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INVESTIGATION OF CORRELATION BETWEEN IMPACT SENSITIVITIES AND BOND DISSOCIATION ENERGIES IN BENZENOID NITRO COMPOUNDS

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The geometries of ten benzenoid energetic materials are fully optimized by employing B3LYP and B3P86 methods with the 6-31G** basis set. Bond dissociation energies (BDEs) for the removal of the NO_2 group in benzenoid molecules are calculated at the same level. The calculation results show that the insertion of an electron withdrawing group increases the stability of the molecules, while the insertion of an electron donating group reduces the stability of the molecules. In addition, the relationship between the impact sensitivities and the weakest BDE values is examined. There exists a good linear correlation between the impact sensitivity and the ratio of the BDE value to the molecular total energy.

K e y w o r d s: density functional theory, bond dissociation energies (BDEs), benzenoid nitro molecules, impact sensitivity.

INTRODUCTION

Energetic materials play an important role in aeronautics, the weapons industry, and other high-tech fields at present [1—3]. Recently, because of many catastrophic explosions resulting from unintentional initiation of munitions by aboard ships, aircraft carriers, munitions trains, impact or shock, continuous strong efforts have been made to develop new materials having good thermal stability, impact and shock insensitivity, better performance, economic and environmentally friendly syntheses in order to meet the requirements of future military and space applications [4, 5]. The nitro group is an important group for energetic materials [6].

As is well known, the bond strength of the weakest bond for an explosive molecule, which may be obtained by calculating the bond dissociation energy (BDE), is of considerable importance in the area of energetic materials, since the rupture of this linkage is believed to be a key factor in many decomposition processes. It was proposed that the bonds in explosives, which play the role of a trigger, are C—NO_2, O—NO_2 and N—NO_2 bonds [7—11]. These bonds usually are the weakest ones in these molecules [10, 12]. In addition, the chemical stabilities and impact/shock sensitivities of energetic materials have frequently been related to the strengths of the weakest bond R—NO_2 (R = C, O, N). Fried *et al*. [6] reported that the ratio (BDE/Ed) of the weakest bond BDE to the explosive decomposition energy (Ed) is a nearly linear function of the logarithm of the impact sensitivity values h_{50}. Rice *et al*. [13] showed that there was a rough correlation between the logarithm of the impact sensitivity values h_{50} and the weakest BDE. Recently, Li *et al*. [14] further substantiates that there is a linear correlation energy between the ratio of the weakest BDE to the molecular total energy and the impact

sensitivity value h_{50} for imidazole derivatives. All the researches mentioned above further indicate that the BDE of the weakest bond of the explosive molecule plays a key role in the initiation event.

Aromatic molecules having nitro groups are generally known as explosives. Through increasing numbers of the groups, the compound densities and the number of moles of gaseous combustion products formed per gram of material can be increased, thereby enhancing the propellant performance. Benzenoid compounds are an important category of energetic compounds. Hakala *et al*. [15] calculated the resonance energies of benzenoid hydrocarbons. Meyer *et al*. [16] thought that some benzenoid nitro compounds had high detonation velocities. The exploration of the microscopic pyrolysis mechanism, which addresses the question of how an important impulse can initiate rapid exothermic reactions leading to the detonation of explosive solids, is always the research target of both theoretical and experimental chemists. Due to the problems of safety, difficulty in purifying, and lack of systematic theoretical studies, a theoretical investigation of the geometry and the property such as the weakest R—NO_2 BDE is of importance.

In this paper, the BDEs of the weakest bond (C—NO_2) for 10 benzenoid nitro compounds have been calculated using density functional theory B3LYP and B3P86 methods with a 6-31G** basis set. The stability caused by the insertion of —NH_2, —CH_3, —OCH_3, Cl, —COOH groups is investigated for the title compounds. In addition, there exists a good linear relationship between BDE/E and h_{50}. These results provide useful information for the molecular design of novel high energetic density materials.

