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Computational studies on nitramino derivatives of 1-Amino-1,2-azaboriridine as high energetic material

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Abstract

In this study, we have applied computational method to determine the thermodynamic and explosive characteristics of nitramino derivatives of 1-Amino-1,2-azaboriridine. Mono, di and tri nitramino derivatives have been designed and considered for detailed study. Structure optimization and frequency calculation of the species have been performed at DFT-B3LYP/6-311++G(d,p) level of theory. The atomization method is employed to calculate the heat of formation (HOF) using electronic energy data calculated at G3 level. Utilizing the WFA program, crystal densities of title compounds were predicted using the data obtained at B3PW91/6-31G(d,p) level. Results show that the number of nitramino group influences the heat of formation of the title compounds. The calculated bond dissociation energies suggest that N-NO_2 bond of the nitramino group is the weakest bond and may be treated as a trigger bond involved in the detonation process. The impact sensitivities (h_{50}) of all the compounds were evaluated and it is found that the designed compound 1-Amino-2,3,3-trinitramino-1,2-azaboriridine is highly insensitive towards impact. Theoretical estimate of the condensed phase density of nitramino derivatives was found to be in the range of 1.60-1.80 g/cm^3. Detonation velocity, D and the detonation pressure, P were found to be 8.0-9.0 km/s and 26.2-35.2 GPa respectively. The present investigation reveals that one of the designed compounds 1-Amino-2,3,3-trinitramino-1,2-azaboriridine met the criteria of high energy density materials.

Keywords DFT, G3 method, azaboriridine, high energy material, detonation velocity, detonation pressure.

Introduction

Search for new high energy materials to be used as explosives and propellants have always drawn attention of research scientists.[1-5] The requisite properties for the materials to fall in the category of high energy materials include high density, high positive heat of formation, low sensitivity and good thermal stability. In the periodic system of elements the elements boron and nitrogen as a group "BN" give [3+5=8] valence electrons and this unit is isoelectronic with a "CC" unit. Thus, in a carbon containing moiety the CC unit can be formally replaced by a BN unit and hence, it is reasonable to expect the possibility of existence of a series of BN analogs with olefinic and aromatic character. Replacing carbons by nitrogens typically increases the crystal density of the compound and also its heat of formation. The greater density can be understood as a result of N atom being smaller than C-H; the increased heat of formation reflects the general weakness of N-N bonds in high N-content energy materials compared to C-N and C-C bonds which make the molecule less stable.[6] N-heterocycles and their derivatives are one of the classes of compounds that have been widely used in developing energetic materials because of the relative stability of N_2 as a combustion product releasing ~946 (kJ/mol) of energy during its formation from N-atoms.[7] Furthermore, compounds containing boron would very likely to form diboron trioxide (B_2O_3) during its combustion which has enthalpy of formation of -1273.5 kJ/mol that comes out to be about 60 kJ of energy given off per gram of boron combusted.[7] Therefore, from the point of view of energy release during combustion, boron and nitrogen containing compounds seem to be a viable choice for developing high energy materials. Recently, Ball and his group[8,9] have done significant computational studies on a series of B-N-C ring compounds and predicted the potentialities of boron-nitrogen-carbon compounds as high energy materials. In addition to the above, Koch and Klapötke[10] also performed computational studies on cyclic and linear three and four membered B and N containing compounds and explored the possibility of using them as potential high energy density materials (HEDMs). Keeping this in mind, we have made an attempt to design azaboriridine systems and studied their thermochemical and explosive characteristics using computational methods. Azaboriridine is commercially available and synthetic routes to the preparation of various substituted B-N-C ring compounds have been documented by Miller[11] and Cernusac *et al.*[12] An amino group is attached at nitrogen in the azaboriridine ring to increase the electron density of the BNC ring because the lone pair of electrons of N atoms may take part in the delocalization and ultimately increasing the electron density of the ring resulting in an easier nitration. Additionally, this amino group has also been found to decrease the sensitivity of high energy materials towards external stimuli. Thus, 1-amino-1,2-azaboriridine as shown in Fig.1 is taken as a moiety and its nitramino derivatives are designed.

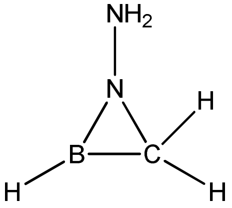
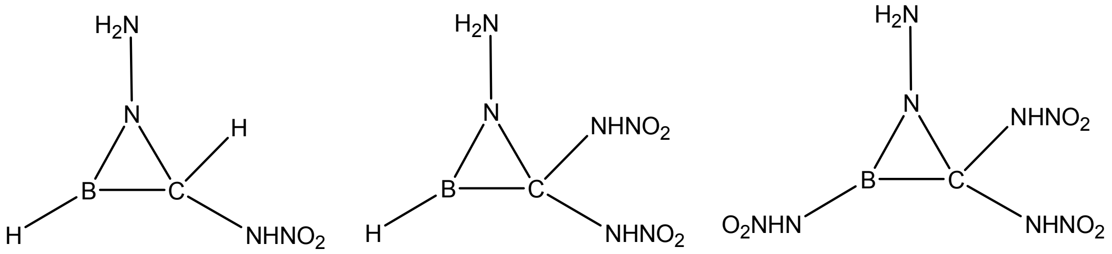


