Thermal stability and quantum chemistry study on octahydro-2,5-bis(nitroimino)imidazo[4,5-d]imidazole

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Abstract

Thermal decomposition of octahydro-2,5-bis(nitroimino)imidazo[4,5-d]imidazole was studied by means of thermogravimetry (TG) and differential thermal analysis (DTA) simultaneously under nitrogen atmosphere. The structure of the compound was also estimated by a B3LYP method based on the 6-31G(d,p) basis set to obtain a stable geometric configuration and the corresponding Wiberg bond order. The results indicate that the compound shows good thermal stability with exothermic decomposition peak at 335°C on DTA, the geometric structure of the compound presents a little contorted configuration and the C(3)—N(22) bond order is weaker than the other N—N or C—N bonds.

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Keywords: octahydro-2,5-bis(nitroimino)imidazo[4,5-d]imidazole; thermal decomposition; TG-DTA; quantum chemistry

1. Introduction

During the past decades, considerable effort has been focused on the development of nitrogen-rich high energy density materials (HEDM) with high performance and decreased sensitivity as well as environmental compatibility[1-2]. One of the most exciting developments in the field of HEDM are N-heterocyclic energetic compounds with high nitrogen content. Octahydro-2,5-bis(nitroimino)imidazo[4,5-d]imidazole (BNNII), shown in Fig. 1, is a homothetic energetic compound of this kind containing two nitroimino groups and it appears to be the future candidate both for civil and military use. Although many properties of BNNII have been known, such as density, detonation velocity, calculated detonation pressure and heats of formation[3], the relationship between its thermal decomposition properties and structure was never reported.

Fig. 1. Chemical structure of BNNII.

Recently, thermal analysis has been used in studying the properties of explosives as a reliable technique to find superior performance explosives and control their quality[4-6]. In particular, works in this field highlight the application of thermal
gravimetric-differential (TG-DTA)[7] and differential scanning calorimetry (DSC)[8-9] techniques. All these methods may provide important information on the properties of substances such as stability, compatibility, sensitivity and so on[10].

On the other hand, quantum chemistry is an important subject that utilizes the quantum mechanics to solve chemistry problems, especially in predicting the properties of unknown hazardous energetic materials. In quantum chemistry, the density functional theory (DFT) method[11-12], which considers the electron correlation, is used to interpret the chemical bond building or breaking, bond property, electron distribution and so on.

Herein, the thermal decomposition properties and the structure of BNNII were investigated by TG-DTA technique and quantum chemistry respectively. The relationship between the two was also discussed.

2. Experimental

2.1. Thermal test

The TG-DTA curves of BNNII were obtained by Mettler Toledo TG-DTA 851e instrument under nitrogen atmosphere at a flow rate of 30.0 mL min\(^{-1}\). The applied heating rate was 15 °C min\(^{-1}\), from 50 °C to 800 °C. The sample with an initial mass of 0.3300 mg was placed to a ceramic crucible. Temperature and calorimetric calibration was done using indium standards.

2.2. Quantum chemistry calculation

Application of density functional theory along with the Lee-Yang-Parr (LYP) nonlocal-correlation functional (B3LYP)[13-15], the geometric structure of BNNII was optimized. Furthermore, a NBO analysis was undertaken to predict the thermal decomposition process. All the work was done on the GAUSSIAN 2003 program package.

3. Results and discussion

3.1. TG-DTA analysis

Fig.2 shows the TG-DTA curves of BNNII under nitrogen stream. The TG curve reveals that the decomposition reaction is a two-stage process: the first stage which starts from 300 °C to 370 °C with about 60.39% mass loss is abrupt and the second stage which is much slower than the former starts immediately with about 28.20% mass loss. Thus, the calculated mass loss of the overall reaction is about 88.59%. In the DTA curve, it presents one sharp exothermic peak with maximum situated in the 300–370 °C temperature range and a small endothermic peak with maximum situated in the 660-690 °C temperature range. Based on the temperature range of weight loss, the exothermic peak can be ascribed to the decomposition of BNNII and the endothermic peak may be ascribed to the sublimation of the residue.

Fig. 2. TG-DTA curves of BNNII.
3.2. Structure analysis

The optimized structure of the BNNII at the B3LYP/6-31G(d,p) level is given in Fig. 3. Table 1 and 2 show the corresponding parameters of BNNII after optimization.

