Journal of Molecular Graphics and Modelling 63 (2016) 85–90

Contents lists available at ScienceDirect

Journal of Molecular Graphics and Modelling

journal homepage: www.elsevier.com/locate/JMGM

Computational assessment of several hydrogen-free high energy compounds

Bisheng Tan[a,*], Ming Huang[a], Xinping Long[b,**], Jinshan Li[a], Guijuan Fan[a]

[a] Institute of Chemical Materials, China Academy of Engineering Physics (CAEP), Mianyang 621900, PR China
[b] China Academy of Engineering Physics (CAEP), Mianyang 621900, PR China

ARTICLE INFO

Article history:
Received 5 August 2015
Received in revised form
29 September 2015
Accepted 6 November 2015
Available online 12 November 2015

Keywords:
Isomerization
Bond-separation energy
Molecular electrostatic potentials
Thermodynamic property
Detonation performance

ABSTRACT

Tetrazino-tetrazine-tetraoxide (TTTO) is an attractive high energy compound, but unfortunately, it is not yet experimentally synthesized so far. Isomerization of TTTO leads to its five isomers, *bond-separation energies* were empolyed to compare the global stability of six compounds, it is found that *isomer* 1 has the highest *bond-separation energy* (1204.6 kJ/mol), compared with TTTO (1151.2 kJ/mol); thermodynamic properties of six compounds were theoretically calculated, including *standard formation enthalpies* (solid and gaseous), *standard fusion enthalpies*, *standard vaporation enthalpies*, *standard sublimation enthalpies*, *lattice energies* and *normal melting points*, *normal boiling points*; their detonation performances were also computed, including *detonation heat* (Q, cal/g), *detonation velocity* (D, km/s), *detonation pressure* (P, GPa) and *impact sensitivity* (h_{50}, cm), compared with TTTO (Q = 1311.01 J/g, D = 9.228 km/s, P = 40.556 GPa, h_{50} = 12.7 cm), *isomer* 5 exhibites better detonation performances (Q = 1523.74 J/g, D = 9.389 km/s, P = 41.329 GPa, h_{50} = 28.4 cm).

1. Introduction

Searching novel high energy density materials (HEDM) will benefit both for the country and the people. But for a HEDM, its energy and safety are mutually contradictory, to a great extent, its development is retarded because of the safety factors. Therefore, compared with other materials, the HEDM's development process is very slow. Conventional high energy density materials are mostly C, H, O, N containing, their energies are approaching the limits, so their developments become more and more difficult. Non-conventional HEDM, which not containing elements hydrogen and carbon (or little carbon), may break through the energy limits and become promising novel HEDMs. All nitrogen compounds [1–8], whose high enthalpies of formation, a great of energies will be released when they decompose, the decomposed products only contain eco-friendly nitrogen gases, they are the most promising HEDMs. However, all nitrogen compounds are very hard to be experimentally synthesized because of their thermodynamic instability and high ring strain energy for ring-shaped compounds, high cage strain energy for cage-shaped compounds. Nonetheless, the attractive properties of all nitrogen compounds still encourage a lot of researchers to diligently study these kinds of materials, we believe that may be experimentally synthesized and applied in the near future.

If all nitrogen compounds are the fourth or fifth generation high-energy explosives, C—H—N—O based heterocyclic high energy compouds [9–11] may be still the third high-energy explosives, they were also designed which have promising detonation performances, and these works may be more close to reality. Tetrazino-tetrazine-tetraoxide (TTTO) [12–14] is one of the research hot spots in the area of energetic materials, once it is synthesized experimentally, the research team will probably occupy the best place in the area of energetic materials.

Therefore, the beautiful structure and the excellent detonation performance of TTTO is still encourage some researchers to dig it further. Our group has being focusing on it and designed five isomers of TTTO (Fig. 1), theoretically studied their detonation performances from the perspectives of standard formation enthalpies, theoretical densities, detonation velocities and detonation pressures; the stability and safety were studied from the views of bond-separation energies, wiberg bond orders and the predicted h_{50} (2.5 kg-drop hammer heights under 50% explosion probability) based on molecular electrostatic potentials. In the research work of explosives, some physical properties of explosives and their relative properties may also play important roles, such as molecular cohesive energies, standard fusion enthalpies, standard vapora-

* Corresponding author.
** Corresponding author.
E-mail address: tanbs_my@caep.cn (B. Tan).

http://dx.doi.org/10.1016/j.jmgm.2015.11.002
1093-3263/

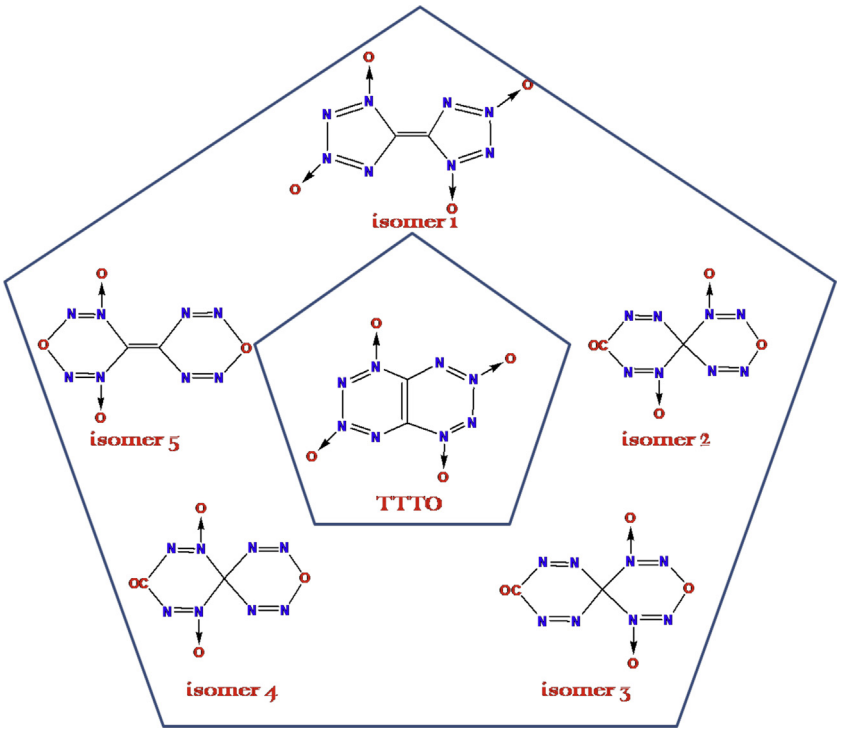

Fig. 1. TTTO and its five isomers.

