Computational and Theoretical Chemistry 992 (2012) 92–96

Contents lists available at SciVerse ScienceDirect

Computational and Theoretical Chemistry

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

Computational studies on the triazole-based high energy materials

Vikas D. Ghule *

Advanced Centre of Research in High Energy Materials (ACRHEM), University of Hyderabad, Hyderabad 500 046, India

ARTICLE INFO

Article history:
Received 3 May 2012
Received in revised form 9 May 2012
Accepted 12 May 2012
Available online 23 May 2012

Keywords:
Density functional theory
Energetic materials
Triazole
Heat of formation
Electrostatic potential
Density

ABSTRACT

In this work, the properties of the dinitro-triazole-based high nitrogen compounds were studied theoretically to facilitate further developments. The gas-phase heats of formation were predicted based on the isodesmic reactions by using the DFT-B3PW91/6-31G(d,p) method. The solid-phase heats of formation and heats of sublimation were estimated in the framework of the Politzer approach. The designed molecules show solid-phase heats of formation above 180.0 kcal/mol. The crystal density has been computed using molecular packing calculations with CVFF force field. Detonation properties of the designed compounds were evaluated by using the Kamlet–Jacobs equation based on predicted densities and heats of formation. Designed triazole-based derivatives show detonation velocity (*D*) over 8.3 km/s and detonation pressure (*P*) above 30 GPa. Thermal stability was evaluated via bond dissociation energies (BDEs) of the weakest C–NO_2 bond at B3PW91/6-31G(d,p) level. Bond dissociation energy analysis revealed that designed molecules are better candidates considering stability.

1. Introduction

The synthesis of nitrogen-rich energetic materials has been a topic of extensive interest and much work has been devoted towards the synthesis of azole-based energetic materials [1–3]. The development of new energetic materials aimed for high positive heat of formation, high detonation velocity and pressure, high thermal stability and low sensitivity towards external forces like impact, friction or electrostatic discharge. Nitrogen-rich compounds constitute a unique class of energetic materials. The greater environmental compatibility of nitrogen-rich compounds is due to the fact that their combustion results mainly in environmental friendly molecular nitrogen. Additionally, a large number of C–N and N–N bonds in a compound leads to a high positive heat of formation and also to high crystalline densities [4,5]. Both heat of formation and density are important for determining the performance of materials and governed by the molecular structure of the compound [6].

Triazole-based energetic materials are most prominent in the nitrogen-rich compounds appear to be the better compromise between high energy, performance and high stability due to nitrogen-catenation and aromaticity. Many papers devoted to the design and preparation of triazole-based energetic materials constantly increases [7–9]. 1H-1,2,4-triazole [7,8], 1H-1,2,3-triazole [10,11], 1H-1,3,4-triazole [12] and 2H-1,2,3-triazole [13,14] derivatives have widely been studied as energetic materials and shown in Fig. 1. The primary reason for this stimulated interest is that nitrotriazole compounds possess more favorable elemental composition with relatively high energetic performance in regard to oxygen balance, density, and other thermodynamic properties when compared to their hydrocarbon analogous aromatic compounds. Triazole derivatives with more than two nitro groups are expected to be potential energetic ingredients for insensitive explosive formulations. Among triazoles, the gas-phase enthalpy of formation of 1,2,4-triazole has been measured by the bomb combustion calorimetry and there are no experimental data on the formation enthalpies of 1,2,3-triazoles in the literature [15–20]. The performance of triazole derivatives can be optimized through substituting hydrogen atoms with nitro explosophore as it improves oxygen balance and density, results in a higher exothermicity of the combustion and detonation process. Hence in the search of novel HEMs, nitroazoles expected to be promising candidates.

The present study aimed to design the triazole-based isomers for the energetic material applications by systematic structure–property relationships. The designed molecules are shown in Fig. 2. Density functional theory (DFT) is used for the prediction of gas phase HOF by employing isodesmic approach. The solid phase HOF is predicted from heat of sublimation using Politzer approach. The crystal density is calculated by force field based packing calculations. The stability of the designed molecules has been attempted by bond dissociation energy (BDE) calculations.

2. Computational details

All DFT calculations were carried out using the Gaussian 03 package [21]. The geometry optimization of the structures and frequency analyses were carried out by using the B3PW91 functional

---

* Tel.: +91 40 23134303; fax: +91 40 23012800.
E-mail address: ghule.vikas@gmail.com

2210-271X/$ - see front matter © 2012 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.comptc.2012.05.007

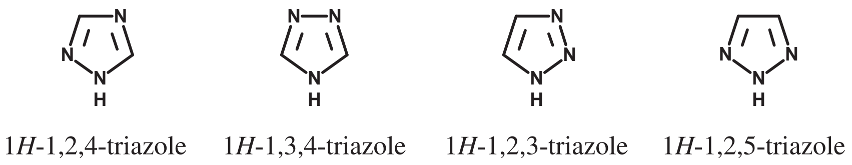

Fig. 1. Triazole moieties used in the development of energetic materials.

