

Articles

Computational Study on Spirocyclic Compounds as Energetic Materials (I)

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The molecular structures of 2,6-diaza-1,3,5,7-tetraoxaspiro[3,3]heptane (**1**) and its dinitro derivative, 2,6-dinitro-2,6-diaza-1,3,5,7-tetraoxaspiro[3,3]heptane (**2**), were fully optimized without symmetry constraints at HF/6-31G* level of theory. A bisected conformation with respect to the ring is preferred with a C_2 symmetric structure. The density of each molecule in the crystalline state was estimated to 1.12 and 2.36 g/cm³ using PM3/VSTO-3G calculations from the molecular volume. The heat of formation was calculated for two compounds at the CBS-4M level of theory. The detonation parameters were computed using the EXPLO5 software: $D = 6282$ m/s, $P_{C-J} = 127$ kbar for compound **1**, $D = 7871$ m/s, $P_{C-J} = 307$ kbar for compound **2**, and $D = 6975$ m/s, $P_{C-J} = 170$ kbar for 60% compound **2** with 40% TNT. Specific impulse of compound **1** in aluminized formulation when used as monopropellants was very similar to that of the conventional ammonium perchlorate in the same formulation of aluminum.

Key Words : Strained-ring, Oxoaza compounds, High-performing energetic materials

Introduction

With the advent of computational capabilities, accurate models and simulations of high-energetic, dense materials (HEDMs) have been continuously pursued.¹ Theoretical approach can be taken to evaluate proposed compounds before undertaking a possibly costly and difficult synthesis. Although there are some successful results on HEDMs that can yield large quantities of energy on dissociation or combustion, the development of new energetic models still continues to be the focus of many researches. Among them, nitrogen-rich compounds containing fewer carbon atoms show better energetic capabilities, because they produce large enthalpies of formation, a positive oxygen balance, and large volumes of environmentally friendly N₂ molecule on decomposing.²

Since the existence of the highly strained-ring hydrocarbon such as spiro-pentane was firmly established in the mid-1940s, a number of synthetic routes to its derivatives and related compounds have been developed.³ Because of highly distorted properties in these compounds, full safety precautions should always be taken in handling them due to their potentially explosive nature. Therefore, it might not be surprising to consider nitrogen-rich compounds with ring strain as explosives.⁴ However, they need to contain high thermal and mechanistic stabilities, while at the same time satisfying the increasing demand for higher outcome. In many cases, high performance and low sensitivity appear to be mutually exclusive, that is why many high performing materials are not stable enough to find practical use and many materials with the desired sensitivity do not possess

the performance requirements of a material to replace a commonly-used explosive.⁵ So far one of the most promising heterocyclic backbones with high-performing energetics is the tetrazole ring compounds.⁶

It has been well known that hydrazine and its diamino and methyl derivative, tetrazane and monomethylhydrazine (MMH), are useful as a solid rocket motor due to the great amount of enthalpies of formation and proton affinities.⁷ Study also showed that the major use of dinitrogen tetraoxide (NTO) was a self-igniting molecule.⁸ So far the mixture is currently used in liquid-fueled rockets.

Therefore, it will be possible to design new solid rocket propellants by combining highly strained nitrogen-rich ring system with the characteristic of dinitrogen tetraoxide and hydrazine analogue within a molecule. In the present study, we evaluate and predict the suitability of 2,6-diaza-1,3,5,7-tetraoxaspiro[3,3]heptane and its dinitro-substituted compound, 2,6-dinitro-2,6-diaza-1,3,5,7-tetraoxaspiro[3,3]heptane, as potential energetic materials using a theoretical method. The structures, energetic properties, detonation and combustion parameters of the compounds will be presented. We will also demonstrate that these models may be promising candidates as new energetic materials based on relatively small molecules.

Results and Discussions

Using the Gaussian G03W (revision B.03) program package, all calculations for structures and energies were performed.⁹⁻¹³ In order to obtain accurate enthalpies and free energies, we applied the complete basis set (CBS) method of

Petterson and coworkers. With a HF/3-21G(d) structure optimization, CBS-4 begins by computing the zero point energy, it then uses a large basis set SCF calculation as a base energy, and a MP2/6-31+G calculation with a CBS extrapolation to correct the energy through second order. To approximate higher order contributions, a MP4(SDQ)/6-31+(d,p) calculation is employed. Here we applied the modified CBS-4M method (M refers minimal population localization) including some additional empirical corrections.^{14,15} To estimate the highest possible density in the crystalline state of the model compounds, semi-empirical PM3/VSTO-3G calculation by scaling the computed molecular volume is used.¹⁶

The detonation parameters were calculated using a EXPLO5 (version 5.04) computer program.¹⁷⁻²⁰ The program is based on the chemical equilibrium, steady-state model of detonation. The calculation of the equilibrium composition of the detonation products is done by applying modified White, Johnson and Dantzig's free energy minimization technique. The program is designed to enable the calculation of detonation parameters at the Chapman-Jouguet (*C-J*) point.

