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Theoretical studies on polynitro-1,3-bishomopentaprismanes as potential high energy density compounds

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ABSTRACT

Based on the fully optimized molecular geometric structures at the DFT-B3LYP/6-31G* level, the densities (ρ), detonation velocities (D) and pressures (P) for a series of polynitro-1,3-bishomopentaprismanes (PNBPPs), as well as their thermal stabilities, were investigated to look for high energy density compounds (HEDCs). The studied PNBPPs have high values of heats of formation (HOFs) and the magnitude is correlative with the number (n) and the space distance of nitro groups. D and P for PNBPPs were estimated by using modified Kamlet–Jacobs equations based on the calculated HOFs and ρ. It is found that ρ, D and P all increase with n and satisfy the group additivity rule. The calculations on the bond dissociation energies of C—NO$_2$ and C—C bonds indicate that both bonds are possible to be the trigger bond in the pyrolysis process, and this interesting phenomenon is related with the molecular structure, especially the strain energy of the skeleton. In conjunction with the energetic performances and thermal stabilities, PNBPPs with $n = 8$–12 are recommended as the preferred candidates of HEDCs. These results would provide basic information for the further studies of PNBPPs.

1. Introduction

Nowadays, high energy density compounds (HEDCs) have been attracting considerable interests because of their superior explosive performances over the currently used materials [1–3]. Looking for HEDCs has become one of the most heated topics and seems to be never-ending to meet with the requirements of national defence and economy. Polynitro-substituted cage compounds are investigated as an important category of HEDCs due to their high strain energies, compact structures and self-contained oxidizability [4]. Typical examples are hexanitrohexaazaisowurtzitane (CL-20) and octanitrocubane (ONC). Recently, our group has carried out theoretical investigations on polynitro-substituted cubane [5], admantane [6] and hexaazaadmantane [7], and some of them have been recommended as potential candidates of HEDCs. These investigations further indicate that cage skeleton is a good parent structure for HEDCs.

The birdcage hydrocarbon, 1,3-bishomopentaprismane (BPP, see Fig. 1 for the structure), is a typical cage compound with good symmetry (C_{2v}) and stability [8–10]. Ever since its first synthesis in 1960 [8], various kinds of its derivatives have been synthesized and investigated in the following decades [11–17]. Polynitro-1,3-bishomopentaprismanes (PNBPPs), which are formed when parts of the H atoms in BPP are substituted by nitro groups, have received greater attention for their potentials as HEDCs [15–17]. Nevertheless, due to the difficulties and expenditure, hitherto only PNBPPs with up to four nitro groups have been successfully synthesized [15–17]. Therefore, theoretical predictions of their structures and explosive performances are of important significance in finding promising candidates for novel HEDCs. However, to the best of our knowledge, there are few theoretical studies focused on the performance of PNBPPs. In the present paper, the potentials for a series of PNBPPs as HEDCs are discussed by systematically predicting their densities, detonation properties and thermal stabilities using density functional theory (DFT). Since there are many isomers for PNBPPs with the same number of nitro groups, only certain kinds of PNBPPs reflecting typical relative position of nitro groups or those having experimental data are chosen as the target compounds.

In the past decade, our group has carried out a series of investigations on the "molecular design" of HEDC for many typical categories of energetic compounds [5–7,18–25]. Based on the results of these studies, a quantitative criteria considering both energy (including density ρ, detonation velocity D and detonation pressure P) and stability (bond dissociation energy BDE of the trigger bond) requirements was suggested to be used to predict the potential of a compound as HEDC, i.e., $\rho \approx 1.9\,\mathrm{g\,cm^{-3}}$, $D \approx 9\,\mathrm{km\,s^{-1}}$, $P \approx 40\,\mathrm{GPa}$ and BDE ≈ 80–$120\,\mathrm{kJ\,mol^{-1}}$ [25]. Therefore, the main content of the present paper is to predict the densities, detonation properties and thermal stabilities of PNBPPs so as to search for new high-energy and insensitive explosives among PNBPPs.

