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Theoretical study of an energetic material di-1H-1,3,4-triazole derivatives

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Abstract

Computations by density functional theory (DFT) method are performed on a series of di-1H-1,3,4-triazole derivatives with different substituents and linkages. The heat of formation (HOF) is predicted by the designed isodesmic reactions. The predicted results reveal that $-N_3$ and $-N{=}N-$ groups are effective structural units for increasing the HOF values of the di-1H-1,3,4-triazole derivatives. The HOMO−LUMO gap is affected by the substituents and linkage groups. Detonation performance is evaluated using the Kamlet−Jacobs approach based on the calculated density and HOF. The results indicate that $-NO_2$, $-NF_2$, $-NH-$, $-NH-NH-$ and $-N{=}N-$ groups are helpful for enhancing the detonation properties of di-1H-1,3,4-triazole derivatives. The bond dissociation energy and bond order of the weakest bonds are analyzed to investigate their stability. It is observed that the $-CH_2-$, $-CH_2-CH_2-$ and $-CH{=}CH-$ groups are effective structural units for improving the stabilities of these derivatives. Considering the detonation performance and the stability, five compounds are screened as the potential candidates for high energy density materials.

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Keywords: Di-1H-1,3,4-triazole; Density functional theory; Heat of formation; Detonation velocity; Detonation pressure

1. Introduction

The synthesis and theoretical study on the nitrogen-rich compounds have received considerable interest in recent years [1−8]. Energetic nitrogen-rich compounds are potential candidates for high energy density materials (HEDMs) due to their large number of N−N and N−C bonds in molecular skeleton, which leads to high density, high positive heat of formation, good oxygen balance, and good stability. Triazole−based energetic materials are most prominent among the nitrogen-rich compounds which appear to be a better compromise with high energy, performance and high stability due to nitrogen catenation and aromaticity [9]. Among them, 1H-1,3,4-triazole is an effective structural unit.

It is well known that properties of high energy, performance and high stability are often improved by making structural modifications. The formation of molecular complexes (e.g., di−, tri, and polymers) is a conceivable way to increase the density and thermostability and improve the material properties of propellants and explosives [10]. Therefore, as we know, triazole connected on the N atom of heterocyclic is more prone to substitution reaction. Hence, it is easily to synthesize the high nitrogen compounds with better comprehensive properties. Thermodynamic calculations conducted at Los Alamos National Laboratory identified 2,5,2′,5′-tetranitro-1,1′-bi-1,3,4-triazole(TNBT) as target molecule was likely to exhibit high performance [11]. 2,5,2′-triazido-1,1′-azo-1,3,4-triazole was synthesized [12], which shows that tetrazene (N−N=N−N) can improve *HOF* but reduce the stability. However, the systematic and comprehensive molecular design still lacks for di-1H-1,3,4-triazole-based high energy density materials.

In this paper, the HOF, electronic structures, energetic properties, and thermal stabilities of a series of di-1,3,4-

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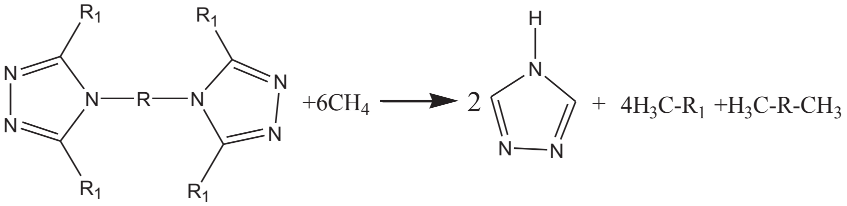
triazole derivatives with various substituents ($-NH_2$,$-NO_2$, $-NF_2$, $-N_3$) and different linkages (−, $-CH_2-$, −NH−, $-CH_2-CH_2-$,−NH−NH−, −CH=CH−, −N=N−) were systematically studied based on the density functional theory (DFT) method.

2. Computational methods

The object molecules, the series of 1H-1,3,4-triazole derivatives of which the molecules are numbered as (A1−A5, B1−B5, C1−C5, D1−D5, E1−E5, F1−F5 and G1−G5), are classified into seven groups, as shown in Fig. 1. The hybrid DFT−B3LYP method [13,14] in combination with 6−31G (*d*, *p*) basis set is used for structure optimization, which has been proved [15−18] to give quite reliable energies, molecular structures, and other properties. All quantum mechanical calculations were performed with Gaussian 03 program package [19]. The optimized structure of each molecule corresponds to only one local energy minimum on the potential energy surface without imaginary frequency.

