

## Theoretical Studies on Vibrational Spectra, Detonation Properties and Stabilities of Polynitroadamantanes

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To look for high energy density compounds (HEDCs), sixteen polynitroadamantanes were designed and their properties were studied. The assigned infrared spectra of polynitroadamantanes were obtained at the DFT-B3LYP/6-31G\*\* level. The frequencies of symmetry stretching vibration of nitro group for polynitroadamantanes have a bathochromic shift with the number of nitro group. However, the frequencies of asymmetry stretching vibration have a contrary trend. The detonation velocity, pressure and heat of 16 polynitroadamantanes were estimated by the Kamlet-Jacobs formula. The stabilities of polynitroadamantanes were studied by the bond dissociation energy and the energy level difference calculation. The number of the nitro group is in direct proportion to the detonation properties. Conversely, it is in inverse proportion to the stability of polynitroadamantanes. Among the polynitroadamantanes having the same number of nitro group, one which the nitro group links with a methylene group has better properties and is unstable than that the nitro group links with a methylidyne group. Consequently, we should balance the stability with energy and density when a new molecule is designed.

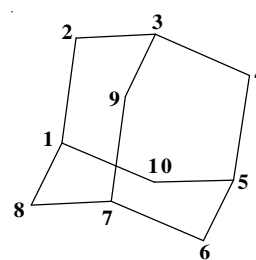
**Keywords:** Properties, Stability, Polynitroadamantanes, Density functional theory.

### INTRODUCTION

Adamantane (**Scheme-I**) is one cage hydrocarbon compound, which is composed of 10 carbon atoms and 16 hydrogen atoms with a large density and a high heat of formation. Recently, one type of adamantane derivative, polynitroadamantane, which possess large energy-density and excellent stability, has being extensively studied<sup>1-8</sup>.

Gilbert and Jack<sup>9</sup> calculated the density, heat of formation and detonation pressure for a series of polynitroadamantanes, which the number of nitro groups range from 2 to 16. Pivina *et al.*<sup>10</sup> predicted the properties of the isomers of hexanitroadamantane. Sýkare and Succeska<sup>11</sup> estimated the detonation parameters for 1,3,5,7-tetranitroadamantane. All above detonation properties are calculated by using the group additivity method, which cannot differentiate the isomers of polynitroadamantanes. Xu *et al.*<sup>12</sup> investigated the vibrational spectra, thermodynamic properties, detonation properties and pyrolysis mechanisms for polynitroadamantanes with the number of nitro groups ranging from 1 to 10 by using DFT-B3LYP /6-31G\* method and Kamlet-Jacobs equation. They recommended 1,2,3,4,5,6,7,8,9,10-polynitroadamantane as the target of HEDM with insensitivity.

In the present work, 16 polynitroadamantanes compounds (Table-1) are designed. Subsequently, the molecular orbit, IR



Scheme-I

spectrum, density, enthalpy of formation, detonation properties and bond dissociation energy are calculated on the basis of optimized structures and the stability is further analyzed.

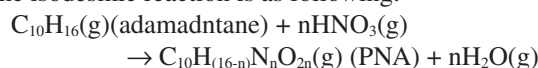
### METHOD OF CALCULATIONS

DFT B3LYP method with 6-31G\*\* basis set was carried out to optimize structures and calculate molecular orbits and IR spectra for 16 polynitroadamantanes using Gaussian 09 (A.02) program<sup>13</sup>. The molar volume of each molecule was calculated by the Monte-Carlo method, followed by formula (1) to obtain its density. The gas phase enthalpies of formation of polynitroadamantanes were derived from an isodesmic reaction. Subsequently, the sublimation enthalpies were calculated by formulae (2)-(6) to further achieve their enthalpies of formation for the solid phase.