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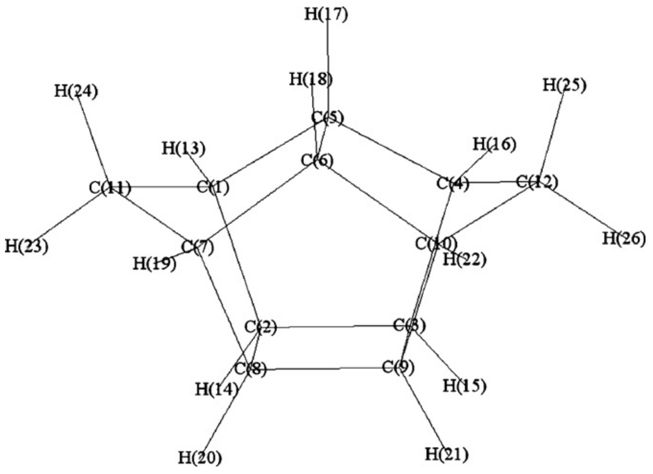

Fig. 1. The structure and atomic numbering for BPP.

2. Computational methods

A series of NPBPPs were studied using Gaussian 03 program [26]. All the molecules and the related radical species were fully optimized without any symmetry restrictions at the DFT-B3LYP level [27,28] with the 6-31G* basis set [29]. The default convergence cutoffs given in the program were used throughout the calculations. To characterize the nature of the stationary points and determine the zero-point vibrational energy corrections, harmonic vibrational analyses were performed subsequently. The computed harmonic vibrational frequencies were scaled uniformly by a factor of 0.96 to take into account the systematic overestimation of vibrational frequencies in the B3LYP/6-31G* calculation [30].

Based on the obtained total energy (E_0), zero-point energy (ZPE) and thermal correction from 0 to 298 K (ΔH_T°), atomization reaction (1) was applied to calculate the heat of formation (HOF) [31]:

$$C_{12}H_{14-n}N_nO_{2n} \rightarrow\ 12C + (14-n)H + nN + 2nO \tag{1}$$

$$\begin{aligned}\Delta H^\circ_{298} &= 12\Delta_f H^\circ_{298,C} + (14-n)\Delta_f H^\circ_{298,H} + n\Delta_f H^\circ_{298,N}\\ &\quad + 2n\Delta_f H^\circ_{298,O} - \Delta_f H^\circ_{298,M}\end{aligned} \tag{2}$$

where M denotes the title compound $C_{12}H_{14-n}N_nO_{2n}$; ΔH°_{298} is the standard enthalpy change of reaction (1) at 298 K; the experimental standard HOFs ($\Delta_f H^\circ_{298}$) of C, H, N and O are known and listed in Table 1 [32]. On the other hand, the following relationship exists:

$$\Delta H^\circ_{298} = \Delta E^\circ_{298} + \Delta(PV) = \Delta E_0 + \Delta ZPE + \Delta H^\circ_T + (\Delta N)RT \tag{3}$$

where ΔE_0, ΔZPE, and ΔH°_T are the change of total energy at 0 K, the change of ZPE and the change of thermal correction from 0 to 298 K between the products and the reactants, respectively. The $\Delta(PV)$ value is the PV work term, and it equals $(\Delta N)RT$ for the reactions of an ideal gas. For reaction (1), it equals $(25+2n)RT$. Besides, the values of ZPE and ΔH°_T of atom are zero, thus Eq. (3) can be derived into Eq. (4):

$$\begin{aligned}\Delta H^\circ_{298} &= 12E_{0,C} + (14-n)E_{0,H} + nE_{0,N} + 2nE_{0,O} - E_{0,M}\\ &\quad - ZPE_M - \Delta H^\circ_{T,M} + (25+2n)RT\end{aligned} \tag{4}$$

