



Full paper/Mémoire

Molecular design of prismane-based potential energetic materials with high detonation performance and low impact sensitivity



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ABSTRACT

To develop new energetic materials, the eleven nitroester substitution derivatives of prismane were investigated at the B3LYP/6-311G** level of density functional theory (DFT). The gas phase heats of formation were calculated by isodesmic reactions and the solid-state heats of formation were obtained by the Politzer approach using the heats of sublimation for the designed compounds. The detonation velocities and pressures of all molecules were calculated by Kamlet–Jacobs equations based on molecular density and heat of detonation. The results show that the nitroester group in prismane is helpful for enhancing molecular detonation properties and power index. Among all molecules, 1,2,3,4-tetrinitroesterprismane has excellent detonation properties (detonation pressure = 40.05 GPa, detonation velocity = 9.28 km/s) and large power index value. The molecular stabilities were evaluated by calculating bond dissociation energies and characteristic heights (H_{50}). The results indicate that the bond dissociation energies of all molecules are above 80 kJ/mol, and all molecules have a larger H_{50} value than hexanitrohexaazaisowurtzitane (CL-20, 12 cm). The obtained structure–property relationships may provide basic information for the molecular design of novel high-energy materials.

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1. Introduction

High-energy density materials (HEDMs) have attracted considerable attention owing to their superior explosive performances over conventional energetic compounds [1–7]. Organic-cage compounds were widely investigated due to their large strain energies, high heat of formation, and compact structures as an important category of HEDMs [8]. Typical examples of these compounds are CL-20 and octanitrocubane (ONC). Octanitrocubanes, which were synthesized in 2000 from heptanitrocubane [9], are derivatives of the strained cubane molecule, have a

high nitrogen content and have been found to have a high density, ranging from 1.98 to 2.06 g/cm³, depending on the nitro group's orientation and to be shock insensitive, as it has been confirmed by hitting the compound with a hammer. However, it is a pity that it cannot be used widely in practical applications because of its production cost nowadays. Furthermore, another two types of organic cage compounds, nitro derivatives of hexaazaadamantane (HAA) and adamantane series, have also been investigated as promising candidates for HEDMs [10,11]. Recently, two novel and super-high energy cage explosives, dodecanitrohexaprismane and hexanitrohexaazaprismane, have also been studied by Zhu et al. [12]. The results indicate that dodecanitrohexaprismane has much higher energetic properties than those of ONC, which may be the most powerful nonnuclear explosive known so far. These

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investigations further indicate that cage skeleton is a good parent structure for HEDMs.

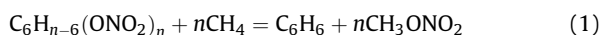
We are interested in another cage structure: prismane, which is a hydrocarbon with a large ring-strain energy of 606.9 kJ/mol [13], and has been synthesized and fully characterized [14,15]. In addition, many prismane derivatives have also been studied in detail with quantum chemistry methods. Such as, azaprismanes were studied by Politzer et al. in 1989 [16]. Their results show that in each set of azaprismane isomers, the most stable is the one having the fewest N–N bonds. Lately, polyisocyanoprismanes and polyazidoprismanes have been studied by Xu et al. [17]. These results indicate that these prismane derivatives have large and positive heat of formation values. However, the detonation performances of derivatives have not been studied in their paper. Otherwise, the nitroprismane derivatives have been calculated in detail at the B3LYP/6-311G** level by Li et al. [18]. The results show that polynitroprismanes with five and six nitro groups meet the demands of practical HEDMs. Furthermore, we also studied the stability and detonation performance of polydinitroaminoprismanes by using density function theory, and found that tridinitroaminoprismanes and tetradinitroaminoprismanes have excellent detonation properties [19].

Recently, a larger number of nitrate ester derivatives were synthesized, which showed high detonation performance and low melting point [20,21]. These works provided an effective strategy for designing energetic materials. In the present work, the H atoms in prismane were systematically replaced with a nitroester group, generating the series of molecules $C_6H_{n-6}(ONO_2)_n$ ($n = 1-6$). The main difference between the nitroester (ONO_2), nitro (NO_2), isocyano (CN), and azido (N_3) functional groups is the amount of oxygen presented. As far as combustion is concerned, the nitroester group has remarkable advantages.

