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**MOLECULAR DESIGN AND PROPERTIES PREDICTION
OF CYCLOTETRAMETHYLENE TETRANITRAMINE (HMX) DERIVATIVES
WITH AMIDO GROUPS**© 2010 **B. Tan**^{1*}, **R. Peng**², **H. Li**², **B. Jin**², **S. Chu**², **X. Long**³¹College of Space Science and Technology, Beijing Institute of Technology, 100081, Beijing, P.R. China²College of Material Science and Engineering, Southwest University of Science and Technology, 621010, Mianyang, Sichuan, P.R. China³China Academy of Engineering Physics (CAEP), 621900, Mianyang, Sichuan, P.R. China

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DFT/BLYP/DNP method was employed to calculate the total energy of cyclotetramethylene tetranitramine (HMX) derivatives modified with amido groups and the bond dissociation energy of the weakest N—NO₂ bond. The bond dissociation energy decreases with the number of amido groups. Isodesmic reactions were used to calculate standard molar enthalpies of formation of the derivatives; these values increase with the number of amido groups but not according to additivity rules. Entropy and heat capacity were also investigated. NBO analysis was applied to study the bond orders and the second perturbation energy of the N—NO₂ bonds; these parameters decrease regularly with the number of amido groups. Taking a single amido derivative as an example to analyze the vibration frequencies, it is shown that all the strongest vibrations are related with the N—NO₂ bonds.

Key words: octogen, bond dissociation energy, enthalpy of formation, bond order.

INTRODUCTION

Cyclotetramethylene tetranitramine (HMX) is one of universal high explosives. With its good parameters invariability and chemical stability, the explosive has attracted a great deal of attention among researchers. Sensitivity is an important parameter defining the invariability of explosives, and in practice it is more important than energy. One is familiar with the fact that if hydrogen atoms on benzene ring of 1,3,5-trinitrobenzene are replaced with two or three amido groups, the resulting DATB and TATB exhibit good invariability and low sensitivity.

In this work we investigated by theoretical calculations whether HMX derivatives modified with amido groups should be new explosives with low sensitivity and high energy. The computations targeted standard molar enthalpy of formation, heat capacity and entropy for a series of compounds, as well as bond order, bond dissociation energy, second order perturbation energy and characteristic vibration frequencies on the weakest N—NO₂ bond in these compounds.

MODELS AND CALCULATION DETAILS

In this paper the thermodynamic parameters and bond dissociation energy were studied using DMol3 [1] mode in Materials Studio package. Generalized Gradient Approximation and DNP (Double Numerical plus Polarization) basic set were adopted in Density Function Theory BLYP [2] calculations. Every molecular structure was optimized to a minimum energy; the greatest gradient converged to 0.004 Ha/Å (Hartrees per Ångström), the greatest displacement to 0.005 Å, energy to 2.0×10⁻⁵ Ha,

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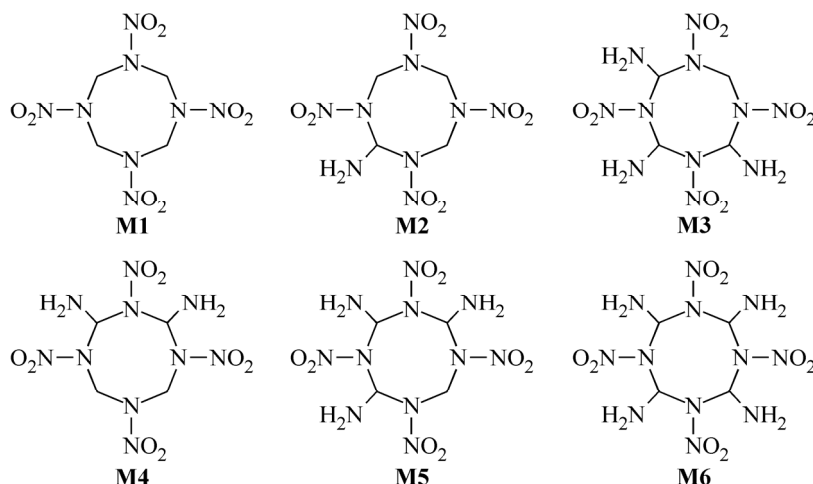