THEORY AND COMPUTATIONAL DETAILS

The density functional theory (DFT) [13, 17] has emerged as a very reliable theoretical method. Hence, it has been used to evaluate BDEs of the molecules of interest. Geometry optimizations, energy and frequency calculations were performed for toluene derivatives using the Gaussian03 package [18]. In this work, ten high explosive molecules were studied. All calculations of the molecular geometry and energy were performed in this work using the DFT method, Becke′s 3-parameter exchange and Lee, Yang and Parr correlation functionals [19, 20] and Perdew′s 86(P86) [21], with the default Gaussian convergence criteria for the ten molecules. The choice of the two methods is not only because B3LYP and B3P86 methods can precisely predict the heats of formation [22, 23] and the latter can produce accurate BDEs [17] for various aromatic nitro compounds, but also because they require less time and computer resources such as disk and memory space. The benzenoid nitro compounds are: (**1**) 1-amino-2,3,4,6-nitrobenzene($C_6H_3O_8N_5$); (**2**) 1-chloro-2,4,6-trinitrobenzene ($C_6HO_6N_3Cl$); (**3**) 1-ethanol-2,4,6-trinitrobenzene ($C_6H_2O_7N_3$); (**4**) 2,4,6-trinitrobenzene ($C_6H_3O_6N_3$); (**5**) 1-carboxy-2,4,6-trinitrobenzene ($C_7H_3O_8N_3$); (**6**) 1-methyl-2,4,6-trinitrobenzene($C_7H_5O_6N_3$); (**7**) 1-amino-2,4,6-trinitrobenzene($C_6H_4O_6N_4$); (**8**) 1-OCH_3-2,4,6-trinitrobenzene ($C_7H_5O_7N_3$); (**9**) 1,3-OCH_3-2,4,6-trinitrobenzene ($C_8H_7O_8N_3$); and (**10**) 1,3-amino-2,4,6-trinitrobenzene ($C_6H_5O_6N_3$). The molecular frameworks of ten title compounds are listed in Fig. 1.

Here, because we assume a homolytic cleavage of the C—NO_2 bond while calculating BDEs, the fragments are radical species. The calculations of the geometry and energy for all fragments were performed with the Pople 6-31G** basis set. Vibrational analysis shows that the optimized structures have no imaginary frequencies. This indicates that the structure of each molecule corresponds to a local minimum on the potential energy surface. The $\langle S^2 \rangle$ values are all very close to 0.75, which shows negligible spin contamination of pure doublet states for fragment open-shell systems. The R—NO_2 bond strength, where R denotes the remainder of the molecule, is obtained by calculating the BDE, defined here as the difference between the total energy of the parent molecule and the energies of the products of the unimolecular dissociation in which an NO_2 group is removed [24]. For example, for 2,4,6-nitrobenzene ($C_6H_3O_6N_3$), the BDE is

$$\text{BDE} = E(C_6H_3O_4N_2) + E(NO_2) - E(C_6H_3O_6N_3). \tag{1}$$

The BDE with ZPE correction is

$$\text{BDE}_{ZPE} = \text{BDE} + \Delta \text{ZPE}, \tag{2}$$

where ΔZPE is the difference between the zero-point energies (ZPE) of the products and the reactants.
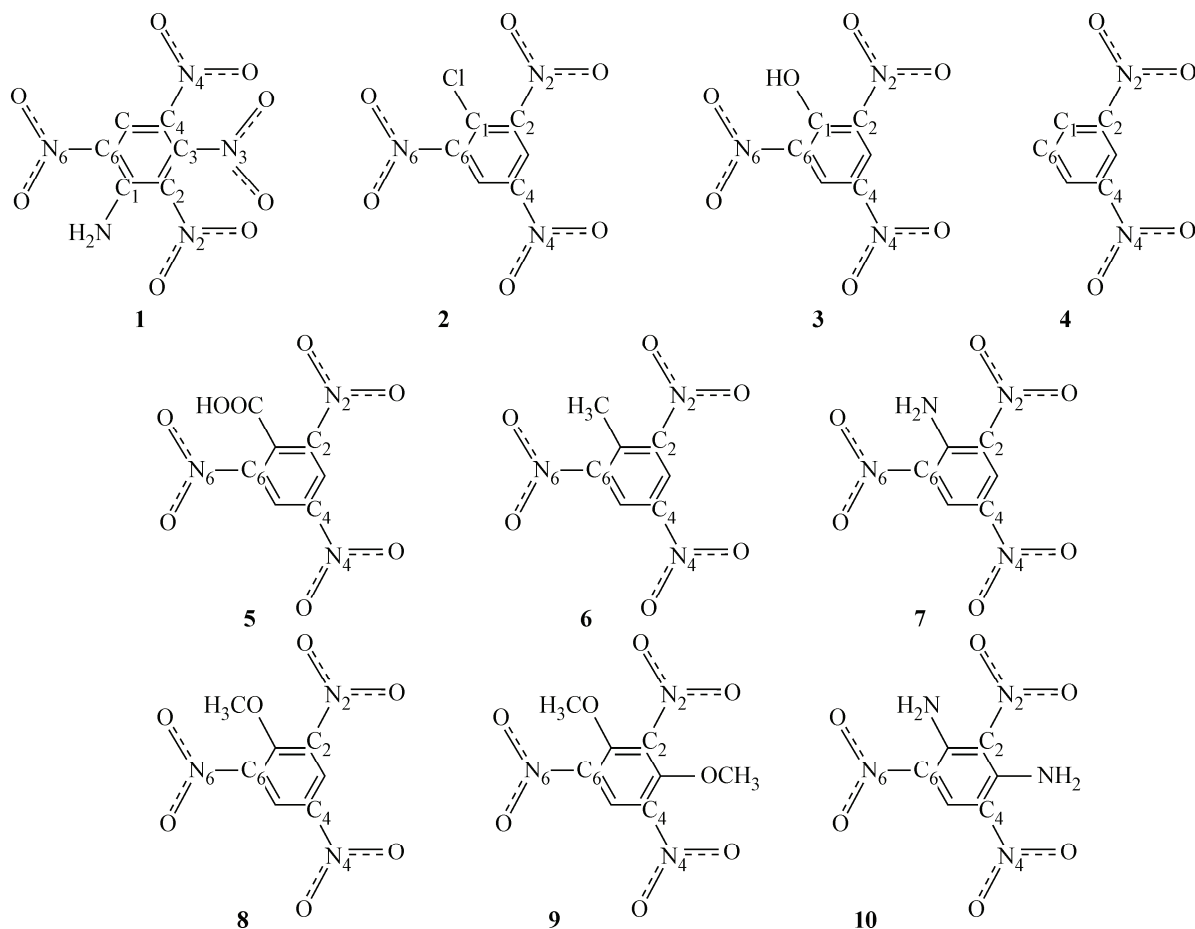
Fig. 1. Structure of the benzenoid nitro molecules considered

