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Theoretically predicted Fox-7 based new high energy density molecules

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ABSTRACT

Computational investigation of *CHNO* based high energy density molecules (HEDM) are designed with FOX-7 (1, 1-dinitro 2, 2-diamino ethylene) skeleton. We report structures, stability and detonation properties of these new molecules. A systematic analysis is presented for the crystal density, activation energy for nitro to nitrite isomerisation and the $C{-}NO_2$ bond dissociation energy of these molecules. The Atoms in molecules (AIM) calculations have been performed to interpret the intra-molecular weak H-bonding interactions and the stability of $C{-}NO_2$ bonds. The structure optimization, frequency and bond dissociation energy calculations have been performed at B3LYP level of theory by using G03 quantum chemistry package. Some of the designed molecules are found to be more promising HEDM than FOX-7 molecule, and are proposed to be candidate for synthetic purpose.

1. Introduction

Potential high energy density molecules (HEDM) [1–9] are typical C–H–N–O explosives where $(CH_2N_2O_2)_n$ fragment is a most fashionable one. Thus, designing of new high energy density molecules become excellent challenge for computational chemist by using only C, H, N and O atoms. The HEDMs have profound application in military and civilian purpose. The basic aspects of modeling of new HEDM based on high heat of reaction, high Crystal density and lower molecular mass of solid reactant as well as gaseous products. Introduction of $-NO_2$ group instead of H-atom in a CH bond increases the oxygen balanced of the corresponding molecule as well as weakens the $C{-}NO_2$ bond. Thus the activation energy for homolysis of $C{-}NO_2$ bond is reduced considerably and the molecule is becoming more reactive. Another aspect of the addition of NO_2 group is to increase the crystal density of the corresponding molecule. As intra-molecular chemical binding force is more stronger than the intermolecular chemical binding force, the effective unit cell volume is reduced and as a result crystal density is increased considerably. Another way to increase the crystal density of a molecule is, designing the molecule in such a way that the molecular volume becomes less.

In this paper we have reported some molecules in which the Fox-7 [10–14] skeleton is one of the major fragments. At first we substituted two hydrogen atoms from two amino groups with an alkene moiety ($-C{=}CH_2$ and $-HC{=}CH-$) giving four member F4M molecule and five member F5M molecules. F6M molecule is modeled by substituting two hydrogen atoms from two amino groups of cis Fox-7 with $-HC{=}CH-$ moiety. All of them are cyclic molecules.

The detonation properties of the designed molecules are explained in terms of the chemical energy of reactions (CER) and crystal density of the corresponding molecule. The velocity of detonation (V_D) and detonation pressure (P_D) are high if the chemical energy of reaction and crystal density are high. The chemical energy of the reaction is analyzed by the exhausted dissociation products of the molecule and in the case of isomeric molecules, it is explained in terms of the energy of the ground state equilibrium structure of the molecule. The CER increases with the increase in number of CO_2 molecule as dissociation products. The crystal density of the molecule is dependent on the molecular weight as well as the molar volume of the molecules. Higher the molecular mass and lower the molar volume are responsible for the higher crystal density. These are the basic aspect of designing HEDMs. The bond dissociation energy (BDE) of $C{-}NO_2$ bond increases with the increase in bond order and the negative charge on $-NO_2$ group. The energy of activation (E_{act}) for the nitro to nitrito isomerisation does not follow the same trend. In most of the cases,

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the E_{act} is getting priority over the BDE. These properties may lead to the stability of the molecules. The Atoms In Molecule (AIM) calculations have been studied extensively for Fox-7 and all new design molecules. The strong covalent and non covalent interactions are analyzed for these molecules. We have achieved to design some molecules whose velocity of detonation are above 9 km/s and one of them has velocity of detonation 9.17 km/s and detonation pressure 37.40 GPa. Advanced theoretical and computational methods are employed to predict the energetics, density and detonation properties more accurately.

2. Theoretical methods and computational details

The optimized equilibrium structure of the electronic ground state of FOX-7 and its derivatives are calculated at the B3LYP [15,16] level of theory employing the aug-cc-pVDZ Gaussian basis set of Dunning [17]. The calculations were performed using the Gaussian-03 program package [18]. The harmonic vibrational frequencies (ω_j) of the electronic ground state of all these molecules are obtained by diagonalizing the B3LYP force field calculated using the aug-cc-pVDZ basis set [17]. The crystal density of these molecules are derived using both Drieding [19] and CVFF [20] force field with the most occurrence 10 space groups C_2, $C_{2/C}$, C_C, $P_{21/C}$, P_1, P_{21}, P_{212121}, P_{bca}, P_{bcn} and P_{na21} among 230 crystal space group present in nature. We have taken the lower density between those force field. We have used our ground state optimized structure to obtained crystal density. All of these calculations are performed in Material Studio of Acceryls package [21]. T. Mondal et al. [22], have found CVFF force field fitted better for nitro molecules compare to experimental crystal density and the Drieding force field works better for all the molecules. Velocity of detonation and detonation pressure for C–H–N–O explosive are obtained by using the empirical Kamlet–Jacob equation [23]. The equations are given below