Fig. 1. Molecular structures of studied HMX derivatives with amido groups

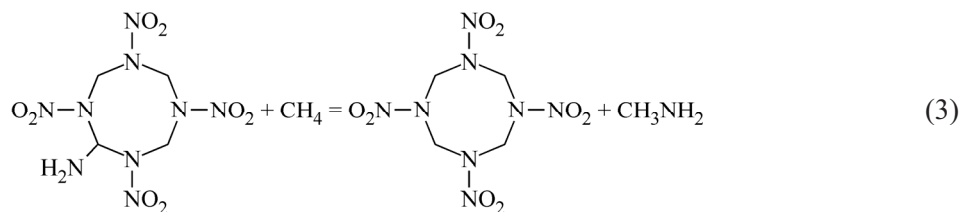
and self-confident field to 1.0×10^{-5} Ha. There were no imaginary frequencies in the frequency analysis. Natural Bond Orbital (NBO) method in Gaussian-03 was applied to calculate bond orders and second order perturbation energies. Enthalpy of formation is a measure of energy content of a compound. It is an important factor in designing new energetic materials or evaluating existing ones. It helps to investigate characteristics of energetic materials as it enters into the calculation of explosive and propellant properties such as detonation velocity, detonation pressure and specific impulse. In order to obtain the accurate standard molar enthalpy of formation of amido-HMXs, five isodesmic reactions were used in calculating parameters. Because the number and types of the chemical bonds were kept the same, any significant systematic errors were avoided and the theoretical values were adjustable to the experimental. The reaction molar enthalpies of isodesmic reactions were described by equations (1) and (2):

$$\Delta_r H_m^\ominus = \sum \Delta_{f,p} H_m^\ominus - \sum \Delta_{f,R} H_m^\ominus = \Delta E_{298.15} + \Delta(pV), \quad (1)$$

$$\Delta E_{298.15} = \Delta E_0 + \Delta ZPVE + \Delta H_T. \quad (2)$$

In equation (1), $\Delta_r H_m^\ominus$ is the reaction molar enthalpy, $\Delta(pV)$ equals ΔnRT under the condition of ideal gas. In the isodesmic reactions, $\Delta n = 0$, so $\Delta(pV) = 0$. The first two items on the right side of equation (2) are the total energy difference between products and reactants, and the energy difference of zero point vibration energy. ΔH_T is temperature change factor, $\sum \Delta_{f,p} H_m^\ominus$ and $\sum \Delta_{f,R} H_m^\ominus$ are standard enthalpies of formation of products and reactants, respectively. Because the experimental enthalpy of formation in gas of referenced molecules including HMX, methylamine and methane are all known [4–6] (HMX: $\Delta_f H_{\text{solid}}^\ominus = 75.0$ kJ/mol; $\Delta_{\text{sub}} H = 161.0 \pm 0.3$ kJ/mol; $\Delta_f H_{\text{das}}^\ominus = \Delta_f H_{\text{solid}}^\ominus + \Delta_{\text{sub}} H = 236.0$ kJ/mol; CH_3NH_2 : $\Delta_f H_{\text{das}}^\ominus = -23.5$ kJ/mol), standard molar enthalpy of formation of target molecules M2–M6 (Fig. 1) can be calculated according to equation (1).