The isodesmic reaction method is employed to calculate *HOF*. Here we design an isodesmic reaction in which the numbers of all kinds of bonds are kept constant to decrease the calculation errors of *HOF*. Because of the electronic circumstances of reactants and products are very similar in the isodesmic reactions, the errors of electronic correction energies can be counteracted, therefore, the errors of calculated *HOF* can be greatly reduced [20]. In these designed reactions, the basic structural unit of 1,3,4-triazole skeleton is kept constant, and the complex molecules are split into sample molecules. This method had been shown to be reliable [3,15,21−23].

The *HOF* of di-1H-1,3,4-triazole derivatives at 298 K was obtained by isodesmic reactions, which is given as follows



(1)

where $R_1 = -H, -NH_2, -NO_2, -NF_2, -N_3$. R = −, $-CH_2-$, −NH−, $-CH_2CH_2-$, −NH−NH−, −CH=CH−, −N=N−.

For the isodesmic reaction, the heat of reaction ΔH_{298} at 298 K can be calculated from the following equation

$$\Delta H_{298\ \mathrm{K}} = \Sigma\Delta H_{\mathrm{f,P}} - \Sigma\Delta H_{\mathrm{f,R}} \tag{2}$$

where $\Delta H_{\mathrm{f,P}}$ and $\Delta H_{\mathrm{f,R}}$ are the *HOF*s of products and reactants at 298 K, respectively. Since the experimental *HOF*s of 1H-1,3,4-triazole, CH_3NF_2, CH_3N_3, and $CH_3N{=}NCH_3$ are unavailable, the additional calculations were carried out. The *HOF* of CH_3NF_2 was calculated by the replacement reaction $CH_3NH_2 + F_2 \rightarrow CH_3NF_2 + H_2$ using G2 theory [17,23].The *HOF* values of 1H-1,3,4-triazole, CH_3N_3 and $CH_3N{=}NCH_3$ were obtained at G2 level from the atomization reaction $C_aH_bO_cN_d \rightarrow aC(g) + bH(g) + cO(g) + dN(g)$. The experimental *HOF*s of reference compounds CH_4, CH_3NH_2, CH_3NO_2, CH_3NHCH_3, CH_3CH_3 , $CH_3CH_2CH_3$, $CH_3CH_2CH_2CH_3$, $CH_3NHNHCH_3$ and $CH_3CH{=}CHCH_3$ are available [24−26].

The *HOF*s of 1H-1,3,4-triazole-based derivatives can be estimated when the heat of reaction $\Delta H_{298\mathrm{K}}$ is known. Therefore, the primary thing is to calculate $\Delta H_{298\mathrm{K}}$. $\Delta H_{298\mathrm{K}}$ can be calculated by using the following expression

$$\Delta H_{298\ \mathrm{K}} = \Delta E_{298\ \mathrm{K}} + \Delta(PV) = \Delta E_0 + \Delta ZPE + \Delta H_{\mathrm{T}} + \Delta nRT \tag{3}$$

where ΔE_0 is the change in total energy between the products and the reactants at 0 K; ΔZPE is the difference between the zero-point energies(ZPE) of the products and the reactants; and ΔH_{T} is the thermal correction from 0 to 298 K. $\Delta(PV)$ equals ΔnRT for the reaction of ideal gas. For the isodesmic reaction here, $\Delta n = 0$, so $\Delta(PV) = 0$.

Since the condensed phases of most energetic compounds are solid, the solid-phase heat of formation ($\Delta H_{\mathrm{f,solid}}$) is required in order to calculate the detonation properties. According to Hess's law of constant heat summation [27], the gas-phase heat of formation ($\Delta H_{\mathrm{f,gas}}$) and heat of sublimation (ΔH_{sub}) can be used to evaluate the solid-phase heat of formation

$$\Delta H_{\mathrm{f,solid}} = \Delta H_{\mathrm{f,gas}} - \Delta H_{\mathrm{sub}} \tag{4}$$

Politzer et al. [28−30] pointed out that the heat of sublimation of energetic compounds correlates well with the molecular surface area and the electrostatic interaction index $\nu\sigma^2_{\mathrm{tot}}$. The empirical expression for this approach is shown below

$$\Delta H_{\mathrm{sub}} = aA^2 + b\left(\nu\sigma^2_{\mathrm{tot}}\right)^{0.5} + c \tag{5}$$

where A is the surface area of the 0.001 electrons/bohr^3 isosurface of the electronic density of the molecule; ν describes the degree of balance between positive and negative potentials on the isosurface; and σ^2_{tot} is a measure of the variability of the electrostatic potential on the molecular surface. The coefficients a, b, and c were determined by Rice et al.:

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