Fig. 1. 1-Amino-1,2-azaboriridine

The superiority of nitramino ($-NHNO_2$) group substituted systems has been envisaged in view of the fact that it increases the nitrogen content that in turn could lead to high crystal density and high heats of formation.[13] The latter are the desired properties for increasing the detonation characteristics of energetic materials. Thus, mono-, di- and trinitramino derivatives as shown in Fig. 2 have been designed and undertaken for detailed study.



1-Amino-3-nitramino-1,2-azaboriridine

1-Amino-3,3-dinitramino-1,2-azaboriridine

1-Amino-2,3,3-trinitramino-1,2-azaboriridine

Fig.2. Schematic representation of the title compounds.

During the present study we attempted to look into the factors that are useful to design new energetic compounds with reduced sensitivity. One of the key factors in assessing the potentialities of an energetic material is the energy that is produced in the decomposition or combustion processes. Ordinarily, this can be estimated if the heat of formation ($\Delta_f H$) of the compound is known. The energy released during detonation process is also related to sensitivity towards detonation. In order to make a reliable estimate of $\Delta_f H$ of the designed compounds we utilized the atomization procedure which has been shown to yield reliable values.[14-16] In order to assess the potentialies of an energetic material, its density and thermodynamic properties in the condensed phase are preferred. Thus, condensed phase densities and heats of formation of the designed compounds were calculated using the procedure developed by Politzer *et al.*[17] and Byrd and Rice.[18] Other explosive characteristics such as oxygen balance (OB_{100}), detonation velocity (D) and detonation pressure (P) have also been calculated to assess the potentialities of the designed compounds.

Computational details

Electronic structure calculations were performed using Gaussian 09 software package.[19] Structures of all the designed compounds were optimized using Becke three-parameter (B3) functional with Lee-Yang-Parr correlation functional with 6-311++G(d,p) basis set. B3LYP hybrid density functional with 6-311++G(d,p) basis set. DFT-B3LYP has been shown to to accurately predict the structural parameters and frequency calculations of many organic compounds and nitro substituted polyaromatic compounds.[20-22] The extended basis set with diffused and polarized functions were used to take into account the highly delocalized electrons of the designed molecules considered during the present investigation. Each optimized structure was subjected to vibrational frequency calculation to ensure that all calculated frequencies were real and positive and the structures belonged to true minima on their potential energy surface. Based on the optimized structures, the other properties of the title compounds such as heat of formation, density, electrostatic potential, detonation pressure and detonation velocity were also determined and the procedure involved in calculating these properties are briefly discussed here as follows:

Heat of formation

The enthalpies of formation of title compounds are needed for the evaluation of the detonation properties of HEDMs. Computational approach has been widely applied and the atomization method has been the choice during several studies.[14-16] The energy and the enthalpy data needed during the calculation were obtained at G3 level composite method [23] which has been shown to accurately predict the heat of formation of a variety of compounds within an accuracy of ± 1 kcal.[24] The procedure followed in calculating it in the case of B-N-C compounds considered during the present study is schematically shown in Fig. 3.

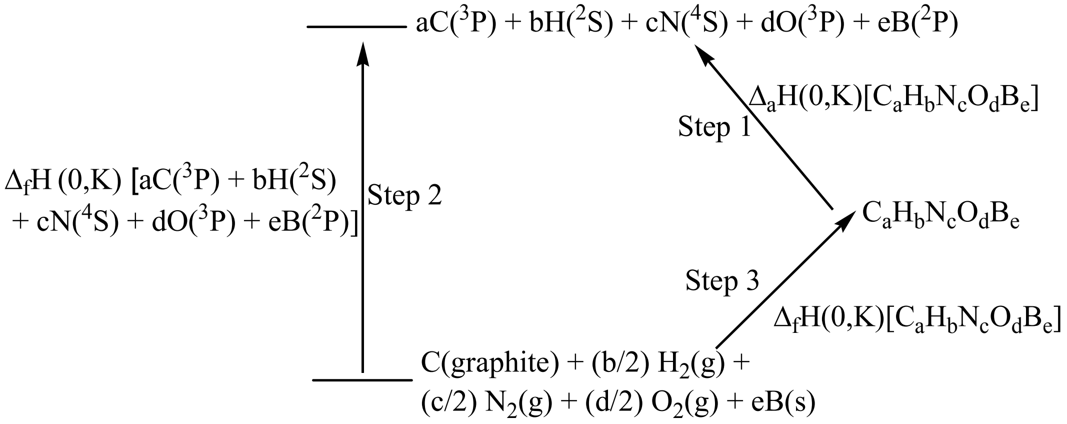


Fig.3 Thermodynamic cycle for the determination of heat of formation using atomization procedure.