Generally, while calculating BDE values, zero point corrected energies have to be used and basis set superposition error (BSSE) calculations have to be performed. In our calculations, the BSSE is considered.

RESULTS AND DISCUSSION

The thermal stability of the title compounds as high energetic explosives should be emphasized. The BDE can evaluate the strength of bonding that is fundamental to the understanding of chemical processes [25], and provide useful information to understand the stability of substituted benzenoid nitro compounds. To elucidate this, we calculated the dissociation energies for the possible initial steps in the pyrolysis route. It should be pointed out that we selected the C—NO_2 bond as the possible breaking bond at B3LYP/6-31G** and B3P86/6-31G** levels. The BDE values are listed in Table 1. The BDE calculated by the B3P86 functional is about 3.9 kcal/mol bigger than the result calculated by the B3LYP functional, which is consistent with the result calculated before [17].

As has been suggested by Chung *et al.* [27], a molecule should have more than a 20 kcal/mol barrier to dissociate in order to be considered as a viable candidate for new high energy density materials. Inspecting Table 1, we can conclude that all the molecules investigated are all viable candidates for new high energy density materials.

It is known that the initial stages in the thermal decompositions of energetic materials can be deduced based on BDEs. From Table 1, the C_2—N_2, C_4—N_4, and C_6—N_6 bonds of compound (**4**) are equivalent and the BDE is 62.7 kcal/mol (B3P86/6-31G**), which is found to give the best experimental C—NO_2 BDE data for nitroalkanes [17] and alkyl nitrate and nitrite compounds [28]. When the —CH_3 group substitutes for the 1-position H atom in compound (**4**), the C_2—N_2 and C_6—N_6 bonds

Bond dissociation energies (BDEs, kcal/mol) for the title compounds at B3LYP/6-31G**
and B3P86/6-31G** *levels*

Compound	B3P86/6-31G**				B3LYP/6-31G**				H_{50} [a]
	C_2—N_2	C_3—N_3	C_4—N_4	C_6—N_6	C_2—N_2	C_3—N_3	C_4—N_4	C_6—N_6	
(1)	65.1	**54.1**	66.9	71.5	60.6	49.8	62.7	67.2	41
(2)	**62.4**	—	73.3	62.4	58.3	—	69.1	58.3	79
(3)	**66.0**	—	72.2	66.0	62.0	—	68.2	62.0	87
(4)	**62.7**	—	62.7	62.7	59.0	—	59.0	59.0	100
(5)	**66.5**	—	69.7	66.5	62.3	—	65.8	62.3	109
(6)T	**64.0**	—	71.0	64.0	60.0	—	67.0	60.0	160
(7)	**72.8**	—	73.8	72.8	68.5	—	69.9	68.5	170
(8)	**60.8**	—	71.2	60.8	57.4	—	67.7	57.4	190
(9)	**55.8**	—	63.2	63.2	52.9	—	59.6	59.6	251
(10)	76.8	—	**76.5**	76.5	72.9	—	72.6	72.6	320

[a] Taken from Ref. [26]. The bold-faced number means that the corresponding bond is most reactive in the studied compound.

are equivalent, and their BDEs are 64.0 kcal/mol for the B3P86 functional, which is smaller than the C_4—N_4 BDE (71.0 kcal/mol). This shows that the rupture of the C_2—N_2 or C_6—N_6 bond is the initial site in the decomposition process. However, when the —Cl group substitutes for the 1-position H atom in compound (4), it is noted that the C4—N4 BDE is 73.3 kcal/mol, which is larger than the C_2—N_2 and C_6—N_6 BDEs. This shows further that the C_2—N_2 or C_6—N_6 bond is the weakest bond and may be the initial site in the decomposition process. Similar analysis can be made for compounds (3), (5), (7), and (8).