According to the analysis of the bond angle and dihedral angle (see Table 1), it is found that the geometric structure of BNNII presents a little contorted configuration and occupies larger dimensional position. It is proved to be in very good agreement with the model of BNNII shown in Fig. 3.

![Fig. 3. Geometric configuration of BNNII after optimization at the B3LYP/6-31G(d,p) level.](image)

| Bond | Bond angle /° | Bond | Dihedral angle /° |
|------|---------------|------|------------------|
| N(10)—C(1)—N(21) | 118.0898 | N(21)—C(1)—N(10)—N(14) | 174.9304 |
| N(10)—C(1)—N(22) | 132.1258 | N(22)—C(1)—N(10)—N(14) | -6.9469 |
| N(21)—C(1)—N(22) | 109.7360 | N(10)—C(1)—N(21)—C(2) | 161.0310 |
| C(3)—C(2)—H(17) | 109.1782 | N(10)—C(1)—N(21)—H(6) | 26.5171 |
| C(3)—C(2)—H(19) | 98.8188 | N(22)—C(1)—N(21)—C(2) | -17.4905 |
| C(3)—C(2)—N(21) | 98.4322 | N(22)—C(1)—N(21)—H(6) | -152.0044 |
| H(17)—C(2)—N(19) | 109.3005 | N(10)—C(1)—N(22)—C(3) | 167.0043 |
| H(17)—C(2)—N(21) | 109.6157 | N(10)—C(1)—N(22)—H(5) | 26.3694 |
| N(19)—C(2)—N(21) | 128.8411 | N(21)—C(1)—N(22)—C(3) | -14.7552 |
| C(2)—C(3)—H(18) | 109.1782 | N(21)—C(1)—N(22)—H(5) | -155.3901 |
| C(1)—C(10)—N(14) | 117.3224 | H(17)—C(2)—C(3)—H(18) | 180.0000 |
| N(10)—N(14)—O(15) | 121.1653 | N(21)—C(2)—C(3)—H(18) | 65.7398 |
| N(10)—N(14)—O(16) | 114.8030 | N(21)—C(2)—C(3)—N(22) | -48.3451 |
| O(15)—N(14)—O(16) | 124.0157 | C(3)—C(2)—N(21)—C(1) | 40.4700 |
| C(1)—N(22)—C(3) | 104.438 | C(3)—C(2)—N(21)—H(6) | 171.0524 |
| C(3)—N(22)—H(5) | 125.5002 | H(17)—C(2)—N(21)—H(6) | 57.1368 |
| C(1)—N(22)—H(5) | 114.2255 | N(19)—C(2)—N(21)—C(1) | 149.0342 |
| C(1)—N(22)—C(2) | 103.7148 | N(19)—C(2)—N(21)—H(6) | -80.3834 |
| C(2)—N(21)—H(6) | 121.3767 | C(2)—C(3)—N(22)—C(1) | 39.0765 |
| C(1)—N(21)—H(6) | 121.3767 | H(18)—C(3)—N(22)—C(1) | -74.9128 |
| | | H(18)—C(3)—N(22)—H(5) | 59.8139 |
| | | N(20)—C(3)—N(22)—H(5) | -77.8081 |
| | | C(1)—N(10)—N(14)—O(15) | -10.6786 |
| | | C(1)—N(10)—N(14)—O(16) | 170.7185 |

As is shown in Table 2, all the C—N bond lengths are range from 1.3073 Å to 1.4517 Å which are between the common C—N single bond (1.47 Å) and the common C≡N bond (1.28 Å). The N—N bond length is 1.3968 Å which is between the common N—N bond (1.45 Å) and the common N≡N bond (1.24 Å). Obviously, all the bond lengths tend to average and make the molecule more stable. On the other hand, the C(3)—N(22) bond order is weaker than the other N—N or C—N bonds. It is indicated that the C(3)—N(22) bond is not stable enough and may be broken firstly when heated or assaulted.
Table 2. Bond length and bond order of BNNII after optimization at the B3LYP/6-31G(d,p) level

| Bond     | Bond length/Å | Bond order |
|----------|---------------|------------|
| C(1)—N(21) | 1.3994       | 1.1301     |
| C(1)—N(22) | 1.3841       | 1.1723     |
| C(1)—N(10) | 1.3073       | 1.5126     |
| C(2)—N(21) | 1.4517       | 0.9712     |
| C(3)—N(22) | 1.4498       | 0.9615     |
| C(2)—C(3)  | 1.5148       | 0.9674     |
| N(10)—N(14) | 1.3968       | 1.0476     |
| N(14)—O(15) | 1.2478       | 1.4090     |
| N(14)—O(16) | 1.2183       | 1.5374     |

