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Polyhedron

Insight into a series of cage-like nitrogen oxides

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ABSTRACT

Molecular structures were optimized by density functional theory B3LYP/6-31g(d,p), total energies were calculated at the level of second order by Møller–Plesset perturbation theory (MP2)/6-311g(d,p), higher accuracy G3MP2B3 method and isodesmotic reactions were employed to investigate the formation enthalpies of eight cage-like nitrogen oxides, including N_2O_3 (D_{3h}), N_4O_4 (D_{2h}), N_4O_6 (D_{2h}), N_4O_6 (T_d), N_6O_6 (D_{3h}), N_6O_9 (D_{3h}), N_8O_8 (D_{4h}), N_8O_{12} (T_d), in which N_8O_8 (D_{2h}) has the highest formation enthalpy, and N_4O_6 (T_d)'s formation enthalpy is the minimum. Their stabilities were measured in terms of cage strain energy, average bond energy, in which N_4O_6 (T_d) is the most stable compound. High positive formation enthalpies and cage strain energies indicate these cage-like nitrogen oxides may be potential high energy density materials.

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1. Introduction

The search for novel high energy density materials (HEDM) is an urgent and long-period work. For a HEDM, its energy and safety are mutually contradictory, to a great extent, its development is retarded by the safety factors. Therefore, compared with other materials, the HEDMs develops very slowly. Conventional high energy density materials contain mostly C, H, O, N elements, the improvement of their energies is strongly limited by the molecular characteristics. Non-conventional HEDM, without hydrogen and carbon elements (or little carbon), may break through the energy limits and become promising novel HEDMs. All nitrogen compounds [1–6], with high formation enthalpies, a great of energies will be released after their decomposition, the decomposed products only contain eco-friendly molecular nitrogen, they are the most promising HEDMs. However, all nitrogen compounds are very hard to be experimentally synthesized because of their thermodynamic instability and high ring strain energy for ring-shaped compounds, high cage strain energy for cage-shaped compounds. Nonetheless, the attractive properties of all nitrogen compounds still attract a lot of researchers to diligently devote their efforts to these kinds of materials, we believe that all nitrogen compounds

may be experimentally synthesized and practically applied in the near future.

In conventional energetic materials, most contain detonation-initiated —NO_2 groups, and nitrogen oxides are typically essential in the process of the synthesis, especially for N_2O_5. Currently, the discovered nitrogen oxides include N_2O, NO, N_2O_2, N_2O_3, NO_2, N_2O_4, N_2O_5 and N_4O, their formation enthalpies are 82.0, 90.2, –, 80.2, 9.16, 11.3, -297.3 kJ/mol (s), – [7], respectively. Few literatures about NO or NN bonds based cage-like nitrogen oxides were reported [8,9], and they were illustrated in Fig. 1, which have higher formation enthalpies (calculated in the following parts), a great deal of energies will be released and a lot of gaseous N_2 and O_2 will be generated after decomposition, and the results indicate that they are promising HEDM candidates. We calculated their formation enthalpies, the cage strain energies, average bond energies to evaluate their energy contents and stabilities.

2. Computational details

All of the electronic structure calculations were performed with density functional theory B3LYP/6-31g(d,p) [10,11], and total energies were calculated at the level of second order Møller–Plesset perturbation theory MP2/6-311g(d,p) [12,13], higher accuracy G3MP2B3 [14,15] method was applied to calculate formation ehthalpies, carried out with GAUSSIAN 09 [16]. Because there are no experimental data for string or cage strain energies, so far, in this work we designed homodesmotic Eq. (1) to calculate string strain energy of chair-type cyclohexane, which is the well-known
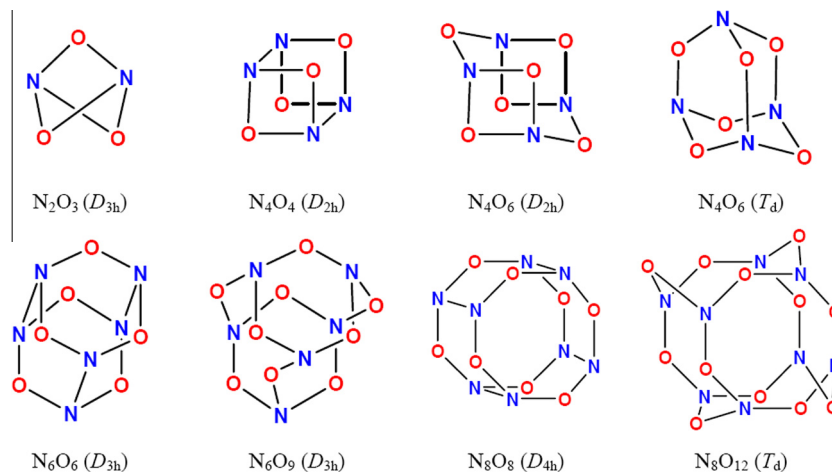
Fig. 1. Molecular structures and the symmetries of eight cage-like nitrogen oxides.

