = \alpha_1 \left(\frac{M}{V(0.001)} \right) + \beta_1 \left(v\sigma_{tot}^2 \right) + \gamma_1 \qquad (1)$$

in which $V(0.001)$ (g cm^{-3}) [39] is the volume of the 0.001 electrons·Bohr^{-3} contour of electronic density of the molecule. Because the crystal density of most compounds in training set are measured at room temperature [29,40], this QSPR model will give crystal density at room temperature.

It is worth mentioning that we took 125000 random points per Bohr^3 for Monte-Carlo calculations of molar volume to make the fluctuation of these volume values smaller than 0.12 g cm^{-3} (Table S1, ESI). The two descriptors $v\sigma_{tot}^2$ is an excellent index of electrostatic interactive tendencies and are particularly significant when the molecules are of the same kind [29]. The accuracy of two descriptors is positively dependent on point numbers in the cubes of electron density and electrostatics potential [38]. In our calculations, we set the grid step as 0.0833 Bohr and the coefficients α_1, β_1, γ_1 are 0.9183, 0.0028 and 0.0443, respectively. The impact sensitivity (h_{50}, cm) means the drop height of 100 cm is equivalent to impact energy of 24.5 J when a 2.5 kg mass is used, which can be estimated by Eqs. (2) and (3) [30,37]:

$$h_{50} = \alpha_2 [V_{eff} - V(0.002)]^{1/3} + \beta_2 (v\sigma_{tot}^2) + \gamma_2 \qquad (2)$$

$$h_{50} = \alpha_3 \sigma_+^2 + \beta_3 v + \gamma_3 \qquad (3)$$

where in Eq. (2), V_{eff} is molar mass of molecules divided by the calculated ρ_{cal}, and $V(0.002)$ (g cm^{-3}) [39] is the volume of the 0.002 electrons·Bohr^{-3} contour of electronic density of the molecule. The fitting parameters of h_{50} vary with different kinds of compounds. And coefficients α_2, β_2, γ_2 are -234.83, $-3.197962.0$, α_3, β_3, γ_3 are -0.0064, 241.42, -3.43, respectively. The h_{50} values of compounds with C-NO$_2$ group are strongly dependent on $V_{eff} - V(0.002)$ and $v\sigma_{tot}^2$ in Eq. (2) and the h_{50} values of N-NO$_2$ compounds can be concisely calculated by Eq. (3) [29,38].

All molecular descriptor such as V_m, v and σ_{tot}^2 in those Pulitzer'sQSPR models were calculated with B3PW91/6-31g(d,p) method. Thus, we also chose B3PW91/6-31g(d,p) to calculate the sensitivity parameters.

Finally, we calculated the activation enthalpy with ANTz as the initial reactant. For the prediction of the decomposition pathways, IRC calculations were performed for each transition state to verify whether it is properly connected the desired reactants and products.

3. Results and discussions

3.1. HOFs of 14 derivatives of Tz

So far, the existing experimental thermodynamic data on Tz and its derivatives are rare. To accurately predict their HOFs for future reference and study the structure-HOFs relationship, we systematically studied 14 derivatives with –NO$_2$ and/or –NH$_2$ substitutes of the two isomers (1*H*- and 2*H*-tetrazole) of Tz with four methods: B3LYP/6-311++g(d ,p), B3LYP/cc-pVTZ, G3 and W1. The comparison with experimental value enables us to attain a most appropriate method which can offer the most exact formation enthalpies. These derivatives and their numbers are listed in Chart 1.

The gas-phase HOFs at 298 K of these 14 derivatives with the atomization reaction approach are shown in Fig. 1 (the numeric values are listed in Table S2, ESI). Gas-phase HOFs, which are calculated at the B3LYP/cc-pVTZ level with two different approaches: atomization reaction approach and isodesmic reaction approach, are shown in Fig. 2 (the numeric values are listed in Table S3, ESI). Figs. 1 and 2 show that these calculated HOFs for the investigated molecules are all positive, which means these compounds can be energetic materials with high energy density. From Fig. 1, it is evident that the four computational methods get the similar trend which respects to the changes of HOFs caused