In the above figure the energy involved in Step 1 is called the atomization energy that is defined as the energy needed to atomize the species to its constituent atoms in their most stable state. This value is calculated at 0 K and therefore, the energy (E) and the enthalpy (H) values are the same. Thus,

$$\Delta_a H\,(0,K) = [aE_{C(^3P)}+bE_{H(^2S)}+cE_{N(^4S)}+dE_{O(^3P)}+eE_{B(^2P)}] - E(G3,0K)\,[C_aH_bN_cO_dB_e] \qquad (1)$$

where E's for the atoms are the total electronic energies at 0 K calculated at G3 level of calculation and a, b, c, d and e are their stoichiometric coefficient present in the molecule. The second term in Eq. (1) is the zero-point corrected total energy for the title molecule also evaluated at G3 level. The second step (Step 2) is the sum of the gas-phase heats of formation of the elements in their most stable state multiplied by their stoichiometric coefficients. Applying the Hess's law, the heat of formation of the molecular species $C_aH_bN_cO_dB_e$ at 0 K can thus be written as

$$\Delta_f H\,(0K)[C_aH_bN_cO_dB_e] = [a\,\Delta_f H\,(0K,C) + b\,\Delta_f H\,(0K,H) + c\,\Delta_f H\,(0K,N) + d\,\Delta_f H\,(0K,O) + e\,\Delta_f H\,(0K,B)] - \Delta_a H\,(0K)[C_aH_bN_cO_dB_e] \qquad (2)$$

where $\Delta_f H$'s of constituent atoms C, H, N, O and B are the experimental heats of formation at 0 K and these are taken from the NIST Web book[7] as 711.19, 216.04, 470.82, 246.79 and 559.91 kJ/mol respectively.

In most of the applications, it is advantageous to have the heat of formation of the molecule at 298 K and therefore, the heats of formation of the desired molecules calculated at 0 K must be changed to 298 K. It is accomplished by adding the increase in enthalpy of the molecule in going from 0 to 298 K and subtracting the corresponding increase for the elements in their standard state. Thus, $\Delta_f H$ (298 K) is determined from the value of the $\Delta_f H$ (0 K) using the following expression,

$$\Delta_f H\,(298\ \mathrm{K})[C_aH_bN_cO_dB_e] = \Delta_f H\,(0\ \mathrm{K})[C_aH_bN_cO_dB_e] + \Delta\Delta H\,[C_aH_bN_cO_dB_e] - [a\,\Delta\Delta H\ \mathrm{C(graphite)} + b/2\,\Delta\Delta H\ H_2(g) + c/2\,\Delta\Delta H\ N_2(g) + d/2\,\Delta\Delta H\ O_2(g) + e\,\Delta\Delta H B(s)] \quad (3)$$

where $\Delta\Delta H'$s are the enthalpy increase of the respective species in going from 0 to 298 K. These values for C(graphite), H_2 (g), N_2 (g), O_2 (g) and B (s) are taken from the NIST Database[7] as 1.050, 8.468, 8.670, 8.680 and 1.213 kJ/mol respectively, whereas the same for the title molecules are taken as the difference of the G3 enthalpies obtained at 298 and 0 K.

Combustion enthalpies (ΔH_{comb}), of the titled molecules were calculated using the following stoichiometric combustion reactions as shown in reactions (4a-c) using the principle of maximum exothermic principle in which we assumed that carbon, hydrogen and boron formed their oxides and nitrogen atoms came off as N_2 gas in the combustion products of the species concerned.

$$CH_5BN_4O_2 + 2\,O_2\,(g) \longrightarrow CO_2\,(g) + 0.5\,B_2O_3(s) + 2.5\,H_2O\,(l) + 2\,N_2\,(g) \quad (4a)$$

$$CH_5BN_6O_4 + O_2\,(g) \longrightarrow CO_2\,(g) + 0.5\,B_2O_3(s) + 2.5\,H_2O\,(l) + 3\,N_2\,(g) \quad (4b)$$

$$CH_5BN_8O_6 \longrightarrow CO_2\,(g) + 0.5\,B_2O_3(s) + 2.5\,H_2O\,(l) + 4\,N_2\,(g) \quad (4c)$$

The enthalpies of formation of water, carbon dioxide and diboron trioxide (B_2O_3) used in above reactions were taken from the NIST database.[7]

