

Are amino groups advantageous to insensitive high explosives (IHEs)?

Xia Cao · Yushi Wen · Bin Xiang · Xinping Long ·
Chaoyang Zhang

Received: 11 April 2012 / Accepted: 16 May 2012 / Published online: 3 June 2012
© Springer-Verlag 2012

Abstract There is usually a contradiction between increasing energy densities and reducing sensitivities of explosives. The explosives with both high energy densities and low sensitivities, or the so-called insensitive high explosives (IHEs), are desirable in most cases. It seems from applied explosives that amino groups are advantageous to IHE but the amount of amino groups contained IHEs is very limited. To make this clear, we present systemic examinations of the effects on the two properties stressed in IHEs after introducing amino groups to different molecular skeletons. As a result, the amino groups on resonant sites to nitro groups in conjugated systems can improve distinctly sensitivities and change energy densities in terms of oxygen balance; while the amino groups in unconjugated systems can hardly increase energy densities and usually cause increased sensitivities. It agrees well with a fact that almost all the molecules of applied amino group contained explosives possess conjugated skeletons. We therefore confirm that if amino groups are introduced resonantly to a nitro group in a conjugated system and the introduction improves *OB*, they are advantageous to IHEs.

Keywords Amino group · Energy density · Insensitive high explosive (IHE) · Sensitivities

Electronic supplementary material The online version of this article (doi:10.1007/s00894-012-1473-5) contains supplementary material, which is available to authorized users.

X. Cao · B. Xiang
College of Chemistry and Chemical Engineering,
Chongqing University,
Chongqing, China 400044

X. Cao · Y. Wen · X. Long · C. Zhang (✉)
Institute of Chemical Materials,
China Academy of Engineering Physics (CAEP),
P.O.Box 919-327, Mianyang, Sichuan, China 621900
e-mail: zcy19710915@yahoo.com.cn

Introduction

The insensitive high explosives (IHEs) [1] are now becoming a hot topic in the field of energetic materials (EMs). It emphasizes the comprehensive performances of an explosive with both a high energy density and low sensitivities. That is, high power and low sensitivity attributed to IHEs lead to a strong desire in the development of EMs. There may be two ways to obtain IHEs: one is to synthesize new pure IHEs and the other is to modify the sensitive explosives synthesized to be desensitized ones. For the first way, there has been limited progress made for the past 50 years. Seldom explosives have been found to be comparable to or even better than HMX from a viewpoint of both energy and safety, even though some new species appeared, such as octanitrocubane (ONC), 2,4,6,8,10,12-hexanitro-2,4,6,8,10,12-hexaazatetracyclo (5.5.0.0^{5,9}.0^{3,11}) dodecane (CL-20), 2,6-diamino-3,5-dinitropyrazine-1-oxide (LLM-105), 1,1-diamino-2,2-dinitroethylene (FOX-7), 1,3,3-trinitro-azetidine (TNAZ), and so forth [2]. It seems that people have greatly succeeded in IHEs via the second means. They obtained the safer explosive formulations compared to the corresponding pure explosives by coating crystals to form plastic bonded explosives (PBX) earlier, and later they obtained the desensitized explosives like hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX) and 1,3,5,7-tetranitro-1,3,5,7-tetraazacyclo-octane (HMX) by enhancing their crystal qualities, that is, reducing the imperfections in their crystals [1, 3].

There is still no authoritative or standard definition of IHE. Considering a fact that the mixed RDX/2,4,6-trinitrotoluene (TNT) has been applied already in many formulations for a long time in which RDX is highlighted for its energy density and TNT is highlighted for its insensitivity [4], we think that IHE may be more powerful than RDX and more insensitive than TNT simultaneously. Accordingly, we define roughly

that the theoretical detonation velocity (D) of an IHE is higher than 8500 m/s, slightly lower than that of RDX, 8800 m/s; and its H_{50} assessing impact sensitivity is higher than 50 cm, lower a bit than that of TNT, 59 cm. Most of applied explosives are summarized into Fig. 1 and divided into four parts according to their D and H_{50} . Explosives in part A with high D and high H_{50} are of IHEs; those in part C conversely with low D and low H_{50} are valueless in practice; and those in part B with high D and low H_{50} and those in part D with low D and high H_{50} take a large occurrence of explosives and show an original contradiction between increasing energy density and decreasing sensitivity. There are only three explosives in part A, LLM-105, FOX-7 and NTO, implying many difficulties in getting a new IHE.

