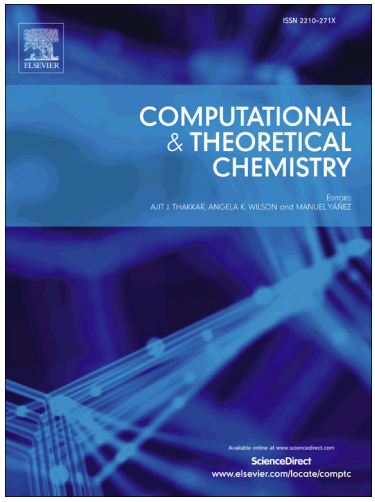

Theoretical Design of Bicyclo[2.2.1]heptane Derivatives for High-Energy Density Compounds with Low Impact Sensitivity

Mingran Du, Xuguang Wang, Ziru Guo

PII: S2210-271X(16)30343-7
DOI: http://dx.doi.org/10.1016/j.comptc.2016.09.008
Reference: COMPTC 2242

To appear in: *Computational & Theoretical Chemistry*

Received Date: 14 June 2016
Revised Date: 11 August 2016
Accepted Date: 6 September 2016

Please cite this article as: M. Du, X. Wang, Z. Guo, Theoretical Design of Bicyclo[2.2.1]heptane Derivatives for High-Energy Density Compounds with Low Impact Sensitivity, *Computational & Theoretical Chemistry* (2016), doi: http://dx.doi.org/10.1016/j.comptc.2016.09.008

Theoretical Design of Bicyclo[2.2.1]heptane Derivatives for High-Energy Density Compounds with Low Impact Sensitivity

Mingran Du*, Xuguang Wang and Ziru Guo

School of Chemical Engineering, Anhui University of Science and Technology, Huainan 232001, China

For new high-energy density compounds, a series of new bicyclo[2.2.1]heptane derivatives were designed and studied by density functional theory (DFT) method. The heat of formation (HOF) was evaluated by the isodesmic reaction. The densities and the heats of sublimation were predicted by the electrostatic potential analysis at B3PW91/6-31G(d,p) and B3LYP/6-311++G(2df,2p) levels, respectively. The detonation performances were predicted by the Kamlet-Jacobs equations. The bond dissociation energies (BDE) and impact sensitivity that is evaluated by the free space per molecule were also studied to give a better understanding of the stability. Results show that HOFs increase with the increasing number of N atoms. When the number of NO_2 groups is larger than 4, HOFs generally increase with the increasing number of NO_2 groups. Even though solid-phase HOF is decreasing, detonation energy is always rising with Oxygen Balance (OB) closing to zero-OB, and positive value of OB will largely reduce detonation energy. Detonation velocity and detonation pressure of the designed compounds are in the range of 5.62-9.46 km/s and 11.72-41.44 GPa, respectively. And detonation velocity and detonation pressure always increase with the increasing number of N atoms or NO_2 groups except when OB is positive value. BDEs of all designed compounds are larger than 20 kcal/mol shows that all designed compounds have a reasonable thermal stability. The calculated impact sensitivities show that all designed HEDCs have acceptable sensitivity. Especially impact sensitivity of C7, D7, E7, F6 and G6 are expected to be very close to Tetryl (h_{50}=25 cm). Considering the thermal stability, impact sensitivity and detonation performance, A8, B8, C7, C8, D7, E7, F6 and G6 might be interesting candidates for use as HEDCs.

Keywords: Density functional calculations; Heats of formation; high-density energy compounds; Detonation properties; Bond energy

1. Introduction

Due to their superior explosive performances over the currently used materials, High energy density compounds (HEDCs) have been used widely for both civilian and military applications [1-4]. Such as, 1,2,4,5-tetrazines,4,4'-azobis-(1,2,5-oxadiazol-3-amine) [1], HMX [2], bis-(triaminoguanidinium)3,3'-dinitro-5,5'-azo-1,2,4-triazolate (TAGDNAT) [3], and bis-tri- aminoguanidinium azotetrazolate (TAGzT) [3]. Nowadays, to meet the requirements of future military and space applications, researchers have always been trying to develop novel HEDCs [5-13]. As is well-known, HEDCs with better explosive performance usually exhibit higher impact sensitivity [14,15]; and with nitro groups may cause great danger to humans and the environment during both their synthesis and performance testing. Thus the foremost objective is to find the molecule having better detonation performance and safety. Theoretical calculation, as an effective way in screening potential explosives without these shortcomings, has been used to design various unknown energetic materials [16-28]. For instance, imidazole, pyrazole, 1,2,3-triazlile-, 1,2,4-triazole- and tetrazole-based

* Corresponding author. E-mail address: dumingranaust@163.com