Density

Density (ρ) plays an important role in determining the explosive properties of high-energy density materials (HEDM). It strongly influences the detonation performance of a HEDM. It can be represented in its simplest form as

$$\rho = M/V_{m(0.001)} \tag{5}$$

where M is the molecular mass in g/molecule, and $V_{m(0.001)}$ is the molecular volume of an isolated gas phase molecule in cm^3/molecule determined at 0.001 electron/$bohr^3$ density space by performing 100 single point calculation by Mote-Carlo integration method on the optimized structures of the molecules. The average volume thus determined was used for the calculation of the density using Eq. (5). However, the most important missing part in using the Monte Carlo integration method is that no allowance was made to take into account the specific intermolecular interaction taking place in the crystal lattice. Politzer *et al.*[17] developed an improved method for determining the crystal density by considering the role played by intermolecular forces in the crystal lattice and gave an expression to determine the crystal density of the designed energetic molecules using ab-initio data as given by Eq. (6).

$$\text{Crystal density } (\rho) = \alpha\,(M/V_{m(0.001)}) + \beta\,(\upsilon\sigma^2_{total}) + \Upsilon \tag{6}$$

where α, β, and ϒ are empirical parameters and υ and σ^2_{total} are the balance parameter and total variance and these are related to electrostatics potentials due to positive and negative charges as follows:

$$\upsilon = \frac{\sigma^2_{+}.\,\sigma^2_{-}}{\sigma^2_{total}} \tag{7}$$

$$\sigma^2_{\mathrm{total}} = \sigma^2_{+} + \sigma^2_{-} \tag{8}$$

Politzer *et al.*[17] determined the values of empirical parameters α , β , ϒ by performing calculations at B3PW91/6-31G(d,p) for a set of "trainee molecules" and fitting the experimental and calculated densities using Eq. (6) and listed them as 0.9183, 0.0028, and 0.0443 respectively. In order to use the values of parametric constants, α , β , and ϒ as listed by Politzer *et al.*[17], we also optimized the structures of the designed molecules at B3PW91/6-31G(d,p) and used these optimized structures to evaluate the value of $V_{m(.001)}$. These structures were also used in the calculation of υ and $\sigma^2_{\mathrm{total}}$ utilizing Electrostatic Potential (ESP) method with WFA-SAS code[25] that are used to evaluate the crystal density using Eq. (6).

Detonation Properties

For known explosives, the energy released during detonation, Q and the density, ρ can be determined experimentally and thus, their performance parameters, the detonation velocity, D and the detonation pressure, P can be calculated using Kamlet-Jacobs equations[26] given by the following expressions,

$$D=1.01\,(NM^{1/2}Q^{1/2})^{1/2}\,(1+1.30\rho) \tag{9}$$

$$P=1.558\rho^2NM^{1/2}Q^{1/2} \tag{10}$$

where D is in km/s and P in GPa. N is the number of moles of gaseous detonation products formed per gram of explosive, M is the average molecular weight of the gaseous products (g/mol), Q is the heat of detonation representing the chemical energy of detonation reaction in (cal/g) of explosive. The heat of detonation Q can be determined as

$$Q = \frac{-[\Delta H_f(\mathrm{products}) - \Delta H_f(\mathrm{reactants})]}{\text{Formula weight of the explosive}} \tag{11}$$

N, M and Q are determined from the stochiometric reactions developed for maximum exothermic principle using arbitrary H_2O-CO_2-N_2-B_2O_3 decomposition assumption. However, in the case of oxygen deficient molecules, the formation of BN was also taken into account. Due to sensitivity and explosive nature of the high energy materials, the experimental determination of their Q and ρ are not very frequent and theoretical approaches have been found to be a viable option. The condensed-phase HOF ($\Delta H_{f(c)}$) can be obtained from the gas-phase HOF ($\Delta H_{f,g}$) and the heat of sublimation (ΔH_{sub}) by applying the Hess's law and it can be written as

$$\Delta H_{f\,(c)} = \Delta H_{f\,(g)} - \Delta H_{sub} \tag{12}$$

In order to determine the heat of sublimation we applied the method developed by Byrd and Rice[18] as given by the expression

$$\Delta H_{sub} = aA^2 + b(\upsilon\sigma^2_{total})^{0.5} + c \tag{13}$$

where A is the surface area of the 0.001 electrons/bohr^3 isosurface of the electronic density of the molecule, υ describes the degree of balance between positive and negative potentials on the isosurface, and σ^2_{total} is a measure of the variability of the electrostatic potential on the molecular surface. The latter two quantities have been shown by Politzer *et al.*[17] to be important in relating macroscopic properties that are dependent on non-covalent electrostatic interactions. The coefficients a, b, and c were determined by Byrd and Rice[18] through a least square fit of Eq. (13) between the known (experimental values) and their theoretically evaluated values by performing the calculations at the optimized structures of a set of "trainee molecules" at B3LYP/6-31G(d) level. These are reported as 0.000267, 1.650087 and 2.966078 respectively. In the present study, the descriptors A, υ and σ^2_{total} are calculated by the computational procedure proposed by Bulat *et al.*[25] In order to use the parametric constants evaluated Byrd and Rice[18], we also performed the calculation on the structures optimized at the same level of theory.