The isodesmic reaction scheme for M2 was designed as (3):



Similarly, other isodesmic reactions were designed as follows:



Table 1

Thermochemical parameters of studied molecules in gas phase

Molekula	E_0 (Hartree)	ZPVE, kJ/mol	$H_{298.15}$, kJ/mol	$\Delta_f H_m^\ominus$, kJ/mol
CH ₄	-40.499	116.232	10.016	-74.400
CH ₃ NH ₂	-95.846	164.243	11.577	-23.500
M1	-1196.880	478.043	46.137	236.000
M2	-1252.235	524.799	53.421	?
M3	-1307.598	563.639	57.049	?
M4	-1307.582	564.070	55.831	?
M5	-1362.933	606.191	60.785	?
M6	-1418.288	651.645	62.254	?



The results are listed in Table 1.

According to the data of Table 1 and equation (1), the standard molar enthalpies of formation of molecules M2 to M6 are 270.365, 272.153, 313.373, 354.273 and 378.521 kJ/mol, respectively. So the standard molar enthalpy of formation of molecules modified with a greater number of amido groups becomes higher (however the tendency is not consistent with a simple group-addition rule). The HMX derivatives M2—M6 should have higher energy than HMX according to the standard molar enthalpies of formation.

CALCULATIONS ON BOND DISSOCIATION ENERGY AND BOND ORDER

From a mass spectrum of HMX in NIST database (<http://webbook.nist.gov/chemistry>), the relative mass of the most abundant group is 46, which is nityl. Therefore the weakest bond in HMX molecule is the N—NO₂ bond. This bond is usually considered as the shock initiation chemical bond in nitroamine molecules, which is evidently related to the shock sensitivity. In fact, the introduction of amido groups changes the N—NO₂ bond length, bond order and bond dissociation energy from the primary HMX molecule (only the weakest N—NO₂ bonds are considered). According to the literature [7—11], the bond dissociation energy and bond order of the weakest N—NO₂ bond in nitroamine molecules have clear relationship with the shock sensitivity. Second order perturbation energy $E(2)$ [13] can also explain the chemical bonds formation in terms of natural molecular orbitals.

The N—NO₂ bond dissociation energy was calculated using equation (8):

$$BDE_{(RN-NO_2)} = E_{(RN)} + E_{(NO_2)} - E_{(RN-NO_2)}. \quad (8)$$

In equation (8) $BDE_{(RN-NO_2)}$ represents bond dissociation of molecule RN—NO₂, $E_{(RN)}$, $E_{(NO_2)}$ and $E_{(RN-NO_2)}$ represent total energy of RN, NO₂ and RN—NO₂, respectively, with RN and NO₂ being radicals. The reactions are homolytical dissociation and the calculation results are for open shell systems. The result from equation (8) is in good agreement with the experimental values [12]. Wiberg bond index is expressed as $W_{AB} = \sum_{\mu \in A} \sum_{\nu \in B} P_{\mu\nu}^2$, where $P_{\mu\nu}$ is a density matrix element between

the atoms A and B. The second order perturbation energy is defined as $E(2) = \Delta E_{ij} = q_i \frac{F_{ij}^2}{\varepsilon_j - \varepsilon_i}$,

where q_i is the donor orbital occupancy, ε_i and ε_j are diagonal elements (orbital energies), and F_{ij} is the off-diagonal NBO fock matrix element. $E(2)$ is a kind of stabilization energy; the greater it is, the more energy the donor orbital supplies to the acceptor orbital. The calculation results are listed in Table 2.

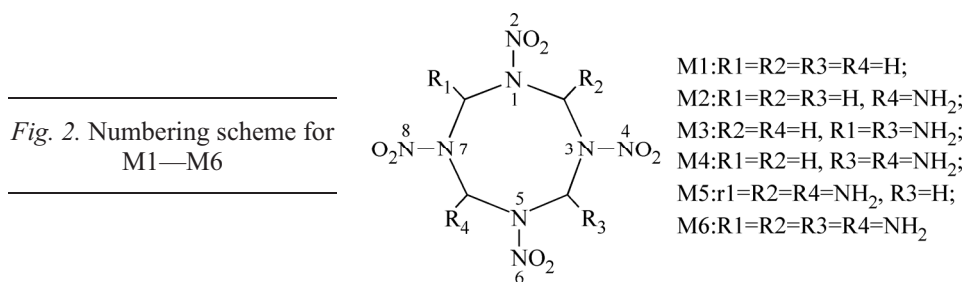


Table 2

The calculated results for M1 to M6 (for numbering scheme see Fig. 2)

