Computational Materials Science xxx (2014) xxx–xxx

Contents lists available at ScienceDirect

Computational Materials Science

journal homepage: www.elsevier.com/locate/commatsci

New $NHNO_2$ substituted borazine-based energetic materials with high detonation performance

Mehdi Zamani [a,b], Mohammad Hossein Keshavarz [b,*]

[a] School of Chemistry, Damghan University, Damghan, Iran
[b] Department of Chemistry, Malek-ashtar University of Technology, P.O. Box 83145/115, Shahin-shahr, Iran

ARTICLE INFO

Article history:
Received 10 June 2014
Received in revised form 6 September 2014
Accepted 13 October 2014
Available online xxxx

Keywords:
Enthalpy of sublimation
Enthalpy of formation
Density
Detonation
DFT

ABSTRACT

Electrostatic potential analysis of molecular surface with the aid of B3LYP, B3PW91 and M06-2X density functional methods was used to estimate the crystal density and enthalpy of sublimation of a series of borazine-based energetic compounds containing nitramino ($-NHNO_2$) substituent. The calculated enthalpy of sublimation was combined with the gas phase enthalpy of formation to predict the solid phase enthalpy of formation. These data in conjugation with the molecular composition of mentioned compounds were used for evaluating the detonation characteristics using Becker–Kistiakowsky–Wilson (BKW) equation of state. The crystal density, detonation velocity and detonation pressure of nitraminoborazines are in the range of 1.373–1.832 g/cm^3, 7274–7851 m/s and 215–261 kbar, respectively. The enthalpies of formation of these compounds are negative, which indicate high thermodynamic stability of nitraminoborazines. Addition of $-NHNO_2$ group to B-substituted borazines including $-NO_2$ and $-N_3$ groups increases the thermodynamic stability of desired compound, whereas they have reverse effect on the N-substituted ones. The molecular structure of novel $-NHNO_2$ substituted borazine-based high energy materials containing $-N_3$ groups with greater performance than conventional organic nitramines i.e. tetryl, DNNT, DANT, RDX and HMX, were also presented. These compounds have high detonation velocity, i.e. near 10,000 m/s.

1. Introduction

The accurate calculation of crystal density (ρ) and the condensed phase enthalpy of formation ($\Delta_f H^\circ$ (c)) are the main factors in prediction of the explosives performance. They enter as input in particular computer codes such as BKW [1], EXPLO5 [2] and EDPHT [3,4] in order to examine the detonation performance of explosives. Politzer et al. [5–10] showed that enthalpy of sublimation (ΔH°_{sub}) and crystal density of solids can be estimated on the basis of molecular surface properties derived from electrostatic potential analysis. This procedure in conjunction with the calculated gas phase enthalpy of formation ($\Delta_f H^\circ$ (g)) can be used for determining the solid phase enthalpy of formation ($\Delta_f H^\circ$ (s)). The mentioned methods were widely used in the literature for investigating the thermochemical and detonation properties of new energetic materials [11–18].

The study of the boron-nitride analogues of organic compounds has been a great amount of interest over the recent years [19–29]. Janning and Ball [28] have studied the structural and thermochemical properties of nitroborazines as novel energetic materials. Nitroborazines were introduced as moderate energetic compounds with high thermodynamic stability [29]. There is no information for predicting thermochemical and detonation performance of nitraminoborazines, which are the subject of the present study.

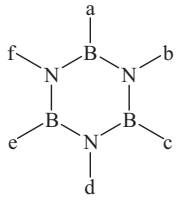
The famous organic explosives containing $-NHNO_2$ substituent are trinitrophenylnitramine **I**, 4,6-dinitro-N-nitro-1,3,5-triazine-2-amine (DNNT) **II** and 4,6-diazido-N-nitro-1,3,5-triazine-2-amine (DANT) **III**. These compounds have high energy content and useful applications. For example tetryl (trinitrophenyl methylnitramine) is used for booster charges and secondary blasting cap charges [30]. DANT is a novel primary explosive and practically unexplored compound [31].

It is important to develop theoretical methods for predicting performance, sensitivity, physical and thermodynamic properties of borazine-based analogues of organic nitramines before their laboratory synthesis. Although preparation of these novel compounds may be not straightforward, but the successful synthesis of some amino and azido derivatives of borazine has been made [22,32]. The purpose of this work is to consider the effect of $-NHNO_2$ substituent on the boron-nitride analogues of conventional organic

* Corresponding author. Tel.: +98 312 522 5071; fax: +98 312 522 5068.
E-mail addresses: keshavarz7@gmail.com, mhkeshavarz@mut-es.ac.ir (M.H. Keshavarz).

http://dx.doi.org/10.1016/j.commatsci.2014.10.025
0927-0256/

nitramines **I–III** (compounds **21–26**). The thermochemical and detonation performance of nitraminoborazines **2–20** are also studied. Since only the little information about DANT and DNNT is available in the literature [33,34], here we clarify the hidden aspects of these novel high energy materials.