2. Computation methods

In our previous studies, we had studied the properties of energetic compounds at the B3LYP and MP2 levels, and the similar calculated results had been obtained at two different levels [22,23]. Therefore, we think that reliable results can be obtained by using B3LYP function. In the present work, structure optimization and frequency calculations were performed with Gaussian 03 package at the B3LYP/6-311G** level [24], and no constraints were imposed on the molecular structure during the optimization process. Heats of formation, detonation performances, and impact sensitivity were studied at the same level, and bond dissociation energies were calculated at the UB3LYP/6-311G** level. All optimization molecular structures are shown in Fig. 1.

The heats of formation in the gas state (HOF_{gas}) of all molecules were evaluated by using an isodesmic reaction.



$$\Delta H_{298} = \Delta E + \Delta ZPE + \Delta H_T = \sum \Delta H_{f,p} - \sum \Delta H_{f,R} \quad (2)$$

where n is the number of $-ONO_2$ groups combined with the C atoms in the cage skeleton, ΔH_{298} is the enthalpy change of the reaction at 298 K, ΔE 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, ΔH_T is the thermal correction from 0 to 298 K, $\sum \Delta H_{f,p}$ and $\sum \Delta H_{f,R}$ are the sums of the heats of formation of the products and the reactants, respectively. As to the reference compound CH_3ONO_2 , its HOF was calculated by G-2 theory, based on atomization energies. The HOF of CH_4 and C_6H_6 can be obtained from NIST.

Since the condensed phases of most energetic compounds are solid, calculating detonation properties requires knowledge of the solid-phase heat of formation (HOF_{solid}). According to Hess' law of constant heat summation, HOF_{gas} and the heat of sublimation (ΔH_{sub}) can be used to evaluate HOF_{solid} :

$$HOF_{solid} = HOF_{gas} - \Delta H_{sub} \quad (3)$$

where ΔH_{sub} is the sublimation enthalpy evaluated using equation (4) suggested by Rice and Politzer et al. [25]:

$$\Delta H_{sub} = \alpha_1(SA)^2 + \beta_1(\nu\sigma_{tot}^2)^{0.5} + \lambda_1 \quad (4)$$

where SA is the area of the isosurface of 0.001 e/Bohr³ electron density of a molecule. ν describes the degree of balance between positive potential and negative potential on the isosurface, and σ_{tot}^2 is a measure of the variability of the electrostatic potential on the molecular surface. The coefficients α_1 , β_1 and λ_1 have been determined by Rice et al.: $\alpha_1 = 1.118 \times 10^{-3}$ kJ·mol⁻¹, $\beta_1 = 6.910$ kJ·mol⁻¹, and $\lambda_1 = 12.416$ kJ·mol⁻¹.

The empirical Kamlet–Jacobs equations [26] are employed to estimate the detonation velocity and pressure for the energetic materials containing carbon, hydrogen, oxygen and nitrogen atoms:

$$D = 1.01 (\overline{NM}^{1/2} Q^{1/2})^{1/2} (1 + 1.30\rho_0) \quad (5)$$

$$P = 1.558 \rho_0^2 \overline{NM}^{1/2} Q^{1/2} \quad (6)$$

D is the detonation velocity (km/s), P is the detonation pressure (GPa). N is the number of moles of gas produced per gram of explosive, and \overline{M} is the mean molecular weight of the gaseous detonation products. Q is the heats of detonation (cal/g). ρ_0 is molecular density (g/cm³), which was calculated from the molar weight (M) divided by the average value molar volume (V). V is defined as a contour of 0.001 electrons/Bohr³ density that was evaluated using a Monte Carlo integration. We performed 100 single-point calculations for each molecule to get an average volume.

But the procedure used to estimate densities can lead to significant errors. Politzer et al. [27,28] considered that the solid molecular density can be adjusted for the electrostatic potential (Eqs. (7)–(11)):

$$\text{Crystal density}(\rho_0) = \alpha(M/W_m) + \beta(\nu\sigma_{tot}^2) + \gamma \quad (7)$$

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