Bond Dissociation Energy

Bond dissociation energy is one of the important parameter of the molecule that has been found to have profound impact on the detonation characteristics of the energetic molecules especially the impact sensitivity and the thermal stability of the compounds.[27-29] BDE is defined as the enthalpy change involved in a chemical bond dissociation process. In the case of a neutral molecule A – B dissociating homolytically into two radicals $A^{\bullet}$ (g) and $B^{\bullet}$(g) shown as

$$A - B(g) \rightarrow A^{\bullet}(g) + B^{\bullet}(g) \qquad (14)$$

the bond dissociation enthalpy DH(A – B) would correspond to the enthalpy of reaction given by the following expression

$$\Delta_{rxn}H_{298} = \Delta_f H\,(A^{\bullet}) + \Delta_f H\,(B^{\bullet}) - \Delta_f H\,(A - B) \qquad (15)$$

where $\Delta_f H$'s are the heats of formation of the corresponding species at 298 K and 1atm pressure. For most of the organic molecules the terms " bond dissociation energy'' (BDE) and "bond dissociation enthalpy'' often appear interchangeably.[30] Therefore, at 0K, the homolytic bond dissociation energy $BDE_0(A - B)$ can be written as

$$BDE_0(A–B) = E_0(A^{\bullet}) + E_0(B^{\bullet}) – E_0(A–B) \qquad (16)$$

where E_0's are the total electronic energies of the species calculated at B3LYP/6-311++G(d,p) level of theory. DFT/B3LYP method has been found to predict reasonably accurate BDEs.[31,32] Using the zero-point corrected total energies of reactant and products, BDE(A–B) can be determined as

$$BDE(A–B)_{ZPE} = BDE_0(A–B) + \Delta ZPE \qquad (17)$$

where ΔZPE is the difference of ZPE's of products and reactants of the bond dissociation process.

Impact Senstivity

The term "sensitivity" refers to an ease with which the initiation of reaction is achieved leading to a self-decomposition process which produce high temperature and pressure. In more specific terms it refers to the vulnerability of the energetic compound when the latter is subjected to external stimuli such as impact, shock, heat, friction, spark etc. Impact sensitivity is commonly measured by the height, h_{50}, from which a mass m dropped on to the compound to produce detonation 50% of the time.[33] The sensitivity is then expressed as either the drop height, h_{50} (usually in cm) or as impact energy mgh_{50}. The larger the value of h_{50}, the lower is the sensitivity. For a 2.5 kg mass, the impact energy for a h_{50} of 100 cm would correspond to 24.5 J. For known explosives experimental tools are available and a statistical value of h_{50} (cm) can be determined. However, for designed molecules which are yet to be synthesized, computational approach has been devised. Pospisil *et al.*[34] have correlated the explosive characteristics of an energetic material to the electrostatic potential of the molecule and proposed an empirical formula relating h_{50} and electrostatic potential of the molecule as given by the following expression

$$h_{50} = \alpha\sigma_{+}^{2} + \beta\upsilon + \gamma \qquad (18)$$

where σ_{+} is the electrostatic potential for the positive charge and υ is the degree of balance between the positive and negative potentials on an isosurface determined at 0.002 electron/bohr^3 of the energetic molecule and defined by Eq. (7). The coefficients α, β and γ are the regression coefficients determined to be -0.0064, 241.42 and -3.43 respectively.[34]

Oxygen Balance

Oxygen balance represented as (OB_{100}) is defined as the ratio of the oxygen content of the compound to the total oxygen required for the complete combustion of all the constituents present in the molecule. It is represented in terms of percentage of oxygen required for complete conversion of carbon to carbon dioxide, hydrogen to water, nitrogen to N_2, and any metal to its oxide. It is calculated as .

$$OB_{100} = \frac{-1600}{Mol.wt.of\ compound}\left(2X + \frac{1}{2}\,Y + \frac{3}{2}\,M - Z\right) \tag{19}$$

where X, Y, Z, and M are the number of C, H, O, and B atoms present in the molecular formula of the compound.

