Theoretical study on the structure and sensitivity of fused aza-cyclic nitro-containing compounds

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Abstract. As the heterocyclic compound with high detonation properties and low sensitivity, fused aza-cyclic energetic compounds have shown great research value and application prospect in recent years. In this paper, two series (30 kinds) of new fused aza-cyclic nitro-containing compounds were designed to be the research target, with good fused aza-cyclic molecules as the basic structure and nitrogen-containing high energy groups of nitro group (-NO2) and amino group (-NH2) as substituents. The DFT-B3LYP/6-31G (d) method was used to optimize the molecular geometry and analyze the vibration frequency. The calculation results show that all derivatives have no virtual frequency, and they are stable structures on the potential energy surface; The nitro group charge of compounds was obtained. The structure-activity relationship between molecular structure and sensitivity was studied. And change relation of the sensitivity and the parent structure of molecule, the type and number of substituting group and configuration was summarized, providing references for relevant researchers.

1. Introduction

High nitrogen compounds have potential application value in energy-containing materials and have received extensive theoretical and experimental attention. As the basic structural units of energy-containing compounds, five-membered nitrogen heterocycles, especially triazole and tetrazole, have become the focus of research due to their high nitrogen content and high heat of formation [1-4]. The nitrogen content of triazole is moderate, showing high heat of formation and stability, while the significant difference of bond energy between nitrogen atoms makes the compound have high energy, such as high heat of formation of 1, 2, 4-triazole ring, and good detonation properties. Previous studies on triazole energy-containing compounds focused on monocyclic derivatives and azo-bonded biocyclic derivatives [5,6], and the heat of formation of zolidazole compounds increased with the increase of nitrogen content, but their stability decreased. The nitrogen-rich cyclic energetic compounds have high energy characteristics and good stability, so it is the focus of energy-containing materials research. Therefore, it is necessary to further study the stability of cyclic compounds containing triazole rings.

In this paper, 30 nitro-containing compounds were generated by automatic assembly of skeleton and functional groups, with each high-energy cyclic compound as the skeleton and nitro (-NO2) and amino (-NH2) as substituents [7]. The compounds were divided into two groups (series A and B) according to the different skeletons. Using density functional theory (DFT) [8-10] to study the molecular geometry and sensitivity at the B3LYP/ 6-31G (d) level and the effects of structural
elements and substituents on sensitivity and their interactions, the regular relationship between the structure, substituents and sensitivity is revealed, which provides theoretical guidance for the sensitivity study, molecular design, synthesis and application of other energy-containing compounds.

2. Calculation principle and method

According to Xiao Heming et al. [11,12], the B3LYP method can provide accurate information of molecular geometry in the study of energy-containing compounds. Conformation optimization was carried out at B3LYP/6-31G (d) level for the cyclic derivatives. The frequency analysis showed that all the optimized configurations had no virtual frequency and were stable structures on the potential energy surface.

Nitro charge ($Q_{NO2}$), a structural parameter, has a good correlation with sensitivity and is commonly used to predict the sensitivity of nitro-containing compounds [13,14]. The more negative the charge, the lower the electron attraction and the more stable the compound. $Q_{NO2}$ is calculated by the following formula. $Q_N$, $Q_{O1}$ and $Q_{O2}$ are the net charges of N and O atoms on the -NO2 connected by the weakest bond of the compound, respectively:

$$Q_{NO2} = Q_N + Q_{O1} + Q_{O2}$$

Read the log file of Gaussian output with Gauss View, view the $Q_{NO2}$ value of each -NO2 in the compound, and select the maximum value of all $Q_{NO2}$ values as the $Q_{NO2}$ value of the compound.

The calculation method and basis group are B3LYP/6-31G (d), and the calculation is completed by Gaussian09 quantum chemical program, and the convergence precision is set within the program.

3. Results and discussion

Table 1 shows the molecular structures of all nitro-containing derivatives in series A and B. Figure 1 compares the nitro charges of all derivatives of the two series. Compounds with $Q_{NO2}$ value less than the $Q_{NO2}$ value of TNT (-0.207e) are found in series A and B, indicating that these compounds have lower sensitivity and better stability. Compared with series B, the $Q_{NO2}$ value of series A tends to be smaller, indicating that the skeleton structure of series A is more stable in these two series. This indicates that benzene fused heterocyclic compounds may have lower sensitivity than fused heterocyclic compounds and have potential applications in stability.