Table 1 also shows that an increase in the number of NO_2 groups on the benzene ring reduces the stability of the molecule, which is characterized by a decrease in the weakest C—NO_2 bond energy. The weakest bond of compound (7) is the C_2—N_2 or C_6—N_6 bond. When the —NO_2 group substitutes for the 3-position H atom in compound (7), the weakest bond is the C_3—N_3 bond and the BDE is 54.1 kcal/mol. A possible explanation for this behavior of compound (1) is that the presence of strong repulsive interactions between O atoms in the adjacent nitro groups attached to C_2 and C_4 on the benzene ring weakens the C_3—N_3 bond strength.

In addition, a different substituted group has a great effect on the BDE. When the electron-withdrawing group —NH_2 substitutes for the 3-position H atom in compound (7), C_4—N_4 and C_6—N_6 bonds are equivalent and the BDEs are all 76.5 kcal/mol, which is smaller than the C_2—N_2 BDE (76.8 kcal/mol). Through the comparison of the weakest bond energies of compounds (4), (7), and (10), it is noted that the insertion of the electron-withdrawing —NH_2 group increases the stability of the molecules.

When the electron donating —OCH_3 group substitutes for the 1-position H atom in compound (4), the C_2—N_2 and C_6—N_6 bonds are equivalent, and their BDEs are 60.8 kcal/mol, which is smaller than the C_4—N_4 BDE (71.2 kcal/mol). When another —OCH_3 group substitutes for the 3-position H atom in compound (8), the C_4—N_4 and C_6—N_6 bonds are equivalent and their BDEs are all 63.2 kcal/mol, which is larger than the C_2—N_2 BDE (55.8 kcal/mol). This shows that the insertion of the electron donating —OCH_3 group reduces the stability of the molecules.

Table 1 also gave the impact sensitivity experimental values [26] of the title compounds. Apparently, there is no linear relationship between BDE and the impact sensitivity; it is clear that there exists a good correlation between the impact sensitivity and the ratio of the BDE to the molecular total energy (BDE/E). Fried *et al.* [6] thought that BDE was not the only factor influencing the sensitivity,

Fig. 2. Relationship between h_{50} and BDE/E for the title compounds

and the relationship involved other factors as well. The energy released by the reaction is determined by the energy of the decomposition into equilibrium products at the standard state (E_d); E_d is a measure of the total energy content of the material. The molecular total energy E, to some extent, reflects the E_d value in the materials and represents the characteristics of the energetic material.

Based on the experimental sensitivity h_{50} available and the calculated BDE/E values for the weakest bond, a plot of h_{50} versus BDE/E is illustrated in Fig. 2. A good linear relationship is observed for the title compounds studied. The function relationship is given by Eq.(**3**), and the linear correlation coefficient is 0.96.

$$h_{50} = -111.81 + 2.09 \times \left(\frac{\text{BDE}}{\text{E}} \right) \times 10^4. \tag{3}$$

It is obvious that the result is in agreement with our previous work [14]. This further substantiates the correlation between the BDE/E and the sensitivity h_{50} in the energetic materials having similar molecular structures.
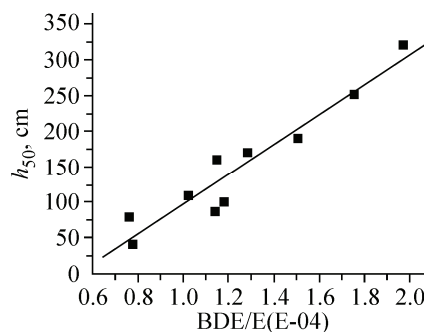
CONCLUSIONS

The BDE for the removal of the NO_2 group in benzenoid molecules were calculated using B3LYP and B3P86 methods with the 6-31G** basis set. It is noted that the insertion of an electron withdrawing group increases the stability of the molecules, while the insertion of an electron donating group reduces the stability of the molecules. In addition, the results show that the ratio of the weakest BDE to the molecular total energy has a good linear correlation with the impact sensitivity values, which indicates that BDE/E is a reasonable practical indicator of explosive sensitivity. We think that the conclusion is useful in the design of new energetic materials.

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