Results and Discussion

Electronic structure and thermal stability

The optimized structures of the titled compounds determined at B3LYP/6-311++G(d,p) level are shown in Fig. 4. The detailed analysis of the structures performed with the Gaussview visualization program[35] reveals that the structural features of the BNC ring remain intact. To elucidate the pyrolysis mechanism of title compounds, the dissociation energy of various possible bond dissociation processes have been determined and the bond associated with the lowest energy has been identified. The latter is designated as the "trigger bond". This bond is presumed to be responsible for the initiation of the detonation process.[36,37] Mainly three different type of bonds viz., Ring-NH_2, Ring-$NHNO_2$ and NH-NO_2 have been taken into consideration. In earlier studies bond order has been used as a measure of the bonding capacity between two atoms, and as a measure of the overall bond strength.[3,11] Bond dissociation energy of a few selected bonds along with its bond order determined by natural bond analysis (NBO)[38,39] are also listed on the optimized structures shown in Fig. 4. Results show that the weakest bond is the N-NO_2 bond associated with the $NHNO_2$ group and we designated it as $P_{NH\text{-}NO2}$. The bond dissociation energy corresponding to $P_{NH\text{-}NO2}$ and the respective bond order are recorded in Table 1. In order to compare our data we also calculated the above two parameters for two well known explosives RDX and HMX. Results show that the trigger bond designated in the designed molecules possesses considerably higher bond dissociation energy and bond order than that of RDX and HMX showing thereby that the designed molecules may be thermally more stable. It has been pointed out in earlier studies[40] that HOMO-LUMO energy gap can be utilized to predict the chemical stability of the compound. Table 2 lists the $\Delta E_{HOMO\text{-}LUMO}$ for the titled compounds determined at B3LYP/6-311++G(d,p) level. The results show that energy gap of all the designed compounds are higher than RDX and very close to HMX showing thereby that the stability of the compounds will be comparable to HMX which is known to be a powerful stable explosive compound.

Heats of formation

The heat of formation in general reflects the energy content of an energetic material. The enthalpy data of the designed compounds are listed in Table 3. The parameters needed for the evaluation of the heats of sublimation of the compounds using the method of Byrd and Rice[18] are also listed in Table 3. In order to use the values of the empirically determined parameters a, b and c of Eq. (13), we used the optimized structures of species concerned at B3LYP/6-31G(d) level which has been used by Byrd and Rice.[18] This was done to use the same level of parameterization. Results show that the heat of sublimation of the titled compounds increased as the number of nitramino groups increased. In the case of mononitramino derivative it is 89 kJ/mol which increased to 109 kJ/mol in the case of trinitramino derivative. This increase in ΔH_{Sub} shows that the presence of nitroamino group increases the stability of the designed molecule. This is also supported by the heat of formation data which also decreased from 194.7 kJ/mol to 143.4 kJ/mol except in the case of dinitroamino compound. A close look at the optimized structure with Gaussview reveals that in the case compound containing two nitramino groups, both of the groups are attached at the same C-atom in the ring and are very near to each other and may yield a very strong repulsive interaction energy causing instability to the molecule and ultimately resulting in a higher heat of formation than the mononitramino derivative. Placing the third nitroamino group at the B atom drastically reduces the heat of formation in the case trinitroamino group. This may be due to the interaction of the empty p-orbital of the boron atom with the additional lone pair of electrons available with the N atom of the nitroamino group bonded to it. The specific enthalpies of combustion of the title compounds are also listed in Table 3. The results show that specific enthalpy of combustion decreases as the number of nitramino group increases. This shows that increase in the number of the substituent group increases the molecular mass more significantly than their energy content.

Explosive performance

The two important explosive characteristics, the detonation velocity, D and the detonation pressure, P calculated using Kamlet-Jacobs equations[26] are listed in Table 4. In order to guess the reliability of the approaches applied during the present investigation to calculate the detonation parameters, we calculated the detonation performances of two well known explosives, RDX (1,3,5-trinitro-1,3,5-triazinane) and HMX (1,3,5,7-Tetranitro-1,3,5,7-tetrazocane) and the values are also listed in Table 4. The calculated values of RDX and HMX using the methods adopted during the present investigation yielded the density and D and P comparable to the experimental values as listed in Table 4. This gave us a confidence that the procedure adopted would yield reliable values of detonation parameters and loading density of the titled molecules. Results show that D and P of the titled compounds are in the range of 8.0 - 9.0 km/s and 26 - 35 GPa respectively. The loading density ρ is in the range of 1.58-1.80 g/cm^3. These loading densities are comparable to commercial explosives RDX (1.82 g/cm^3). For the three title compounds considered during the present investigation, OB_{100} values are also listed in Table 4. The results show that increase in the number of nitramino group drastically increases the oxygen balance. In the case of trinitramino derivative, OB_{100} value is calculated to be 0.00. This shows that the trinitroaminoderivative of 1-Amino-1,2-azaboriridine would be considered to be a preferred compound in terms of the maximum exothermic heat release.

Impact sensitivity

Impact sensitivity of the title compounds measured in terms of h_{50} (cm) are listed in Table 5. Lower values of h_{50} signify the compounds to be more sensitive towards impact. In order to assess the reliability of the calculation of impact sensitivity on the basis of Eq. (18), the same is calculated for known commercial explosives such as RDX and HMX and is found to be 28 and 47 cm respectively. The predicted value of RDX is in close agreement with the experimental value (29 cm) whereas for HMX the predicted value is slightly higher than the experimentally determined one (33 cm). This gives us a confidence that use of Eq. (18) for determining the impact sensitivity of designed or yet to be synthesized high energetic materials would yield reliable values. Results recorded in Table 5 show that the values of h_{50} of the title molecules are in the range of 52 - 30 cm. The results show that trinitramino derivative has explosive properties comparable to HMX.