strain-free six-membered string. The calculated string strain energies of chair-type cyclohexane is only 1.25 kJ/mol in terms of Eq. (I), it is well in agreement with our chemical intuitions about chair-type cyclohexane, and the details were displayed in Table 1. In a homodesmotic reaction, bond types, bond valences, atomic hybridization types and molecular conformations are kept the same at both sides, the systematic errors caused by the electron-correlation energies and electron-exchange energies may be reduced to a significant extent. Accordingly, Møller–Plesset perturbation theory MP2/6-311g(d,p) and some homodesmotic reactions were carried out to calculate cage strain energies and formation enthalpies of the cage-like nitrogen oxides.

$$H_2C-C(H_2)-CH_2 \cdots + 6\,H_3C-CH_3 \longrightarrow 6\,H_3C-C(H_2)-CH_3 \tag{1}$$
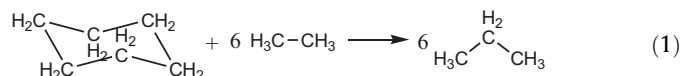
$$E_S = \sum_i n_i(E_{0,i}(R) + ZPE_i(R)) - \sum_j n_j(E_{0,j}(P) + ZPE_j(P)) \tag{I}$$

Formation enthalpy, a basic parameter of a compound, is a computational challenging physical quantity for wavefunction based electronic structure *ab initio* methods so far [17,18], especially for some larger molecules. Despite semiempirical methods can directly calculate formation enthalpy, but the accuracy could not be achieved. Homodesmotic reaction-based density functional theory calculations [19–22] for gaseous phase formation enthalpy are still effective and reliable methods, which are designed along the route where the compounds contain experimental values, formation enthalpies can be calibrated to the level of experimental values under 298.15 K.

3. Results and discussion

The properties of HEDMs are mainly determined by two factors: enthalpy of formation and density [23]. The higher the formation

enthalpy is, the more heat will be released when a HEDM decompose; the higher the density is, the more heat and gaseous products will be released, and the higher the detonation velocity and the detonation pressure will be achieved. The detonation pressure changes with the rapid growth of exponential relationship.

Isodesmotic reactions (1)–(8) and Eqs. (II)–(IV) were considered to calculate formation enthalpies. In the homodesmotic reactions, the compounds' experimental formation enthalpies are well known except the cage-like nitrogen oxides, so the unknown formation enthalpies may be calculated and calibrated to the experimental level, the related results were listed in Table 2. In Eqs. (II)–(IV) $\Delta H_{298}, \sum \Delta_f H_P, \sum \Delta_f H_R, \Delta E_{298}, \Delta E_0, \Delta ZPE, \Delta H_T$ are the reaction enthalpy change at 298 K, the sum of formation enthalpies of products and reactants, he reaction thermodynamic energy change at 298 K, energy change at 0 K, zero point vibration energy change and temperature-dependent enthalpy change, respectively. All gaseous molecules in the isodesmotic reaction are regarded as ideal gases, hence, $\Delta(pV) = \Delta nRT$. The theoretical formation enthalpies were displayed in Table 3.
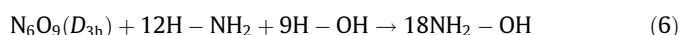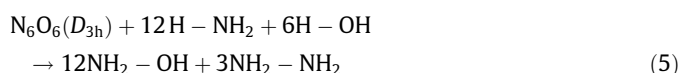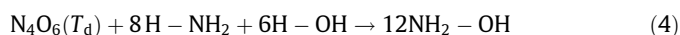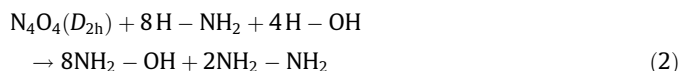
$$N_2O_3(D_{3h}) + 4\,H-NH_2 + 3\,H-OH \rightarrow 6NH_2-OH \tag{1}$$

$$N_4O_4(D_{2h}) + 8\,H-NH_2 + 4\,H-OH \\ \rightarrow 8NH_2-OH + 2NH_2-NH_2 \tag{2}$$

$$N_4O_6(D_{2h}) + 8\,H-NH_2 + 6\,H-OH \rightarrow 12\,NH_2-OH \tag{3}$$

$$N_4O_6(T_d) + 8\,H-NH_2 + 6\,H-OH \rightarrow 12\,NH_2-OH \tag{4}$$

$$N_6O_6(D_{3h}) + 12\,H-NH_2 + 6\,H-OH \\ \rightarrow 12NH_2-OH + 3NH_2-NH_2 \tag{5}$$

$$N_6O_9(D_{3h}) + 12\,H-NH_2 + 9\,H-OH \rightarrow 18NH_2-OH \tag{6}$$
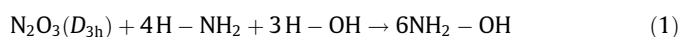
Table 1
Total energies and zero-point energies of the *chair*-type cyclohexane related compounds involved in homodesmotic reaction (1).

Molecules	Total energy (Hatree)	Homodesmotic reaction	E_S (kJ/mol)
(cyclohexane)	$E_{tot} = -235.168021$ $E_{zpe} = 0.170549$	$C_6H_{12} + 6CH_3CH_3 \rightarrow 6CH_2(CH_3)_2$	1.25
CH_3CH_3	$E_{tot} = -79.570857$ $E_{zpe} = 0.07935$		
$CH_2(CH_3)_2$	$E_{tot} = -118.765964$ $E_{zpe} = 0.103717$		