



Computational screening of several silicon-based high-energy hexanitrohexaazaisowurtzitane-like derivatives



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ARTICLE INFO

Article history:

Received 31 October 2013

Received in revised form 25 November 2013

Accepted 2 December 2013

Available online 11 December 2013

Keywords:

Silicon-based CL-20 derivatives

Cage strain energy

Homodesmotic reactions

Formation enthalpy

Fluorine balance

ABSTRACT

Silicon-based hexanitrohexaazaisowurtzitane (CL-20) derivatives, including nitro ($-\text{NO}_2$) and difluoro-amino ($-\text{NF}_2$) group containing derivatives, may become important high-energy compounds. Density Functional Theory Becke exchange plus Perdew correlation (BP) with triple numerical set plus polarization functions (TNP) and homodesmotic reactions were employed to calculate cage strain energies, gaseous phase formation enthalpies of several silicon-based CL-20 derivatives. Comparative studies were carried out between silicon-based CL-20 nitro and difluoroamine derivatives. The structural stability of these silicon-based CL-20 derivatives were evaluated in terms of N- NO_2 or N- NF_2 bond dissociation energies and Mulliken charges of $-\text{NO}_2$ or $-\text{NF}_2$ groups by means of density functional theory revised versions of the Perdew–Burke–Ernzerhof (RPBE) with TNP functions, and the exchange component of Perdew and Wang's 1991 functional (PW91) with TNP functions, two theoretical methods were chosen according to experimental data. The theoretical studies show that their performances are better than CL-20 in terms of detonation velocities, detonation pressures and explosion temperatures. Structural stability of these silicon-based CL-20 derivatives is higher than CL-20 according to N- NO_2 or N- NF_2 bond dissociation energies and cage strain energies. This work will lay some foundations for the future explorations of novel high-energy silicon-based compounds.

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1. Introduction

Since 1990 the luminescence properties of porous silicon were discovered by Canham [1], it has attracted more and more research interests in this area, such as the aspect of porous silicon-based energetic materials [2]. In 1992, Bard and his colleagues of Texas University in U.S. reported porous silicon-based energetic materials firstly [3]. Later, Lazarouk et al. found the fast oxidation process of porous silicon in the air is in the form of combustion or detonation [4]. After 2007, Monuko [5] and Churaman [6] further studied the energetic properties of porous silicon.

The basic principle of silicon derived high-energy explosives is based on the mix of porous silicon and the given oxidants and forms a detonation component. To achieve the highest detonation power on the given surface and in the given volume, it must meet the requirement of high porous density in the premise of the

proper size of mixed oxidant molecules, that is, as much as possible effective detonation reactive superficial areas of nano-silicon should be ensured.

The silicon-based high-energy materials or devices mentioned above are porous silicon and oxidants separated systems. However, so far, there are fewer silicon-based high-energy compounds reported which combined two components into one compound. Klapötke experimentally synthesized and theoretically studied a silicon-pentaerythritol tetranitrate (Si-PETN), $\text{Si}(\text{CH}_2\text{ONO}_2)_4$, which is a sensitive high-energy compound, it was designed and synthesized on the basis of carbon-based high-energy and sensitive compound pentaerythritol tetranitrate (PETN), $\text{C}(\text{CH}_2\text{ONO}_2)_4$ [7–9]. Currently, this is an attractive strategy which reduces the risk of synthesis and usage. The development of exploring high-energy compounds is of a long and hard way, for hundreds of years, there are only several high-energy explosives in practical use. It is expected that silicon-based high-energy compounds may play more important role because of very negative formation enthalpies of SiO_2 (s), -910.8 kJ/mol, or SiF_4 (g), -1614.9 kJ/mol, which are the main products after silicon-based high-energy explosive burns or detonates, and it will release a large amount of heat.

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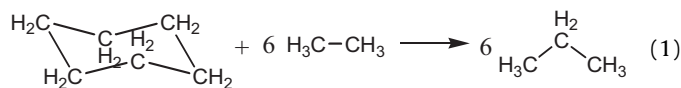
CL-20, a cage-shaped polynitro high explosive, is now commonly in military and civil use. Some of the properties of CL-20 are: theoretical density 2.04 g/cm³, detonation velocity 9380 m/s, standard formation enthalpy 416 kJ/mol (solid), and differential scanning calorimetry (DSC) decomposition temperature 228 °C [10]. If the carbon atoms in CL-20 are partly or wholly substituted by silicon atoms, and difluoramino groups (–NF₂) instead of nitro groups (–NO₂), will the energy become higher or the molecular structure become more stable?

In this paper, we designed a series homodesmotic reactions to calculate formation enthalpies of silicon-based CL-20 derivatives in terms of the experimental enthalpy of formation of CL-20, accordingly, the energy levels of silicon-based CL-20 derivatives were established; another homodesmotic reactions to calculate cage strain energy, Mulliken charge of nitro groups and bond dissociation energy of N–NO₂ and N–NF₂, hereby, the stabilities of silicon-based CL-20 derivatives were determined.