TABLE-1  
16 DESIGNED POLYINITROADAMANTANES COMPOUNDS

|     |  |
|-----|--|
| C1  | 1,3,5,7-Tetranitroadamantane             |
| C2  | 2,4,6,8-Tetranitroadamantane             |
| C3  | 2,2,4,4-Tetranitroadamantane             |
| C4  | 1,2,3,5,7-Pentanitroadamantane           |
| C5  | 2,4,6,8,9-Pentanitroadamantane           |
| C6  | 1,2,3,4,5,7-Hexanitroadamantane          |
| C7  | 1,2,3,5,6,7-Hexanitroadamantane          |
| C8  | 2,4,6,8,9,10-Hexanitroadamantane         |
| C9  | 2,2,4,4,6,6-Hexanitroadamantane          |
| C10 | 1,2,3,4,5,6,7-Heptanitroadamantane       |
| C11 | 2,2,4,6,8,9,10-Heptanitroadamantane      |
| C12 | 1,2,3,4,5,6,7,8-Octanitroadamantane      |
| C13 | 2,2,4,4,6,6,8,8-Octanitroadamantane      |
| C14 | 1,2,3,4,5,6,7,8,9-Nonanitroadamantane    |
| C15 | 2,2,4,4,6,6,8,8,9-Nonanitroadamantane    |
| C16 | 1,2,3,4,5,6,7,8,9,10-Decanitroadamantane |

The isodesmic reaction is as following:



$$\rho_{\text{crystal}} = a \left( \frac{M}{V_m} \right) + b(\nu_{\text{tot}}^2) + c \quad (1)$$

$$\Delta H_{\text{sub}}(298 \text{ K}, \text{ kcal/mol}) = aA^2 + b(\nu_{\text{tot}}^2)^{0.5} + c \quad (2)$$

$$\sigma_{\text{tot}}^2 = \sigma_+^2 + \sigma_-^2 = \frac{1}{m} \sum_{i=1}^m [V^+(r_i) - \bar{V}_s^+]^2 + \frac{1}{n} \sum_{j=1}^n [V^-(r_j) - \bar{V}_s^-]^2 \quad (3)$$

$$\nu = \frac{\sigma_+^2 \sigma_-^2}{[\sigma_{\text{tot}}^2]^2} \quad (4)$$

$$\bar{V}_s^+ = \frac{1}{m} \sum_{i=1}^m V^+(r_i) \quad (5)$$

$$\bar{V}_s^- = \frac{1}{n} \sum_{j=1}^n V^-(r_j) \quad (6)$$

The detonation velocity, detonation pressure and detonation heat were estimated by the Kamlet-Jacobs formula<sup>14</sup>.

The weakest bond in each molecule was confirmed by the structure analysis and its bond dissociation energy (BDE) was calculated<sup>15</sup>.

## RESULTS AND DISCUSSION

IR spectrum closely related with the structure of a compound and is the external manifestation of a structure. The frequencies of symmetry and asymmetry stretching vibration for 16 polynitroadamantanes are shown in Table-2. It is shown that the frequencies of symmetry stretching vibration of nitro group for polynitroadamantanes decrease (a bathochromic shift) with the increasing of nitro group numbers. However, the frequencies of asymmetry stretching vibration of nitro group for polynitroadamantanes increase (a hypsochromic shift) with the number of nitro group. The main reason may be an inductive effect. As a strong electron withdrawing group, nitro group could draw the electron orbit of another nitro group