In the above mentioned three IHEs, FOX-7 and LLM-105 contain amino groups. Other explosives in part D in Fig. 1, for example, 1-amino-2,4,6-trinitrobenzene (TNA), 1,3-diamino-2,4,6-trinitrobenzene (DATB), 1,3,5-triamino-2,4,6-trinitrobenzene (TATB) and nitroguanidine (NQ), contain amino groups too and possess high H_{50} much above 50 cm. It seems that amino groups can make explosives insensitive. Furthermore, as illustrated in Table 1, after introducing one, two and three amino groups respectively to 1,3,5-trinitrobenzene (TNB) to form TNA, DATB, and TATB, the melt points, packing densities (d) and H_{50} increase gradually [4]. And comparing TNA, DATB and TATB with TNB, it can be found that the theoretical D increases little after the introduction [5–7]. It seems that the amino groups can enhance both H_{50} and D , that is, improve both energy densities and sensitivities, suggesting the advantageousness of amino groups to IHEs [8–11].

However, the amount of applied explosives with amino groups is very limited. There are few besides the above mentioned FOX-7, LLM-105, TNA, DATB, TATB and NQ.

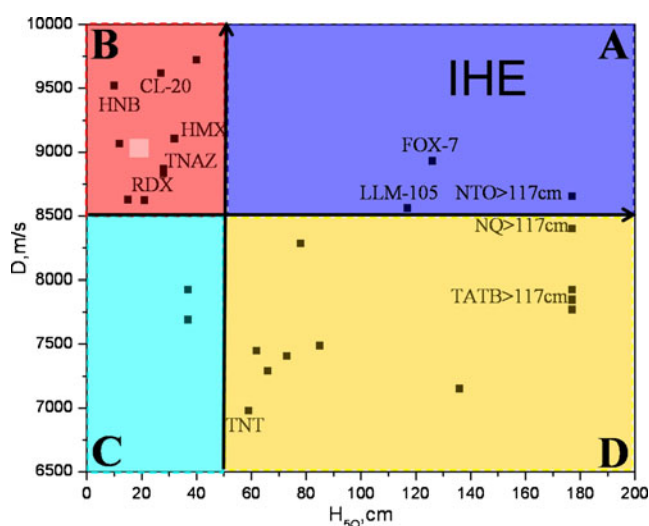


Fig. 1 Coordinates of applied explosives according to their detonation velocities (D) and impact sensitivities (H_{50}). The origin of coordinate is (50 cm, 8500 m/s)

This leads to a seeming puzzle: amino groups are advantageous to IHE but involved limitedly in IHE even in applied explosives. As a matter of fact, the presence of hydrogen atoms is beneficial in some ways, for instance, it can allow hydrogen bonding, which is likely to decrease sensitivity. On the other hand, it also uses up oxygen atoms that could be better employed in forming CO_2 . The formation of CO_2 is a major factor in promoting good detonation properties [12].

Spontaneously, we will be concerned about whether the above RDX and TNT can be aminated to form new compounds as shown in Fig. 2 with improved properties to meet the requirements of IHEs. It needs beforehand predictions for confirmation.

This is actually a sense of molecule design. As a matter of fact, reliable predictions by accurate calculations and correct structure-property correlations can have been finished already before preparation of a material [13, 14], which is the so-called rationality stressed in syntheses. In the past decades, metrological methods and quantum chemical and/or molecular force-field calculations were used to examine the structure-property correlations of explosives. For example, some characteristics, including oxygen balance (OB) [15], strength of the weakest linkage in a molecule [16], charges on an active group like a nitro or azide group [17, 18], interaction energy among the substitutes linked a molecular skeleton [19], energy gap between HOMO and LUMO [20, 21], molecular electrostatic potential [22], and so forth, have been related with the explosive safety evaluated usually by the so-called sensitivities to external stimuli. At the same time, the group addition method [23–26], the *ab initio* calculation method [27] and the molecular electrostatic potential method [28–30] were employed to predict the d of explosives, and further to predict their detonation properties by combining the known heat of formation (HOF) and equations of state. By these means, many properties of numerous potential explosive molecules have been predicted. Actually, the safety and the detonation properties of above mentioned ONC, CL-20, LLM-105, FOX-7 and TNAZ had been already predicted before they came into being.