Based on assumptions (i) the constant pressure in the combustion chamber and the chamber cross-section area, (ii) the applicable energy and momentum conservation equations, (iii) the zero velocity of the combustion products at the combustion chamber, (iv) no temperature and velocity lag between condensed and gaseous species, (v) the isentropic expansion in the nozzle, the theoretical rocket performances were calculated. Using the EXPLO5 software, the combustion calculations were carried out under isobaric conditions.

Structures. Because of the existence of a spiro carbon atom, a bisected conformation is preferred with respect to the ring. The molecular structures of CH₂N₂O₄ and its dinitro compound, CN₄O₈, were fully optimized without symmetry constraints at HF/6-31G* level of theory to give a C₂ symmetry (Fig. 1). The tetrahedral carbon representing the spiro-centre has external bond angle with mean value of 117.7° and internal one is found to be 93.9°. These values are far from the perfect tetrahedron, due to the fact that the carbon is included into a less flexible and more strained ring.²¹ The average bond angle of C-O-N or O-N-O linkage in the ring is within the range of 88.21-89.13°. For CH₂N₂O₄

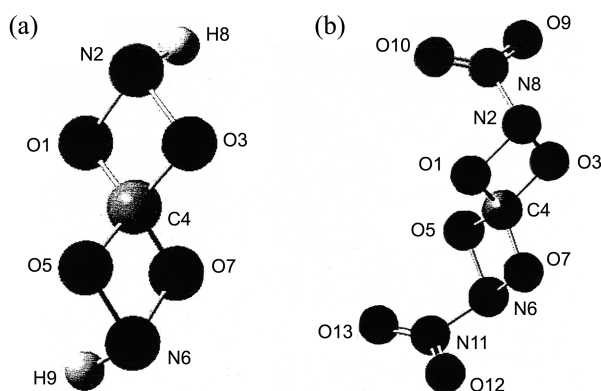


Figure 1. Optimized molecular structure for (a) 2,6-diaza-1,3,5,7-tetraoxaspiro[3,3]heptane (CH₂N₂O₄) and (b) 2,6-dinitro-2,6-diaza-1,3,5,7-tetraoxaspiro[3,3]heptane (CN₄O₈).

molecule, the mean C-O distance is 1.406 Å and the average O-N distance is 1.505 Å. Each four-membered ring against a spiro carbon center is not virtually planar with deviation of 4.245° from the plane defined by the O1, N2, O3, and C4 atoms. The C-O distance is a little shorter by comparing with that of the 1,3-dioxetane and 1,3,5,7-tetraoxaspiro[3,3]pentane (1.420 Å). For CN₄O₈ molecule, with the presence of a spiro center at C4 atom, the average C-O distance and the O-N one is 1.411 Å and 1.486 Å. The four-membered ring made by C, O, N, and O atom of CN₄O₈ molecule is more deviated from the planarity than CH₂N₂O₄ one by 0.928°.

Energetic Properties. The enthalpy of formation of a gas-phase molecule was computed according to the atomization energy method.²²⁻²⁴ In Eq. (1), $\Delta_f H^{\circ}(g, \text{CH}_2\text{N}_2\text{O}_4)$ stands for the gas-phase enthalpy of formation of CH₂N₂O₄, $H(\text{CH}_2\text{N}_2\text{O}_4)$ represents the CBS-4M calculated enthalpy of CH₂N₂O₄, ΣH° denotes the CBS-4M calculated enthalpies for the individual atoms, and $\Sigma \Delta_f H^{\circ}$ indicates the experimentally reported literature values for the enthalpies of formation for the corresponding atoms, $\Delta_f H^{\circ}$.²⁴

$$\Delta_f H^{\circ}(g, \text{CH}_2\text{N}_2\text{O}_4) = H(\text{CH}_2\text{N}_2\text{O}_4) - \sum_{\text{atoms}} H^{\circ} + \sum_{\text{atoms}} \Delta_f H^{\circ} \quad (1)$$

Using computed data and the values in literature, the gas phase enthalpy of formation of 2,6-diaza-1,3,5,7-tetraoxaspiro[3,3]heptane (CH₂N₂O₄) can be calculated to $\Delta_f H^{\circ}(g, \text{CH}_2\text{N}_2\text{O}_4) = +27.8$ kcal/mol. The enthalpy of formation of the gas-phase 2,6-dinitro-2,6-diaza-1,3,5,7-tetraoxaspiro[3,3]heptane (CN₄O₈) was also computed following the same procedure and can be obtained: $\Delta_f H^{\circ}(g, \text{CN}_4\text{O}_8) = +9.5$ kcal.