TABLE-2  
CALCULATED FREQUENCIES ( $\text{cm}^{-1}$ ) OF SYMMETRY AND ASYMMETRY STRETCHING VIBRATION FOR  $\text{NO}_2$

| Compd. | Symmetry stretching vibration | Asymmetry stretching vibration |
|--------|-------------------------------|--------------------------------|
| C1     | 1291, 1289                    | 1503, 1502, 1499               |
| C2     | 1293                          | 1509, 1502, 1497               |
| C3     | 1288, 1242                    | 1530, 1517                     |
| C4     | 1290, 1286, 1284              | 1508, 1504                     |
| C5     | 1289, 1287, 1282              | 1527, 1511, 1505, 1498         |
| C6     | 1286, 1283                    | 1518, 1511                     |
| C7     | 1283, 1281, 1277              | 1527, 1523, 1519               |
| C8     | 1290, 1289, 1279              | 1534, 1533, 1514, 1503         |
| C9     | 1239, 1229                    | 1536, 1527, 1519               |
| C10    | 1279                          | 1528, 1514                     |
| C11    | 1287                          | 1540, 1539, 1533               |
| C12    | 1276, 1275, 1272              | 1540, 1532, 1526               |
| C13    | 1246                          | 1538, 1535, 1535               |
| C14    | 1281, 1278, 1267              | 1557, 1549, 1544, 1539, 1529   |
| C15    | 1275                          | 1556, 1545, 1540               |
| C16    | 1269, 1250                    | 1564, 1557, 1550, 1545, 1535   |

at *ortho*-position to the nitrogen atom which should concentrate on oxygen atom. As a result, the electron density of  $\text{N}=\text{O}$  increased. Among the polynitroadamantanes having the same number of nitro group, one which the nitro group links with a methylene group has slightly bigger frequency of asymmetry stretching vibration of nitro group than that the nitro group links with a methylidyne group. It is because that alkyl, as a weak electron releasing group, could repel the electron orbit of nitro group to the oxygen atom. As a result, the electron density of  $\text{N}=\text{O}$  decreased.

**Density and detonation property:** Detonation velocity (D), detonation pressure (P) and detonation heat (H) are the important parameters to evaluate the performances of energetic compounds. However, density ( $\rho$ ) and enthalpy of formation ( $\Delta H_f$ ) are of importance to calculate above detonation properties using the Kamlet-Jacobs formula. The properties for 16 polynitroadamantanes were listed in Table-3.

TABLE-3  
DENSITIES ( $\text{g cm}^{-3}$ ), ENTHALPY OF FORMATION ( $\text{kJ mol}^{-1}$ ), DETONATION VELOCITY ( $\text{m s}^{-1}$ ), DETONATION PRESSURE (GPa), AND DETONATION HEAT ( $\text{kJ kg}^{-1}$ ) FOR 16 POLYINITROADAMANTANES

| Compd. | Density | Enthalpy of formation | Detonation velocity | Detonation pressure | Detonation heat |
|--------|---------|-----------------------|---------------------|---------------------|-----------------|
| C1     | 1.59    | -374.29               | 6615                | 17.96               | 4652            |
| C2     | 1.84    | -342.84               | 7439                | 25.11               | 4751            |
| C3     | 1.83    | -238.97               | 7450                | 24.86               | 5080            |
| C4     | 1.83    | -358.83               | 7696                | 26.53               | 5143            |
| C5     | 1.93    | -345.16               | 8006                | 29.62               | 5181            |
| C6     | 2.00    | -336.77               | 8527                | 34.27               | 5541            |
| C7     | 1.87    | -345.35               | 8119                | 29.91               | 5520            |
| C8     | 2.08    | -342.32               | 8768                | 37.03               | 5528            |
| C9     | 1.94    | -226.08               | 8443                | 33.03               | 5814            |
| C10    | 1.97    | -315.59               | 8684                | 35.25               | 5858            |
| C11    | 2.02    | -290.14               | 8864                | 37.24               | 5915            |
| C12    | 1.98    | -261.62               | 8940                | 37.46               | 6184            |
| C13    | 2.07    | -152.65               | 9313                | 41.67               | 6404            |
| C14    | 2.00    | -215.25               | 9183                | 39.75               | 6441            |
| C15    | 2.04    | -64.52                | 9415                | 42.24               | 6720            |
| C16    | 2.12    | -146.86               | 9749                | 46.24               | 6697            |

It can be seen that the density, detonation velocity, pressure and heat are in direct proportion to the number of the nitro group. Among the polynitroadamantanes with the same number of nitro group, one which the nitro group links with a methylene group has better properties than that the nitro group links with a methylidyne group. In other words, for the sake of a higher energy density, we should increase the number of nitro group and link the nitro group with a methylene group to the best of our abilities.