Molecula	l_{N-N} , Å	BO_{N-N}	BDE, kJ/mol	$E_{LUMO} - E_{HOMO}$, eV	$E(2)$, kJ/mol
M1	$l_{12} = 1.435$	0.9760	196.85	3.402	164.60
M2	$l_{12} = 1.444$	0.9673	191.80	3.399	133.01
M3	$l_{78} = 1.420$	1.0140	194.99	3.174	159.33
M4	$l_{78} = 1.449$	0.9981	191.02	3.186	153.97
M5	$l_{78} = 1.454$	0.9729	174.84	3.118	60.375
M6	$l_{56} = 1.479$	0.9277	161.44	2.535	44.308

From Table 2 one can find that bond length, bond order, bond dissociation energy and $(\sigma_N \rightarrow \sigma_{N-O}^*)$ second order perturbation energy of the weakest N—NO₂ bonds in HMX molecule change regularly with the introduction of amido groups; N—NO₂ bonds become longer, the bond orders and bond dissociation energy become smaller, $(\sigma_N \rightarrow \sigma_{N-O}^*)$ second order perturbation energies and energy gap of the frontier orbitals of the molecules all become smaller. Some deviations happen in the changing process, such as those for M3, the diamido derivative with the groups opposed to each other: bond length and other relevant parameters are on the high side. From the evidences above, one can conclude that the new compounds should be unstable due to the introduction of amido groups.

VIBRATIONAL ANALYSIS AND CALCULATIONS OF HEAT CAPACITY AND ENTROPY

Heat capacity (C_p) and entropy (S) are also significant properties of high energy compounds. These quantities were described as follows:

$$C_p = C_{tra} + C_{rot} + C_{vib}(T), \quad (9)$$

$$C_{vib} = R \sum_i \frac{(h\nu_i / kT)^2 \exp(-h\nu_i / kT)}{[1 - \exp(-h\nu_i / kT)]^2}, \quad (10)$$

$$S = S_{tra}(T) + S_{rot}(T) + S_{vib}(T). \quad (11)$$

The heat capacities of M1—M6 at constant pressure and 298.15 K were worked out without any corrections; they were 267.64, 305.36, 331.01, 324.26, 354.28, 372.32 J/mol·K, respectively.

The variational trends of heat capacity and entropy from 25 K to 1000 K are shown in Figures 3 and 4.

The heat capacities (Fig. 3) have the tendency to rise with the increasing number of amido groups, especially on going from HMX to the monoamide derivative. Heat capacities change slower after 500 K, the contribution to heat capacity being mainly from molecular vibration.

As to the entropies (Fig. 4), they increase in nearly linear fashion. It is understandable as the translation, rotation and vibration components all comprise a temperature factor.