| Derivative | Molecular Structure          |
|------------|-----------------------------|
| A1: $R_{1,2}$ =H; $R_3$ =NO2 | B1: $R_{1,3}$ =H; $R_2$ =NO2 |
| A2: $R_{1,3}$ =H; $R_2$ =NO2 | B2: $R_{1,2}$ =H; $R_1$ =NO2 |
| A3: $R_3$ =H; $R_1$ =NO2 | B3: $R_3$ =H; $R_1$ =NH2; $R_2$ =NO2 |
| A4: $R_2$ =H; $R_1$ =NH2; $R_3$ =NO2 | B4: $R_1$ =H; $R_2$ =NH2; $R_3$ =NO2 |
| A5: $R_1$ =H; $R_2$ =NH2; $R_3$ =NO2 | B5: $R_1$ =H; $R_3$ =NH2; $R_2$ =NO2 |
| A6: $R_2$ =H; $R_1$ =NH2; $R_3$ =NO2 | B6: $R_{1,2}$ =NH2; $R_1$ =NO2 |
| A7: $R_1$ =H; $R_3$ =NH2; $R_2$ =NO2 | B7: $R_{1,3}$ =NH2; $R_2$ =NO2 |
| A8: $R_3$ =H; $R_1$ =NH2; $R_2$ =NO2 | B8: $R_1$ =H; $R_{2,3}$ =NO2 |
| A9: $R_1$ =H; $R_3$ =NH2; $R_2$ =NO2 | B9: $R_3$ =NH2; $R_{2,3}$ =NO2 |
| A10: $R_1$ =NH2; $R_3$ =NO2 | B10: $R_3$ =NH2; $R_{1,2}$ =NO2 |
| A11: $R_2$ =NH2; $R_1$ =NO2 | B11: $R_{1,2,3}$ =NO2 |
| A12: $R_{1,3}$ =NH2; $R_2$ =NO2 | |
| A13: $R_1$ =H; $R_{2,3}$ =NO2 | |
Table 2 shows the nitro charges of series A and series B derivatives. The following laws can be obtained: 1) When the substituents of series A are 1 -NH₂, 1 -NO₂ and 1 -H, the Q_{NO2} value of each compound is: A7 < A4 < A5 < A6 < A9 < A8, that is, the sensitivity of each compound increases and the stability decreases in this order. A5 and A7 are the connection structures of substituents of -NH₂ and -NO₂ and benzene ring. It can be known that the Q_{NO2} value substituted by -NH₂ and -NO₂ on C atom is smaller than the Q_{NO2} value substituted by -NH₂ and -NO₂ on N atom. Therefore, A5 and A7 have smaller Q_{NO2} value. Moreover, because of intramolecular hydrogen bonds, A7 has a smaller Q_{NO2} value, lower sensitivity and more stable. The Q_{NO2} value of A8 and A9 increases sharply, which may be caused by the presence of N-NO₂ structure in the molecule, which greatly increases the sensitivity of the compound. And A9 is less sensitive than A8 probably because A9 forms intramolecular hydrogen bonds. The N-NH₂ structure of A6 also gives it a larger Q_{NO2} value and a higher sensitivity. Compared with A6, A4 has a lower sensitivity and a smaller Q_{NO2} value. This may be because the electronegativity of N atoms in -NH₂ makes -NH₂ form an intramolecular hydrogen bond with -NO₂. Moreover, the stabilization effect of this hydrogen bond is far greater than the unstable effect of the N-NH₂ structure in the molecule. 2) When the substituents of series A are 1 -NH₂ and 2 -NO₂, the Q_{NO2} value of each compound decreases successively in the order of A18, A16 and A17, and the sensitivity decreases successively. A16 and A18 may have larger Q_{NO2} value and higher sensitivity because of the N-NO₂ structure, and A16 is more stable than A18, because the stability increases with the distance between -NO₂ increases in isomers. 3) When A series of substituent are 2 -NH₂, 1 -NO₂, compound sensitivity reduces and the stability increases by the order of A11, A10, A12. The N-NH₂ structure of A10 molecule increases its sensitivity and A10 does not contain hydrogen bond, while the N-NO₂ structure in A11 molecule also increases its sensibility and the intramolecular hydrogen bond decreases its sensitivity, but the sensitivity of A11 is still much higher than that of A10. We reasonably speculate that this may be because the N-NO₂ functional group can increase the compound energy more effectively than N-NH₂ in the modification of the N-position on the azole ring, thus dramatically increasing the compound sensitivity. 4) When the substituents of series A are 1 -NO₂ and 2 -H, the
Q_{NO2} value of A3 is significantly larger than the Q_{NO2} value of A1 and A2, that is, the sensitivity of A3 is higher, indicating that the N-NO2 functional group introduces an N-N bond more than C-NO2, which can effectively increase the energy of the compound and increase the sensitivity of the compound. 5) When the substituents of series A are 2 -NO2 and 1 -H, the Q_{NO2} value of each compound increases successively in the order of A13, A14 and A15. A14 and A15 have higher sensitivity because of the N-NO2 structure, while A14 has lower sensitivity than A15. It can be seen that in the isomers containing the same N-NO2 functional group, the sensitivity of the compound decreases when the distance between -NO2 increases. 6) In series A, for compounds whose Q_{NO2} value is greater than RDX's Q_{NO2} value (-0.115e), -NO2 is substituted on N atom, while for compounds whose Q_{NO2} value is less than TNT's Q_{NO2} value (-0.207e), -NO2 is substituted on C atom. It can be seen that C-NO2 has lower energy and is more stable than N-NO2. 7) When series A contains 1 -NO2, in compounds whose Q_{NO2} value is less than TNT's Q_{NO2} value, the compound has a smaller Q_{NO2} value and the compound is more stable when -NO2 is substituted at the R2 substitution site. It may be because when -NO2 is substituted at R2, -NO2 can form an intramolecular hydrogen bond with H at the R1 substitution site at the N atom of the azole ring.