The melting point of 2,6-diaza-1,3,5,7-tetraoxaspiro[3,3]heptane was taken to be equal to that of 1,3,5,7-tetraoxaspiro[3,3]heptane (44 °C), which was available in the literature.²⁵ Considering a close melting point of piperidine and cyclohexane replacing CH₂ by NH, it is not unreasonable for CH₂N₂O₄ and C₃H₄O₄ results in a similar one. The enthalpy of sublimation for CH₂N₂O₄ was estimated according to Trouton's rule, $\Delta H_{\text{sub}} = 188T_m$, and the validity of the rule reflects the fact that the entropy of vaporization is approximately constant for many compounds and that $\Delta H_{\text{sub}} \approx \Delta H_{\text{vap}} + \Delta H_{\text{fusion}}$, with $\Delta H_{\text{vap}} \gg \Delta H_{\text{fusion}}$ so that $\Delta H_{\text{sub}} \approx \Delta H_{\text{vap}}$.²⁶

With the estimated sublimation enthalpy, the enthalpy of formation for solid 2,6-diaza-1,3,5,7-tetraoxaspiro[3,3]heptane can be calculated to $\Delta_f H^{\circ}(s, \text{CH}_2\text{N}_2\text{O}_4) = +88.8$ kJ/mol, then $\Delta U_f^{\circ}(s, \text{CH}_2\text{N}_2\text{O}_4) = +78.9$ kJ/mol using the correlation $U_m = H_m - nRT$.²⁷ Same procedure was applied to get $\Delta_f H^{\circ}(s, \text{CN}_4\text{O}_8)$ and $\Delta U_f^{\circ}(s, \text{CN}_4\text{O}_8)$ for 2,6-dinitro-2,6-diaza-1,3,5,7-tetraoxaspiro[3,3]heptane, which result in +12.2 kJ/mol and +26.3 kJ/mol. The maximum density of each CH₂N₂O₄ and CN₄O₈ in the crystalline state was estimated to 1.12 g/cm³ and 2.36 g/cm³ using PM3/VSTO-3G calculations from the molecular volume (V_{max}).¹⁶

Detonation Parameters. With the heat of formations obtained in an extensive computational study and by using the EXPLO5 software, the detonation parameters of CH₂N₂O₄ and its dinitro compound, CN₄O₈, were calculated. Although the model compounds have a positive oxygen balance, Table

Table 1. Detonation parameters for 2,6-diaza-1,3,5,7-tetraoxaspiro[3,3]heptane (CH₂N₂O₄) and 2,6-dinitro-2,6-diaza-1,3,5,7-tetraoxaspiro[3,3]heptane (CN₄O₈) depending on its density^a

| | 100% CH ₂ N ₂ O ₄ | 100% CN ₄ O ₈ | 100% RDX |
|-----------------------------|----------------------------------------------------|-------------------------------------|----------|
| ρ (g/cm ³) | 1.12 | 2.36 | 1.80 |
| Ω (%) | +15.1 | +49.0 | -21.6 |
| Q_v (kJ/kg) | -6473 | -2145 | -6111 |
| T_{ex} (K) | 5308 | 2462 | 4390 |
| P_{C-J} (kbar) | 127 | 307 | 337 |
| D (m/s) | 6282 | 7871 | 8868 |
| V_0 (L/kg) | 750 | 686 | 739 |

^a ρ = density, Ω = oxygen balance, Q_v = heat of detonation, T_{ex} = detonation temperature, P_{C-J} = detonation pressure, D = detonation velocity, V_0 = volume of detonation gases, RDX = 1,3,5-trinitrohexahydro-1,3,5-triazine.

1 shows that detonation temperature and heat of detonation for CH₂N₂O₄ are comparable to the conventional explosive 1,3,5-trinitrohexahydro-1,3,5-triazine (RDX) with slightly negative oxygen balance.