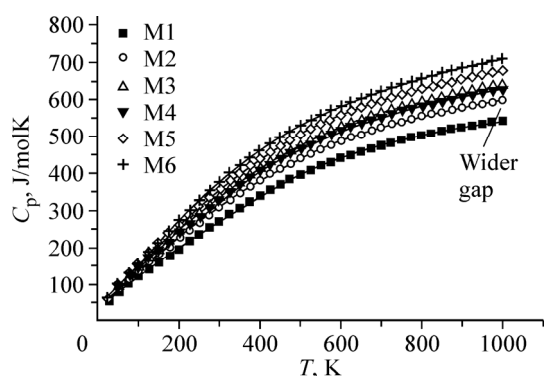


Fig. 3. Heat capacities of M1 to M6 versus temperature

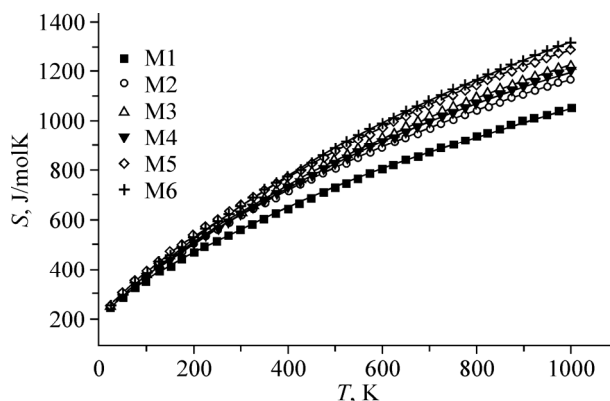


Fig. 4. Entropies of M1 to M6 versus temperature

In order to investigate the vibrational characteristics, the HMX derivative M2 was considered as an example and its vibration frequencies and their intensities were obtained as shown in Fig. 5.

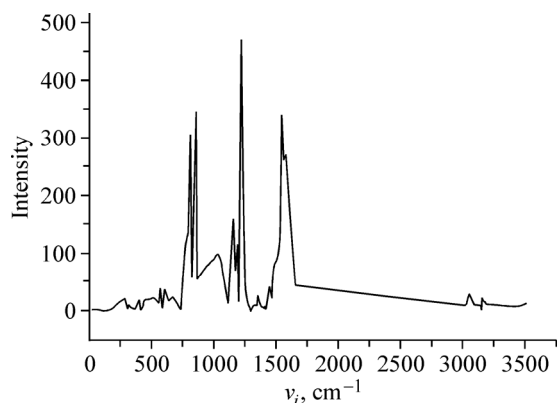
There are 84 characteristic vibrational modes in compound M2. Among them the stronger characteristic vibration modes 769.9 cm^{-1} corresponding to N—H bond shearing vibration in amido group; 790.3 and 802.2 cm^{-1} due to C—N stretching vibration in the heterocycle; 808.9 , 833.9 , 849.0 , 1218.8 and 1222.6 cm^{-1} due to N—N bond stretching vibration (1218.8 cm^{-1} is the strongest); 1525.8 , 1537.3 , 1549.1 and 1574.4 cm^{-1} due to N—O bond asymmetric stretching vibration in NO_2 group.

Bader [14] and Laurence [15] considered that there probably are some internal relationship between shock wave sensitivity of explosives and some characteristic vibration frequencies in explosive molecules. All these strong vibration modes calculated are related to N— NO_2 , so it can convince one that N— NO_2 is the most significant point affecting the shock sensitivity of nitroamine molecules.

CONCLUSION

From BLYP/DNP method and isodesmic reactions calculations, the standard molar enthalpies of formation of M2 to M6 were obtained; they are 270.365, 272.153, 313.373, 354.273 and 378.521 kJ/mol, respectively, indicating a tendency to increase. The heat capacities and entropies were also investigated. The weakest N— NO_2 bonds dissociation energies from M1 to M6 are 196.85, 191.80, 194.99, 191.02, 174.84 and 161.44 kJ/mol, respectively, presenting a downtrend. The frontier orbital energy gaps also present a downtrend. Natural bond orbital analysis indicates that the bond orders (Wiberg bond index) of the weakest N— NO_2 bonds are gradually reduced from monoamide-HMX to tetraamide-HMX, $\sigma_{\text{N}} \rightarrow \sigma_{\text{N}-\text{O}}^*$ second order perturbation energies change exhibiting a similar trend.

From the calculations and analyses of this work one can conclude that the introduction of amido groups to HMX is advantageous in terms of energy. However, as evident from bond dissociation energy of the weakest bond in the molecule, the addition of amido groups to HMX leads to unstable compounds.



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Fig. 5. Frequencies and their intensity for M2

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