Table 2. Calculated nitro group charge (Q_{NO2}) of A and B series of derivatives.

| Comp. | Q_{NO2} (e) | Comp. | Q_{NO2} (e) | Comp. | Q_{NO2} (e) | Comp. | Q_{NO2} (e) | Comp. | Q_{NO2} (e) |
|-------|------------|-------|------------|-------|------------|-------|------------|-------|------------|
| A1    | -0.268     | A7    | -0.294     | A13   | -0.243     | A19   | 0.074      | B6    | -0.255     |
| A2    | -0.289     | A8    | -0.057     | A14   | -0.008     | B1    | -0.220     | B7    | -0.191     |
| A3    | -0.039     | A9    | -0.071     | A15   | 0.049      | B2    | -0.245     | B8    | -0.194     |
| A4    | -0.277     | A10   | -0.277     | A16   | -0.041     | B3    | -0.185     | B9    | -0.160     |
| A5    | -0.274     | A11   | -0.089     | A17   | -0.248     | B4    | -0.253     | B10   | 0.036      |
| A6    | -0.272     | A12   | -0.280     | A18   | 0.028      | B5    | -0.227     | B11   | 0.094      |

The relationship between the nitro charge of series A and the substitution sites of substituents is shown in figure 2. As can be seen from the figure, in series A, when -NO2 is substituted at R2 or R3 (on C atom), the compound has a smaller Q_{NO2} value and lower sensitivity. It can be seen that when -NO2 is substituted at C atom, the energy of the compound is relatively small and the sensitivity is relatively low. This is mutually confirmed by the above laws obtained from table 2, and the introduction of -NH2 into the compound is beneficial to the reduction of sensitivity.

Figure 3 and figure 4 show the relationship between the nitro charge of A and B series and the number of substituents. Since the substituent sites of A and B series are R1-R3 in their parent ring structures, the number of substituents -NH2 and -NO2 in figure 3 and figure 4 is less than or equal to three. As shown in the figure, the influence of different functional groups on nitro charge is as follows: the introduction of -NH2 is beneficial to increase the -Q_{NO2} value of the compound, that is, to reduce the sensitivity. The -Q_{NO2} value of series A and B compounds increases with the number of -NH2 and decreases with the number of -NO2. This suggests that we can introduce the high-energy group -NO2 into the molecular structure to improve the energy properties, and -NH2 to increase its stability. It is also found from figure 3 and figure 4 that the compound has a large -Q_{NO2} value and low sensitivity when the number of -NO2 is 1. It indicates that when the number of substituents of -NO2 is small, the superconjunction of -NO2 can stabilize the molecular skeleton.
4. Conclusion

Based on the DFT calculation, the nitro charges of fused aza-cyclic nitro-containing derivatives were compared, the relationship between the sensitivity of compounds and the types and number of substituents was studied, and the structure-activity relationship was established. The following conclusions were obtained. 1) The skeleton structure of series A is more stable than that of series B, indicating that the stability of benzene fused heterocyclic compounds is more promising than that of fused heterocyclic compounds. 2) The $Q_{NO2}$ value replaced by -NH$_2$ and -NO$_2$ on the C atom is smaller than the $Q_{NO2}$ value replaced by it on the N atom, because compared with C-NO$_2$ and C-NH$_2$, the functional groups of N-NO$_2$ and N-NH$_2$ introduce more N-N bonds to increase the energy of the compound more effectively, increasing the $Q_{NO2}$ value and sensitivity of the compound. 3) Intramolecular hydrogen bond makes the compound less sensitive. 4) The electronegativity of N atoms in -NH$_2$ substituents causes -NH$_2$ to form intramolecular hydrogen bonds with -NO$_2$. 5) In the modification of the N position on the azole ring, the N-NO$_2$ functional group can increase the compound energy more effectively than N-NH$_2$, thus dramatically increasing the sensitivity. 6) In isomers with the same N-NO$_2$ functional group, the sensitivity of the compound decreases with the increase of the distance between -NO$_2$. 7) Generally, the $-Q_{NO2}$ value of the compound increases with
the number of -NH₂ and decreases with the number of -NO₂. The value of \( Q_{\text{NO2}} \) indicates that the molecular stability increases with the number of -NH₂ and decreases with the number of -NO₂. Therefore, -NO₂ can be introduced into the molecular structure to improve the energy property and -NH₂ to reduce the sensitivity. 8) When the number of substituents of -NO₂ is small, the superconjugation of -NO₂ can stabilize the molecular skeleton.

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