It also shows performance characteristics with a predicted detonation velocity of 6282 m/s and a predicted detonation pressure of 127 kbar, both of which are lower than for RDX (8868 m/s, 337 kbar). Because of suffering from a low density, it results in a poor performance. However, CH₂N₂O₄ and CN₄O₈ molecules are similar to RDX in volume of detonation gases. For CN₄O₈, detonation pressure and velocity which are two important performance parameters for an energetic material are close to RDX. However, detonation temperature and heat of detonation are far lower to RDX.

Based on the existence of vibrationally stable minimum on the potential energy hypersurface and considering the lowest energy isomer, computed molecular volumes was obtained using semi-empirical PM3/VSTO-3G calculations. It is well established that the computed molecular densities correlate well with the highest observed experimental densities.¹⁶ As shown in Table 1, CN₄O₈ is higher density molecule than RDX. Predicted heat of detonation and detonation temperature of CN₄O₈ are much lower than RDX, however, those values of CH₂N₂O₄ comparable to RDX. Previous studies using H₃N₃O₃ model showed that values of detonation pressure, detonation velocity and volume of detonation are higher than CH₂N₂O₄ and CN₄O₈, although the density is 1.60 g/cm³.²⁸

In this regard, CN₄O₈ compound would be a good candidate as an explosive with reasonable detonation pressure and velocity. It will be worth to point out that the nitro group in nitro-substituted spiro compound not only allows a molecule to self-oxidize, but it can also react to make elemental nitrogen, liberating energy as it does so. However, the increased nitro content of a parent molecule increases its enthalpy of combustion or decomposition on a molar basis but not on a gram basis; that is, the mass of the poly-nitro compound increases proportionately faster than its enthalpy of reaction.²⁹

Because CN₄O₈ compound is also an oxidizer with the positive oxygen balance, the value should be close to zero by

Table 2. Detonation parameters for 2,6-dinitro-2,6-diaza-1,3,5,7-tetraoxaspiro[3,3]heptane (CN₄O₈) and a Formulation with TNT

| | 90% CN ₄ O ₈ , 10% TNT | 80% CN ₄ O ₈ , 20% TNT | 70% CN ₄ O ₈ , 30% TNT | 60% CN ₄ O ₈ , 40% TNT |
|-----------------------------|-------------------------------------------------|-------------------------------------------------|-------------------------------------------------|-------------------------------------------------|
| ρ (g/cm ³) | 1.43 | 1.52 | 1.63 | 1.71 |
| Ω (%) | +6.18 | -2.72 | -11.63 | -20.52 |
| Q_v (kJ/kg) | -6780 | -7120 | -7114 | -6904 |
| T_{ex} (K) | 5540 | 5664 | 5559 | 5252 |
| P_{C-J} (kbar) | 104 | 124 | 146 | 170 |
| D (m/s) | 5914 | 6259 | 6558 | 6975 |
| V_0 (L/kg) | 749 | 742 | 735 | 713 |

using a negative oxygen balance material to be an explosive. Explosive trinitrotoluene (TNT) has an oxygen balance of ca. -74%, accordingly it needs an oxidizer. Table 2 shows that detonation parameters for the neat 2,6-dinitro-2,6-diaza-1,3,5,7-tetraoxaspiro[3,3]heptane (CN₄O₈) with TNT formulations in which the TNT content has been varied in order to achieve optimal performance.

The increased TNT content of a parent molecule increases its detonation pressure and velocity, but decreases detonation volume proportionately. A formulation of 40% TNT stands for better predicted detonation parameters with the detonation pressure of 170 kbar, the detonation velocity of 6975 m/s, and the detonation volume of 713 L/kg. As shown in Table 1, 6:4 ratio of CN₄O₈ and TNT is quite similar to RDX in the values of an oxygen balance and a predicted heat of detonation. However, the performance data for RDX are out of reach. The calculated detonation velocities of all compounds in TNT formulations are in the range of 104 and 170 m/s and are well below the commonly used explosive RDX (337 m/s). Usually a good oxygen balance results in more negative heat of detonation and therefore leads to a better performance of the explosive. It is unexpected that CN₄O₈ compound can perform as RDX. Table 2 also shows that a predicted density increases by adding TNT content of a parent molecule and calculated detonation temperature and heat of CN₄O₈ in TNT formulations are coming and going.

Combustion Parameters. For a solid rocket propellant, the combustion products into space (or atmosphere) is freely expanded at constant pressure, as one can assume. Therefore, the combustion proceeds as isobaric, of which $\Delta U = Q_p - p\Delta V$ is a good approximation.³⁰ In this study, we assumed firing the rocket motor against ambient atmosphere as it is commonly the case for tactical missiles.