2. Computational details

All of the electronic structure calculations were performed using the DMol3 [11,12] numerical-based density-functional computer software implemented in the Materials Studio 5.0 package [13] distributed by Accelrys, Inc. Because there are no experimental data for string or cage strain energies, so far, in this work we select the suitable functions from eight classes of functions [14–20] according to the well-known fact that the chair-type cyclohexane is strain-free, the results indicated that BP functions together with homodesmotic reaction (1) may be more suitable to calculate the ring strain energies of chair-type cyclohexane. Strain energies were calculated in terms of Eq. (1), and the details were displayed in Table 1. In a homodesmotic reaction [21–24], bond types, bond valences, atomic hybridization types and molecular conformations are kept the same at both sides, the systematic errors caused by the electron-correlation energies and electron-exchange energies may be reduced to a significant extent. Accordingly, BP/TNP functions

and some homodesmotic reactions were carried out to calculate cage strain energies and formation enthalpies of CL-20 and their Si-based derivatives.



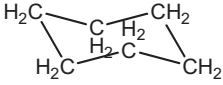
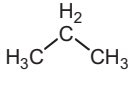
$$E_S = \sum_i n_i (E_{0,i}(R) + ZPE_i(R)) - \sum_j n_j (E_{0,j}(P) + ZPE_j(P)) \quad (1)$$

Formation enthalpy, a basic parameter of a compound, is a challenging physical quantity for wave function based electronic structure ab initio methods so far [25,26], especially for some larger molecules. Despite semi-empirical methods can directly calculate formation enthalpy, but the accuracy could not be achieved. Homodesmotic reaction-based density functional theory calculations for gaseous phase formation enthalpy are still effective and reliable methods, which are designed along the route where the compounds contain experimental values, formation enthalpies can be calibrated to the level of experimental values under 298.15 K.

3. Results and discussions

According to homodesmotic (1) and Eq. (1), the calculated string strain energies of chair-type cyclohexane range from –13.4 kJ/mol to 24.8 kJ/mol, BP/TNP's result (3.2 kJ/mol) is most agreeable with our knowledge with respect to chair-type cyclohexane. In equation (1), *R* and *P* denote reactants and products, respectively; *i* and *j*, a reactant and a product, *n_i* and *n_j*, coefficient of reactant *i* and product *j*, respectively. Accordingly, the similar designs were considered to calculate the cage strain energies of silicon-based CL-20 derivatives. The homodesmotic reactions were shown in (2)–(8), here *R* group represents nitro group (–NO₂) or difluoramino group (–NF₂) and the results were shown in Tables 2–4.

Table 1
The string strain energy calculations of chair-type cyclohexane by means of eight classes of functions.

Functions	Energies		H ₃ C–CH ₃	
PW91/TNP	<i>E</i> ₀ (Hartree)	–235.853443	–79.810824	–119.120296
	<i>ZPE</i> (kJ/mol)	437.312	189.221	261.877
	<i>E</i> _S (kJ/mol)	10.3		
BP/TNP	<i>E</i> ₀ (Hartree)	–235.928212	–79.842869	–119.164067
	<i>ZPE</i> (kJ/mol)	439.810	189.259	261.571
	<i>E</i> _S (kJ/mol)	3.2		
PBE/TNP	<i>E</i> ₀ (Hartree)	–235.630625	–79.732288	–119.004575
	<i>ZPE</i> (kJ/mol)	436.521	187.991	262.810
	<i>E</i> _S (kJ/mol)	–4.3		
BLYP/TNP	<i>E</i> ₀ (Hartree)	–235.819964	–79.801722	–119.105327
	<i>ZPE</i> (kJ/mol)	441.738	187.920	261.638
	<i>E</i> _S (kJ/mol)	3.8		
BOP/TNP	<i>E</i> ₀ (Hartree)	–235.815773	–79.806869	–119.109361
	<i>ZPE</i> (kJ/mol)	436.278	188.322	262.148
	<i>E</i> _S (kJ/mol)	–8.8		
VWM-BP/TNP	<i>E</i> ₀ (Hartree)	–235.939573	–79.846836	–119.169928
	<i>ZPE</i> (kJ/mol)	439.253	189.456	261.450
	<i>E</i> _S (kJ/mol)	4.6		
RPBE/TNP	<i>E</i> ₀ (Hartree)	–235.978959	–79.861844	–119.192001
	<i>ZPE</i> (kJ/mol)	437.102	188.774	264.718
	<i>E</i> _S (kJ/mol)	–13.4		
HCTH/TNP	<i>E</i> ₀ (Hartree)	–235.997972	–79.882311	–119.215885
	<i>ZPE</i> (kJ/mol)	456.529	200.895	274.357
	<i>E</i> _S (kJ/mol)	24.8		

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