Therefore, based on the calculated results, the standard HOF of the compound M, $\Delta_f H^\circ_{298,M}$, can be obtained from Eqs. (2) and (4). To decrease the influence of the size and structure of the molecules on the results, the HOFs for 49 energetic compounds whose experimental HOFs are available were calculated at the same theoretical level [33]. By comparing the experimental and calculated results, correction equation was obtained with a good linear correlation coefficient ($R = 0.990$):

$$\Delta_f H^\circ_{298,M,corrected} = -75.79 + 0.98\Delta_f H^\circ_{298,M} \tag{5}$$

The empirical Kamlet–Jacobs (K–J) equations [34], which were raised by Kamlet and Jacobs in 1968, are widely used to estimate the detonation properties (D and P) of CHNO explosive due to the facility and reliability of the method. The expressions are as follows:

$$D = 1.01(N\bar{M}^{1/2}Q^{1/2})^{1/2}(1 + 1.30\rho) \tag{6}$$

$$P = 1.558\rho^2 N\bar{M}^{1/2}Q^{1/2} \tag{7}$$

In the above equations, N is the moles of gaseous detonation products per gram of explosive, $\bar{M}$ is the average molecular weight of gaseous products, Q refers to the detected chemical energy of the detonation reaction, and ρ denotes the experimental loading density of explosive. Obviously, the experimental values of Q and ρ cannot be obtained for energetic compounds that have not been synthesized. In order to predict the detonation properties of potential HEDCs, we recommend that modified K–J equations based on the calculation results of quantum chemistry be used [25]. In detail, ρ can be replaced by the theoretical density of a compound crystal (ρ_{cal}), while Q can be calculated as the difference between the HOFs of products and reactants of the detonation reaction (Q_{cal}). The expressions of the modified K–J equations are as follows:

$$D = 1.01(N\bar{M}^{1/2}Q_{cal}^{1/2})^{1/2}(1 + 1.30\rho_{cal}) \tag{8}$$

$$P = 1.558\rho_{cal}^2 N\bar{M}^{1/2}Q_{cal}^{1/2} \tag{9}$$

Here, the products for the explosive reaction are N_2, H_2O, CO_2 and O_2 in turn if the content of oxygen is enough; otherwise, those H atoms that cannot produce H_2O due to the lack of oxygen will turn into H_2 gas, while those C atoms unable to produce CO_2 will exist in the form of solid C. The detailed calculation methods for parameters N, $\bar{M}$ and Q_{cal} for the compounds with different compositions are listed in Table 2 [35].

Considering that crystal is not easy to be compressed and there are vacancies in the loading attachment of actual explosive, ρ_{cal} is always larger than ρ [25]. Besides, since the explosive reaction is designed according to the maximal exothermic principle, Q_{cal} is larger than Q [25]. Therefore, it is comprehensible that the obtained D and P are theoretically the largest values for the title compounds. Previous studies [5–7,18–25] reveal that the modified K–J equations are reliable if the value of ρ_{cal} is close to the experimental one. Therefore, it is noticeable that the reliability of ρ_{cal} is the key factor in the prediction of detonation properties.

As well known, accurate prediction of crystal density is of much difficulty. "Group or volume additivity" method [36,37], although simple and rapid, cannot give reliable results owing to its inherent drawbacks; while the "crystal packing" method [38,39], which is more reliable, has its limitation in routine calculation due to its extensive requirement in computational resources. Recently, an

Table 1
The experimental standard heats of formation ($\Delta_f H^\circ_{atom}$)^{34} and calculated total energy (E_0) for C, H, N and O atoms at the B3LYP/6-31G* level.

$\Delta_f H^\circ_{atom}$ (kJ mol^{-1})				E_0 (a.u.)			
C	H	N	O	C	H	N	O
716.7	218.0	472.7	249.2	−37.84628	−0.50027	−54.58449	−75.06062