From the analysis of the expansion of the combustion products through the nozzle, the theoretical characteristics of the rocket motor propellant may be derived. The parameters in the combustion chamber and the isentropic expansion through the nozzle should be obtained in the calculation of the theoretical rocket performance. The options that composition of combustion products remains unchanged and is in instantaneous chemical equilibrium during the expansion through the nozzle are provided by the EXPLO5 code.¹⁷

Table 3 summarized the combustion parameter of the neat propellants covalent CH₂N₂O₄ used as monopropellants and

Table 3. Combustion properties (solid rocket motor) of Neat 2,6-diaza-1,3,5,7-tetraoxaspiro[3,3]heptane ($\text{CH}_2\text{N}_2\text{O}_4$) and a formulation with 30% Al (frozen expansion)^a

| | $\text{CH}_2\text{N}_2\text{O}_4$ | 70% $\text{CH}_2\text{N}_2\text{O}_4$, 30% Al | 70% AP, 30% Al |
|-----------------------------------|-----------------------------------|---------------------------------------------------|-------------------|
| condition | isobaric | isobaric | isobaric |
| p (bar) | 70 | 70 | 70 |
| ρ (g/cm^3) | 1.60 | 2.46 | 2.18 |
| Ω (%) | 25.8 | 7.59 | -2.85 |
| Q_p (kJ/kg) | -5697 | -6565 | -6787 |
| T_{comb} (K) | 3721 | 4818 | 4290 |
| I_{sp}^* (s) | 283 | 240 | 243 |

^a Ω = oxygen balance, Q_p = heat of isobaric combustion, T_{comb} = combustion temperature, I_{sp}^* = specific impulse

for aluminized formulations assuming rocket propellant conditions (isobaric conditions with a chamber pressure of 70 bar), in which the aluminum content has been varied in order to achieve optimal performance and compare the corresponding values for a conventional AP/Al formulation. The formulations of $\text{CH}_2\text{N}_2\text{O}_4$ with Al give better performance than the neat propellant and have generally higher combustion temperature.

The results also show that a formulation of 30% Al gives optimal performance from the comparison of the same formulation of AP/Al. The change of the impulse per propellant mass unit is described as the specific impulse I_{sp}^* , which is an important parameter for the characterization of rocket propellants and can be interpreted as the effective exhaust velocity of the combustion gases when exiting the expansion nozzle. The specific impulse and heat of isobaric combustion of the same formulation of covalent $\text{CH}_2\text{N}_2\text{O}_4$ with Al are slightly lower than those of the AP/Al formulation. The specific impulse of 80% $\text{H}_3\text{N}_3\text{O}_3$ and 20% Al formulation is much higher than that of the 70%/30% of $\text{CH}_2\text{N}_2\text{O}_4/\text{Al}$.²⁸ A 30% Al formulation mixture may be the most promising candidate as environmentally benign oxidizer to be used in solid rocket motors.³¹ Typical values for the specific impulse of solid boosters are 250 s, whereas for bipropellants they are found at approx. 450 s.³⁰ In that regards, a 70% $\text{CH}_2\text{N}_2\text{O}_4$ and 30% Al mixture may be useful as solid rocket motors. Monopropellants are endothermic liquids, which decompose exothermically in the absence of oxygen. They possess a relatively small energy content and are only used in small missiles and small satellites (I_{sp}^* (hydrazine) = 186 s). To be solid rocket motors, they should be chlorine or perchlorate-free, close to $2.0 \text{ g}/\text{cm}^3$ in density, low vapor pressure, and less sensitive than PETN (pentaerythritol tetranitrate). Therefore, our results indicate that a formulation of 30% Al might be the promising candidate for solid rocket motors.

Conclusions

From this theoretical study on 2,6-diaza-1,3,5,7-tetraoxaspiro[3,3]heptane and 2,6-dinitro-2,6-diaza-1,3,5,7-tetraoxa-

spiro[3,3]heptane, it can be concluded: (i) the suggested 2,6-diaza-1,3,5,7-tetraoxaspiro[3,3]heptane molecule shows comparable detonation parameters to RDX. (ii) formulation of 60% 2,6-dinitro-2,6-diaza-1,3,5,7-tetraoxaspiro[3,3]heptane with 40% TNT gives the best results as explosives. (iii) the specific impulse of the chlorine and perchlorate-free formulation of 70% of 2,6-diaza-1,3,5,7-tetraoxaspiro[3,3]heptane with 30% of aluminum shows similar calculated performances to those of the conventional AP/Al formulation. All the results obtained should encourage synthetic works to prepare on a laboratory scale and to evaluate their properties experimentally, first and foremost their thermal stability.

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