Conclusion

On the basis of theoretical studies, we have studied the electronic structure, enthalpy of formation, enthalpy of combustion and thermal stability of nitramino deivatives of 1-Amino-1,2-azaboriridine. On the basis of overall performance parameters we find that 1-Amino-2,3,3-trinitramino-1,2-azaboriridine fall in the category of HEDMs. The present study shows that BNC ring compounds have a great potential to be used as HEDMs.

Acknowledgement

One of the authors (SG) is thankful to University Grants Commission (UGC), New Delhi for providing DSA (BSR) fellowship under its SAP program sanctioned to the Chemistry Department. Authors are also thankful to Uttar Pradesh State Government for providing financial support under its Center of Excellence Program for the upgradation of the computational facility.

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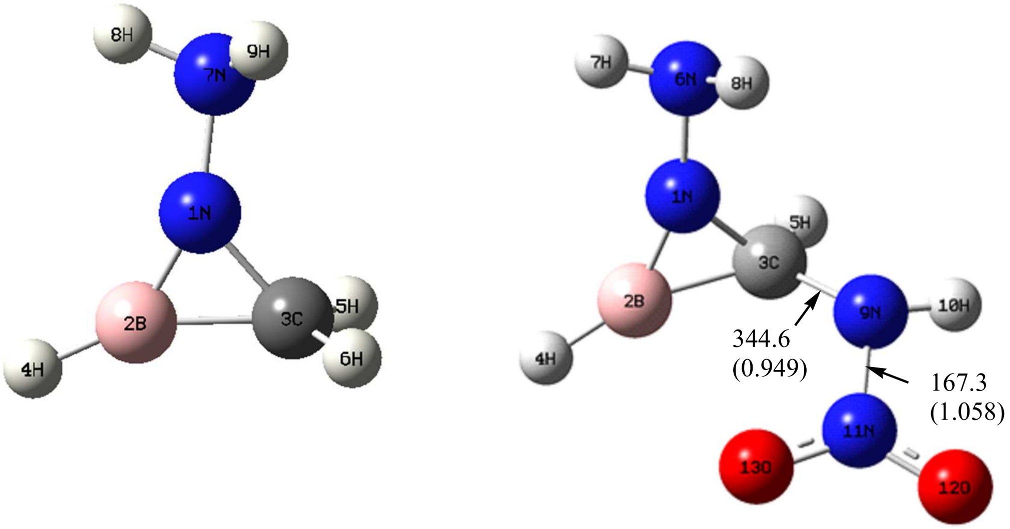
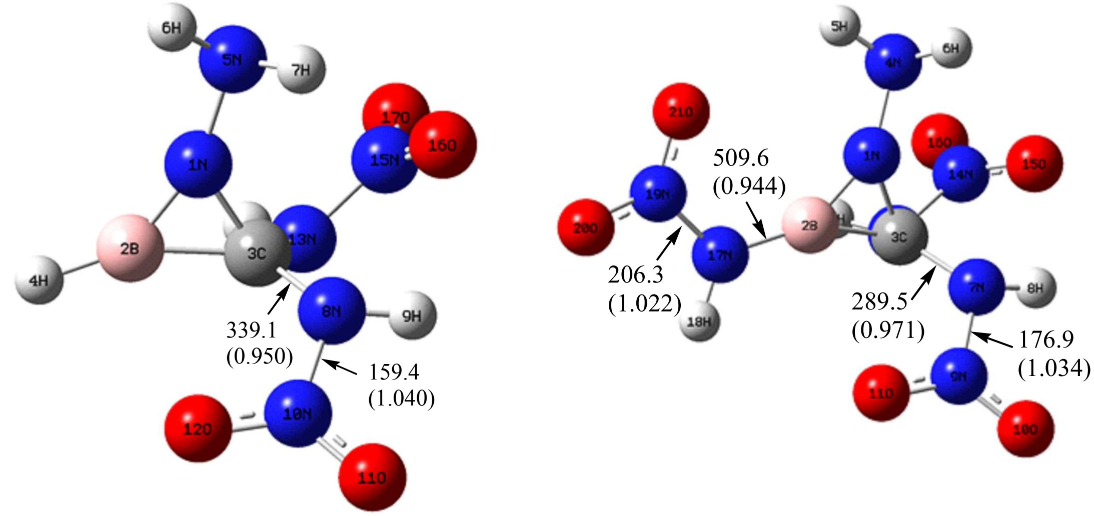


1-Amino-1,2-azaboriridine 1-Amino-3-nitramino-1,2-azaboriridine



1-Amino-3,3-dinitramino-1,2-azaboriridine 1-Amino-2,3,3-trinitramino-1,2-azaboriridine

Fig. 4. Optimized structures of title compounds at B3LYP/6-311++G(d,p). Values represent BDE (without parentheses) and bond order (within parentheses).