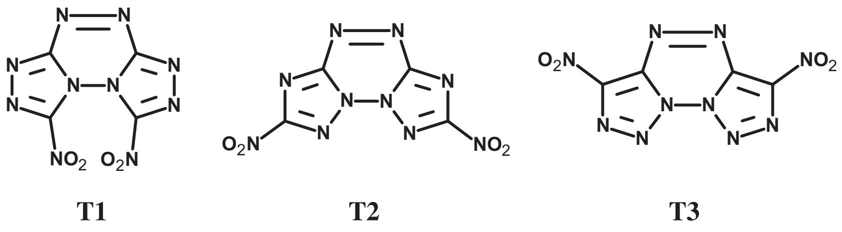

Fig. 2. Molecular structure of designed triazole derivatives.

with the 6-31G(d,p) basis set. All of the optimized structures were characterized to be true local energy minima on the potential-energy surface without imaginary frequencies. The heat of formation and density are important parameter in evaluating the performance of energetic materials. The gas phase heat of formation ($\Delta_f H^o_{Gas}$) have been predicted by designing appropriate isodesmic reactions [22,23]. The designed isodesmic reactions for the prediction of $\Delta_f H^o_{Gas}$ are given in supporting information. For estimation of the potential performance of the energetic material, it is also significant to calculate their solid phase heat of formation ($\Delta_f H^o_{Solid}$) because it is related directly with the detonation characteristics. According to Hess' law, $\Delta_f H^o_{Solid}$ can be obtained by;

$$\Delta_f H^o_{Solid} = \Delta_f H^o_{Gas} - \Delta H_{Sub}$$

where ΔH_{Sub} is the heat of sublimation and can be evaluated by the Byrd and Rice method [24] in the framework of the Politzer approach [25,26], using the following empirical relation,

$$\Delta H_{Sub} = \beta_1 A^2 + \beta_2 (\nu \sigma^2_{tot})^{0.5} + \beta_3$$

where A is the area of the isosurface of 0.001 electrons/bohr^3 electronic density, ν indicates the degree of balance between the positive and negative surface potentials, σ^2_{tot} is a measure of variability of the electrostatic potential, and β_1, β_2, and β_3 are determined through a least-squares with the experimental $\Delta_f H^o_{Solid}$ of a selected set of known materials [24]. Surface area, degree of balance between the positive and negative surface potentials and variability of the electrostatic potential are calculated using WFA program [27]. The crystal densities of all triazole derivatives are predicted by the molecular packing calculations using polymorph module of Material Studio Suite [28]. The calculation involves defining a molecule in an asymmetric cell unit, packing into a crystal under a given space group symmetry, geometry optimization to achieve energy minimized structure and removal of duplicate crystal structures by the clustering process as implemented in the polymorph module. The empirical Kamlet–Jacobs [29–31] equations were employed to estimate the values of D and P for the high energy materials containing C, H, O and N as following equations:

$$D = 1.01(NM^{0.5}Q^{0.5})^{0.5}(1 + 1.30\rho_o) \text{ and } P = 1.55\rho_o^2 NM^{0.5}Q^{0.5}$$

where in above equations D is detonation velocity (km/s), P is detonation pressure (GPa), N is moles of gaseous detonation products per gram of explosives, M is average molecular weights of gaseous products, Q is chemical energy of detonation (kJ/mol) defined as the difference of the HOFs between products and reactants, and ρ_o is the density of explosive (g/cm^3). The thermal stability of the designed compounds has been evaluated by calculating the bond dissociation energy (BDE) of the weakest C–NO_2 bonds. BDE is the difference between the zero point energy corrected total energies at 0 K of the parent molecules and those of the corresponding radicals in the unimolecular bond dissociation [32,33].

3. Results and discussion

The present study investigates important properties of energetic materials including heats of formation, densities, detonation performance and stability by employing density functional theory. A systematic structure–property relationship has been established by varying triazole backbone in the structure and the hydrogen atoms are replaced with –NO_2 groups (Fig. 2). The predicted energetic properties of triazole derivatives are compared with the benchmark explosives like, TNT (2,4,6-trinitrotoluene), TATB (2,4,6-trinitro-1,3,5-triaminobenzene), RDX (hexahydro-1,3,5-trinitro-1,3,5-triazine) and HMX (octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine).

3.1. Heat of formation

Heat of formation is one of the most important thermo-chemical properties of energetic materials because it is related directly with detonation parameters. In this section, the effect of triazole backbone, nitro substituent, and different linkages positions on heat of formation has been investigated. Table 1 lists the total

Table 1
Total energy (E_0), zero point energy (ZPE) and thermal correction (ΔH_T) at the B3PW91/6-31G(d,p) level and experimental $\Delta_f H^o_{Gas}$ for the reference compounds.

Compd.	E_0 (a.u.)	ZPE (a.u.)	ΔH_T (a.u.)	$\Delta_f H^o_{Gas}$ (kcal/mol)
CH_4	−40.459760	0.0451	0.0038	−17.83[a]
NH_3	−56.499062	0.0346	0.0038	−10.97[b]
CH_3NO_2	−244.866353	0.0503	0.0052	−19.40[c]
NH_2NH_2	−111.767104	0.0533	0.0045	22.79[d]
CH_3NNCH_3 (cis)	−189.104491	0.0840	0.0062	47.38[e]
1*H*-1,2,4-triazole	−242.100678	0.0604	0.0045	46.06[f]
1*H*-1,3,4-triazole	−242.090161	0.0595	0.0046	53.53[e]
1*H*-1,2,3-triazole	−242.074950	0.0596	0.0045	64.94[e]

[a] Ref. [39].
[b] Ref. [40].
[c] Ref. [41].
[d] Ref. [42].
[e] Values calculated using G3 calculations.
[f] Ref. [43].