**Bond dissociation energy and stability:** It is absolutely critical that a compound is stable and safe for use. Xiao *et al.*<sup>15</sup> reported that bond dissociation energy can be used to estimate the stability of a high energy density compound. The energy level difference, length and dissociation energy of the weakest C-N bond for 16 polynitroadamantanes are listed in Table-4. It can be seen that the number of nitro group is in inverse proportion to the energy level difference and bond dissociation energy and in direct proportion to the length of the weakest C-N bond. It indicates that poly-nitroadamantanes' stabilities decrease with the increasing of the nitro group number. Among the polynitroadamantanes with the same number of nitro group, one which the nitro group links with a methylene group has lower energy level difference and bond dissociation energy than that the nitro group links with a methylidyne group. However, an opposite instance occurs in the weakest C-N bond length. In other words, for the sake of polynitroadamantanes' stabilities, we should decrease the nitro group and link the nitro group with a methylidyne group. It is similar to the most energetic compounds that the stability of polynitroadamantanes conflict with its energy and density. Consequently, we should balance the stability with energy and density when a new molecule is designed.

TABLE-4  
ENERGY LEVEL DIFFERENCE (ev), LENGTH (Å) AND  
DISSOCIATION ENERGY (kJ mol<sup>-1</sup>) OF THE WEAKEST  
C-N BOND FOR 16 POLYNITROADAMANTANES

| Compd. | Energy level difference | Weakest C-N bond                 |        |                          |
|--------|-------------------------|----------------------------------|--------|--------------------------|
|        |                         | Bond                             | Length | Bond dissociation energy |
| C1     | 5.410                   | C <sub>5</sub> -N <sub>23</sub>  | 1.536  | 237.05                   |
| C2     | 5.387                   | C <sub>1</sub> -N <sub>23</sub>  | 1.533  | 237.16                   |
| C3     | 4.805                   | C <sub>20</sub> -N <sub>29</sub> | 1.567  | 133.74                   |
| C4     | 5.305                   | C <sub>11</sub> -N <sub>25</sub> | 1.542  | 218.87                   |
| C5     | 5.231                   | C <sub>1</sub> -N <sub>22</sub>  | 1.534  | 230.33                   |
| C6     | 5.190                   | C <sub>14</sub> -N <sub>21</sub> | 1.544  | 214.67                   |
| C7     | 5.221                   | C <sub>12</sub> -N <sub>19</sub> | 1.542  | 215.18                   |
| C8     | 5.110                   | C <sub>1</sub> -N <sub>21</sub>  | 1.533  | 220.49                   |
| C9     | 4.824                   | C <sub>1</sub> -N <sub>27</sub>  | 1.568  | 110.85                   |
| C10    | 5.141                   | C <sub>5</sub> -N <sub>17</sub>  | 1.545  | 194.43                   |
| C11    | 4.293                   | C <sub>1</sub> -N <sub>38</sub>  | 1.565  | 133.39                   |
| C12    | 4.792                   | C <sub>4</sub> -N <sub>19</sub>  | 1.549  | 196.42                   |
| C13    | 4.783                   | C <sub>12</sub> -N <sub>40</sub> | 1.569  | 101.27                   |
| C14    | 4.959                   | C <sub>16</sub> -N <sub>26</sub> | 1.555  | 171.11                   |
| C15    | 4.264                   | C <sub>12</sub> -N <sub>36</sub> | 1.587  | 47.65                    |
| C16    | 4.881                   | C <sub>9</sub> -N <sub>17</sub>  | 1.567  | 161.02                   |

## Conclusion

It can be seen from above results that the frequencies of symmetry stretching vibration of nitro group for polynitroadamantanes have a bathochromic shift with the increasing numbers of nitro group. However, the frequencies of asymmetry stretching vibration have a contrary trend. The number of the nitro group is in direct proportion to the detonation properties. Conversely, it is in inverse proportion to the stability. Among the polynitroadamantanes with the same number of nitro group, one which the nitro group links with a methylene group has better properties and is unstable than that the nitro group links with a methylidyne group. Consequently, we should balance the stability with energy and density when a new molecule is designed.

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