tion enthalpies, standard sublimation enthalpies, lattice energies, normal melting points or normal boiling points. Accordingly, we studied TTTO and their five isomers both from the physical (thermodynamics and mechanics of explosion) and chemical aspects, to evaluate and screen some desired isomers.

Bond-separation energy [15] is a kind of absorded energy that all the covalent bonds between heavy atoms (except for hydrogen or its isotopes) in one mole molecules are separated into simple σ type single bonds or π type double bonds or π type triple bonds based small molecules, which is expressed as isodesmic reactions [16]. The higher the *bond-separation energy*, the stronger the molecular framework. This expression may separate σ and π bonds and isolate electons' delocalization, and it may not only be applied in conjugated or non-conjugated rings based molecular structures, but also be used in conjugated or non-conjugated chain-shaped molecular structures. On the right side the isodesmic reaction, they are simple sigle bonds and double bonds related small molecules, such as ethane, ethene, aminomethane and hydroxylamine etc., just like factorization in mathematics, such as $(x^2-y^2)=(x+y)(x-y)$. These small molecules and their relative energies may be included in a molecular library, it is easy to build computer programme and transfer between computers on internet.

2. Theory based on molecular surface electrostatic potential

Eqs. (1)–(5) based on molecular surface electrostatic potential were proposed by Politzer et al. [17].

$$V(\mathrm{r}) = \sum_A \frac{Z_A}{|\mathrm{R_A} - \mathrm{r}|} - \int \frac{\rho(\mathrm{r'})\mathrm{dr'}}{|\mathrm{r'} - \mathrm{r}|} \tag{1}$$

Where $V(\mathrm{r})$– molecular electrostatic potential, Z_A–charge of A atomic nucleus located R_A,$\rho(\mathrm{r})$-density of electrons.

$$\sigma_{\mathrm{tot}}^2 = \sigma_+^2 + \sigma_-^2 = \frac{1}{r}\sum_{i=1}^{r}\left[V_s^+(\mathrm{r}_i) - \overline{V}_s^+\right]^2 + \frac{1}{s}\sum_{j=1}^{r}\left[V_s^-\left(\mathrm{r}_j\right) - \overline{V}_s^-\right]^2 \tag{2}$$

$$\overline{V}_s^+(\mathrm{r}_i) = \frac{1}{r}\sum_{i=1}^{r} V_s^+(\mathrm{r}_i),\ \overline{V}_s^- = \frac{1}{s}\sum_{j=1}^{s} V_s^-\left(\mathrm{r}_j\right) \tag{3}$$

Where σ_+^2 and σ_-^2 are positive and negative standard deviation respectively. $\sigma_{\mathrm{tot}}^2 = \sigma_+^2 + \sigma_-^2$, $V_S^+(\mathrm{r}_i)$ and $V_S^-(\mathrm{r}_j)$ are positive and negative molecular electrostatic potential respectively. Π denotes the average deviation of the surface electrostatic potential.

$$\nu = \frac{\sigma_+^2\sigma_-^2}{[\sigma_{\mathrm{tot}}^2]^2} \tag{4}$$

$$\Pi = \frac{1}{2}\sum_{i=1}^{n}|V(r_i) - \overline{V}_S| \tag{5}$$

Formula (6)–(8), derived from molecular electrostatic potential proposed by Politzer et al. [18,19] were applied to compute vaporization enthalpies, sublimation enthalpies, fusion enthalpies, Formula (9) and (10) were employed to calculate molecular cohesive energy and lattice energy, respectively [20]. Some related coefficients in Eqs. (6), (7), (7) and (11) were listed in the brackets $\{(\alpha_1, \alpha_2, \alpha_3)=(1.355, 1.1760, -10.4331), (\beta_1, \beta_2, \beta_3)=(4.4307\times10^{-4}, 2.0599, -2.4825), (\gamma_1, \gamma_2, \gamma_3)=(0.1046, 1.872, 60.74), (\delta_1, \delta_2, \delta_3)=(-0.0064, 241.42, -3.43)\}$, proposed by Politzer et al..

$$\Delta_{\mathrm{vap}}H^\circ = \alpha_1 As^{0.5} + \alpha_2(\nu\sigma_{\mathrm{tot}}^2)^{0.5} + \alpha_3 \tag{6}$$

$$\Delta_{\mathrm{sub}}H^\circ = \beta_1 As^2 + \beta_2(\nu\sigma_{\mathrm{tot}}^2)^{0.5} + \beta_3 \tag{7}$$

$$\Delta_{fus}H^\circ = \gamma_1 As + \gamma_2\nu\Pi + \gamma_3 \tag{8}$$

$$E_{\mathrm{coh}} = \Delta U_{\mathrm{vap}} - p\Delta V \approx \Delta H_{\mathrm{vap}} - RT \tag{9}$$

$$E_{\mathrm{latt}} = -\Delta H_{\mathrm{sub}}(T) - 2RT \tag{10}$$