$$P_D = 15.58\rho^2 N M^{\frac{1}{2}} Q^{\frac{1}{2}}$$
$$V_D = 1.01\left(N M^{\frac{1}{2}} Q^{\frac{1}{2}}\right)^{\frac{1}{2}}(1 + 1.30\rho) \quad (1)$$

where V_D is the detonation velocity, expressed in millimeter per milliseconds, P_D is the detonation pressure (in kilobars unit), N is the number of moles of gases per gram of explosive in moles, M is the average molecular mass of the gaseous products in grams, Q is the chemical energy of detonation (calories per gram) and ρ_0 is the crystal density in gram per cubic centimeter. The standard enthalpy of reaction is obtained by using the following equation [24].

$$\Delta H^{298.15} = \Delta E^{298.15} + \Delta PV$$
$$\Delta H^{298.15} = \Delta E_0 + \Delta ZPVE + \Delta H_T + \Delta nRT \quad (2)$$

E_0 is the total molecular electronic energy of the ground state equilibrium electronic structure, $\Delta ZPVE$ is the zero point energy, Δn is the mole difference between gaseous products and gaseous reactants, R is gas constant and T is absolute temperature. ΔH_T is the thermal correction to enthalpy and it was calculated by the use of statistical mechanics [25] and it is the sum of translational thermal energy, rotational thermal energy and vibrational thermal energy. Thus ΔH_T is given by the following equation

$$\Delta H_T = \Delta H_{Trans} + \Delta H_{Rot} + \Delta H_{Vib} \quad (3)$$

$$\Delta H_{Trans} = [H(T) - H(0)]_{Trans} = \frac{5}{2}RT \quad (4)$$

$$\Delta H_{Rot} = [H(T) - H(0)]_{Rot} = \frac{3}{2}RT \quad (5)$$

$$\Delta H_{Vib} = H(T) - H(0)$$
$$= RT\sum_{i=1}^{f}\left(\frac{h\nu_i}{kT}\right)\frac{\left(\exp^{-\frac{h\nu_i}{kT}}\right)}{\left(1 - exp^{-\frac{h\nu_i}{kT}}\right)} \quad (6)$$

where f is the number of degree of freedom, k is Boltzmann constant, ν_i is the i^{th} vibrational frequency. E_0, ZPVE and ν_i are taken from Density functional theory (DFT) calculation.

Heat of formation (HOF) of any molecule can be calculated using the following equation

$$\Delta H^{298.15} = \sum_{Product} HOF - \sum_{Reactant} HOF \quad (7)$$

The enthalpy of reaction or the enthalpy of combustion was derived by the following way. The entire nitrogen atom is converted to N_2, hydrogen atom is eliminated as a H_2 O vapour, the carbon atom is coming out as a CO or as CO_2 if oxygen is excess. We are using these formulas for calculating the enthalpy of reaction for those molecules which have oxygen balanced (OB) zero or positive. We have calculated OB for Fox-7 and our isomeric molecules which are zero and 60.00, respectively. We have taken the formula for calculating the OB from the Z. Chaoyang et al. paper [26].

3. Results and discussion

3.1. Detonation properties

We have calculated the detonation properties of well known Fox-7 molecule and literally unknown newly designed three Fox-7 derivatives which are basically unsaturated ring molecules, one of them is four member, another is five member and third one is six member ring molecule. These cyclic molecules are designated as F4M, F5M and F6M molecule. The picture of these following molecules are shown in Fig. 1. Table 1 represents the detonation properties of these following molecules including crystal density and chemical energy of detonation (Q). According to the equation (1), it is well known that the velocity of detonation and detonation pressure increases with increase in the chemical energy of detonation and increase in the crystal density of the molecule. All of these design molecules F4M, F5M and F6M have detonation properties higher than parent Fox-7 molecule. 1, 1-diamino, 2, 2-dinitro ethylene (Fox-7) is a small and relatively symmetric energetic [11] molecule compared with the typical C–H–N–O explosive. The crystal structure of Fox-7 [27] is also very simple, consisting of a small crystal unit cell (monoclinic unit cell with space group P21/c) containing four molecules. Experimentally known crystal density of Fox-7 [27,28] is 1.86 g/cc, detonation velocity is 8.66 km/s and detonation pressure is 34 GPa. But our results show that the crystal density, V_D and P_D for Fox-7 are 1.77 g/cc, 8.26 km/s and 30 GPa, respectively. Thus our theoretically predicted values are little lower than the experimental values. The major two factors play crucial role for calculating detonation properties, one is the crystal density and another is the chemical energy of detonation. F6M has highest crystal density among these following molecules, thus, it has high velocity of detonation (9.17 km/s) and high detonation pressure (37.40 GPa). F4M and F5M have velocity of detonation above 8.91 km/s which is the experimental velocity of detonation for HMX. Thus these molecule F4M, F5M and F6M may serve as a better high energy density molecules than other known HEDM.