Table 1. Calculated bond dissociation energies (BDE) and the bond order of the trigger bond in designed and reference molecules.

Compound	Trigger Bond	Bond order	BDE^0 (kJ/mol)	BDE_{ZPE} (kJ/mol)
1-Amino-3-nitramino-1,2-azaboriridine	$P_{NH\text{-}NO2}$	1.0583	187.89	167.30
1-Amino-3,3-dinitramino-1,2-azaboriridine	$P_{NH\text{-}NO2}$	1.0399	179.87	159.43
1-Amino-2,2,3-trinitramino-1,2-azaboriridine	$P_{NH\text{-}NO2}$	1.0338	197.16	176.92
RDX (1,3,5-trinitro-1,3,5-triazinane)	Ring-NO_2	1.0187	157.14	137.06
HMX (1,3,5,7-Tetranitro-1,3,5,7-tetrazocane)	Ring-NO_2	0.9898	174.74	154.85

Table 2. HOMO, LUMO energies and $\Delta E_{LUMO-HOMO}$ of title compounds calculated at B3LYP/6-311++G(d,p) level. Values are in a.u.

Compound	E_{HOMO}	E_{LUMO}	$\Delta E_{LUMO-HOMO}$
1-Amino-3-nitramino-1,2-azaboriridine	-0.24438	-0.04714	0.19724
1-Amino-3,3-dinitramino-1,2-azaboriridine	-0.26385	-0.07030	0.19355
1-Amino-2,2,3-trinitramino-1,2-azaboriridine	-0.26714	-0.08681	0.18033
RDX*	-0.31361	-0.08820	0.15618
HMX*	-0.30542	-0.09996	0.20546

* Values for these molecules are calculated during the present study.

Table 3. Parameters involved in the estimation of sublimation enthalpies using WFA program using the structures of the designed molecules optimized at B3LYP/6-31G(d).

Compound	υ	σ^2_+	σ^2_-	SA ($Å^2$)	ΔH_{sub} (kJ/mol)	$\Delta_f H^0(g)$ (kJ/mol)	$\Delta_f H^0(s)$ (kJ/mol)	$\Delta H_{sp,comb}$ (kJ/g)
1-Amino-3-nitramino-1,2-azaboriridine	0.24	155.88	98.45	145.42	89.66	284.37	194.71	16.7
1-Amino-3,3-dinitramino-1,2-azaboriridine	0.18	180.40	57.73	183.17	95.67	317.83	222.16	11.2
1-Amino-2,2,3-trinitramino-1,2-azaboriridine	0.14	196.61	40.43	224.97	108.93	252.35	143.41	8.0

Table 4. Detonation properties of the title compounds.

Compound	OB_{100}	ρ (g/cm^3)	Q (cal/g)	D (km/s)	P (GPa)
1-Amino-3-nitramino-1,2-azaboriridine	-55.17	1.58	1913.72	8.0	26.17
1-Amino-3,3-dinitramino-1,2-azaboriridine	-18.18	1.71	1863.62	9.0	34.14
1-Amino-2,2,3-trinitramino-1,2-azaboriridine	0.00	1.80	1800.50	9.0	35.17
RDX[a]	-21.62	1.80[a] 1.82[b]	1488.28	8.70[a] 8.75[b]	33.26[a] 34.00[b]
HMX[a]	-21.62	1.90[a] 1.91[b]	1477.02	9.0[a] 9.10[b]	35.15[a] 39.00[b]

[a] Values are calculated during the present study.

[b] Values are taken from Ref. 41.

Table 5. Density Data and impact sensitivity (*h*$_{50}$/cm) of the designed molecules along with the reference compounds.

Compound	υ	σ^2_+	σ^2_-	σ^2_{total}	$\upsilon\sigma^2_{total}$	$V_{(0.001)}$ Å^3	ρ (g/cm^3)	h_{50} (cm)
1-Amino-3-nitramino-1,2-azaboriridine	0.23	163.69	98.97	262.66	61.68	129.56	1.58	52.21
1-Amino-3,3-dinitramino-1,2-azaboriridine	0.18	186.97	58.20	245.16	44.38	173.72	1.71	39.08
1-Amino-2,2,3-trinitramino-1,2-azaboriridine	0.14	199.68	41.28	240.96	34.21	217.98	1.80	29.57
RDX *	0.13	164.19	30.75	194.94	25.90	204.52	1.80	27.59
HMX *	0.21	127.16	55.24	182.39	38.51	264.76	1.90	46.73

* Calculated values during the present study.

DFT calculations performed on 1-Amino-2,3,3-trinitramino-1,2-azaboriridine show it to be a potential high energetic material with detonation performance comparable to HMX.