Borazine:
a-f= H (**1**)

Mononitramino:
a= $NHNO_2$; b-f= H (**2**)
b= $NHNO_2$; a, c-f= H (**3**)

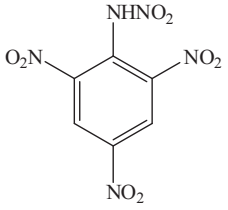
Dinitramino:
a, b= $NHNO_2$; c-f= H (**4**)
a, c= $NHNO_2$; b, d-f= H (**5**)
b, d= $NHNO_2$; a, c, e, f= H (**6**)
a, d= $NHNO_2$; b, c, e, f= H (**7**)

Trinitramino:
a, c, e= $NHNO_2$; b, d, f= H (**8**)
b, d, f= $NHNO_2$; a, c, e= H (**9**)
a, b, f= $NHNO_2$; c, d, e= H (**10**)
a-c= $NHNO_2$; d-f= H (**11**)
a, b, d= $NHNO_2$; c, e, f= H (**12**)
a, b, e= $NHNO_2$; c, d, f= H (**13**)

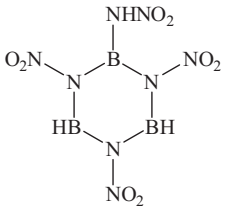
Tetranitramino:
a-d= $NHNO_2$; e, f= H (**14**)
a, b, c, e= $NHNO_2$; d, f= H (**15**)
a, b, d, e= $NHNO_2$; c, f= H (**16**)
a, b, d, f= $NHNO_2$; c, e= H (**17**)

Pentanitramino:
a-e= $NHNO_2$; f= H (**18**)
a-d, f= $NHNO_2$; e= H (**19**)

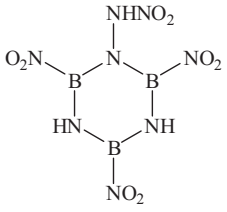
Hexanitramino:
a-f= $NHNO_2$ (**20**)



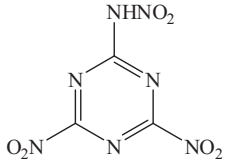
I



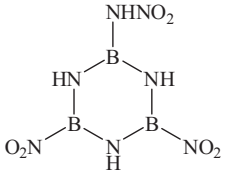
21



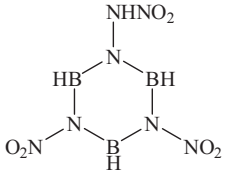
22



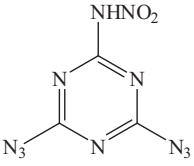
II



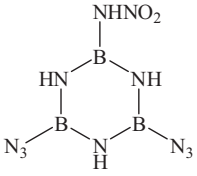
23



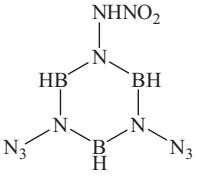
24



III



25



26

2. Computational details

All quantum chemical calculations of this work were done using Gaussian-09 software package [35]. Geometry optimization and frequency calculations of all studied compounds **I–III** and **1–26** were performed at M06-2X/6-311G(d,p) level of theory. There is no imaginary frequency for all optimized structures. This meta-hybrid density functional method, which is recommended for applications relating main-group thermochemistry [36], was employed to calculate gas phase enthalpy of formation of nitraminoborazines **2–20** through the following isodesmic reaction:

$$B_3N_3H_6 + xNH_2NO_2 \rightarrow B_3N_3H_{6-x}(NHNO_2)_x + xH_2 \quad (1)$$

For calculating the $\Delta_f H^\circ$ (g) of organic nitramines **I–III** and their boron-nitride analogues (compounds **21–26**), Eqs. (2)–(4) and Eqs. (5)–(7) were used, respectively:

$$C_6H_6 + 3NO_2 + NH_2NO_2 \rightarrow C_6H_2(NO_2)_3(NHNO_2) + (5/2)H_2 \quad (2)$$

$$C_3N_3H_3 + 2NO_2 + NH_2NO_2 \rightarrow C_3N_3(NO_2)_2(NHNO_2) + 2H_2 \quad (3)$$

$$C_3N_3H_3 + 2N_3 + NH_2NO_2 \rightarrow C_3N_3(N_3)_2(NHNO_2) + 2H_2 \quad (4)$$

$$B_3N_3H_6 + 3NO_2 + NH_2NO_2 \rightarrow B_3N_3H_2(NO_2)_3(NHNO_2) + (5/2)H_2 \quad (5)$$

$$B_3N_3H_6 + 2NO_2 + NH_2NO_2 \rightarrow B_3N_3H_3(NO_2)_2(NHNO_2) + 2H_2 \quad (6)$$

$$B_3N_3H_6 + 2N_3 + NH_2NO_2 \rightarrow B_3N_3H_3(N_3)_2(NHNO_2) + 2H_2 \quad (7)$$

Two stages have been followed to determine the values of $\Delta_f H^\circ$ (g): (1) the standard enthalpy of reaction was calculated; (2) the calculated value along with the benchmark $\Delta_f H^\circ$ (g) data of