4. Conclusions

The combination of TG-DTA technique and quantum chemistry were applied to the thermal analysis and structural characterization of BNNII respectively. It is concluded that the thermal decomposition process consists of one main stage when the primary quantity of heat is giving out and another slow stage with a small endothermic peak. The onset of the exotherm starts at 300 °C with the peak maximum at 335 °C and the onset of endotherm starts at 660 °C with the peak maximum at 670 °C. The process of the overall reaction involves about 88.59% mass loss.

The optimized geometric configuration and the Wiberg bond order of the BNNII were calculated at the B3LYP/6-31G(d,p) level. It is seen that the geometric structure of the BNNII presents a little contorted configuration and the C(3)—N(22) bond order is weaker than other N—N or C—N bonds which may be broken firstly when heated or assaulted.

Acknowledgements

The authors gratefully acknowledge the Analysis and Testing Center of Nanjing University of Science and Technology for providing supports to carry out the work.

References

[1] Schmidt, M. W., Gordon, M. S., Boatz, J. A., 2005. Triazolium-based energetic ionic liquids, Journal of Physical Chemistry 109, p. 7285.
[2] Muthurajan, H., Sivabalan, R., Talawar, M. B., Venugopalan, S., Gandhe, B. R., 2006. Computer code for the optimization of performance parameters of mixed explosive formulations, Journal of Hazardous Materials 136, p. 475.
[3] Dagley, I. J., Kony, M., Walker, G., 1995. Properties and impact sensitiveness of cyclic nitramine explosives containing nitroguanidine groups, Journal of Energetic Materials 13, p. 35.
[4] Zhang, G. X., Weeks, B. L., 2010. A device for testing thermal impact sensitivity of high explosives, Propellants, Explosives, Pyrotechnics 35, p. 440.
[5] Piazzon, N., Rosenthal, M., Bondar, A., Spitzer, D., Ivanov, D. A., 2010. Characterization of explosives traces by nanocalorimetry, Journal of Physics and Chemistry of Solids 71, p. 114.
[6] Li, Y. C., Cheng, Y., 2010. Investigation on the thermal stability of nitroguanidine by TG/ DSC-MS-FTIR and multivariate non-linear regression, Journal of Thermal Analysis and Calorimetry 100, p. 949.
[7] Poulomi, S., Fathollahi, M., Hajimirsadeghi, S. S., Hosseini, S. G., 2006. Thermal behavior of aluminum powder and potassium perchlorate mixtures by DTA and TG, Thermochimica Acta 443, p. 129.
[8] Berger, A., Wehrstedt, K. D., 2010. Azodicarboxylates: Explosive properties and DSC measurements, Journal of Loss Prevention in the Process Industries 23, p. 734.
[9] Turcotte, R., Vachon, M., Kwok, Q. S. M., Wang, R. P., Jones, D. E. G., 2005. Thermal study of HNIW (CL-20), Thermochimica Acta 443, p. 105.
[10] Cides, L. C. S., Araújo, A. A. S., Santos-Filho, M., Matos, J. R., 2006. Thermal behaviour, compatibility study and decomposition kinetics of glimepiride under isothermal and non-isothermal conditions, Journal of Thermal Analysis and Calorimetry 84, p. 441.
[11] Becke, A. D., 1993. A new mixing of Hartree-Fock and local density functional theories, Journal of Chemical Physics 98, p. 1372.
[12] Kohn, W., Becke, A. D., Parr, R. G., 1996. Density functional theory of electronic structure, Journal of Physical Chemistry 100, p. 12974.
[13] Johnson, B. G., Gill, P. M. W., Popele, J. A., 1993. The performance of a family of density function method, Journal of Chemical Physics 98, p. 5612.
[14] Jimmie, C. O., James, L. S., Heng, C., 2002. Thermal decomposition of high-nitrogen energetic compounds—dihydrazido-S-tetrazine salts, Thermochimica Acta 384, p. 91.
[15] Bauschlicher, Jr. C. W., Partridge, H., 1995. The sensitive of B3LYP atomization energies to the basis set and a comparison of basis set requirements for CCSD (T) and B3LYP, Journal of Chemical Physics Letters 240, p. 533.