All these lead to a possibility to predict reliably some key properties of interested compounds after introducing amino groups and to an instruction to IHE syntheses. In fact, there is no report detailing the effect of introducing amino groups to nitro compounds according to our knowing. This work intends to provide a systemic study on the effect in systems with different molecular skeletons, in which the energy density and sensitivity are accounted.

Methodologies

To examine systemically the effect of introduced amino groups on the sensitivity and energy density, we first chose some representative skeletons contained in almost all

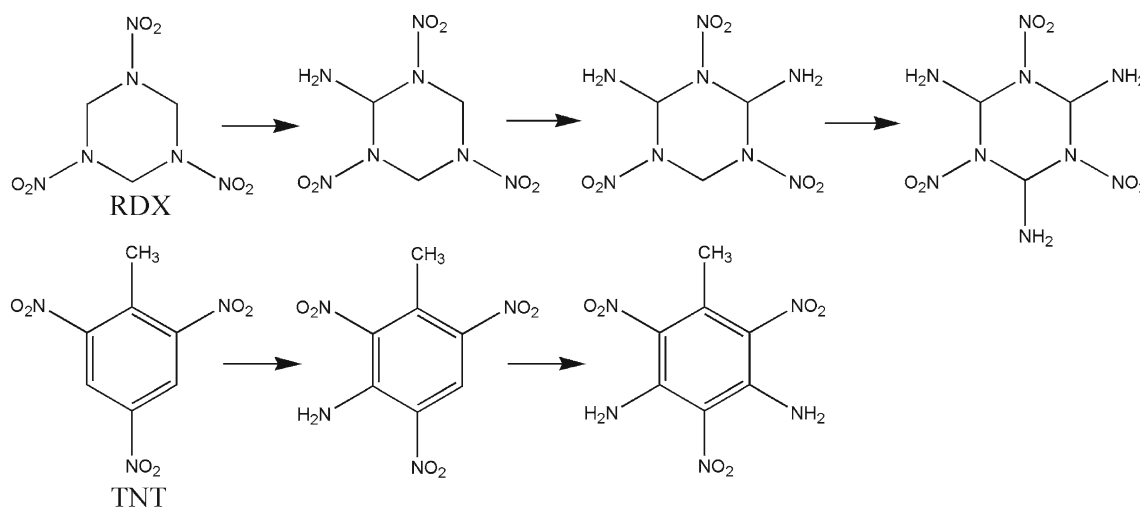
Table 1 Comparison of some properties of TNB, TNA, DATB and TATB. The data are cited from ref [4]

Compound	TNB	TNA	DATB	TATB
Structure formula				
Melt point, K	394	463	559	603
Packing density, g/cm ³	1.690	1.773	1.837	1.938
H_{50} , cm	100	177	320	490
Theoretical D , m/s	7432	7926	7770	7845

applied nitro explosives including acyclic hydrocarbons, aliphatic heterocycle, cage and aromatic ring. By bonding these skeletons with nitro and/or amino groups, we can get the molecules of many existing explosives or their analogues. The sensitivity of a nitro compound is assessed based on molecular stabilities. That is, the extensively applied indexes including the nitro group charges (Q), the bond length (R) and the bond dissociation energy (BDE) involved in the weakest bond in a compound are adopted for sensitivity assessment [31]. Zhang and Li have always related the nitro group charges and the bond dissociation energy with the impact sensitivities of nitro explosives respectively [32, 33]. It should be emphasized that if the weakest linkage does not involve a nitro group, only the related R and BDE will be concerned. For example, in the nitro derivatives of ONC, the weakest bonds are C-C bonds rather than C-N bonds, therefore, R and BDE of C-C bonds are paid attention to.

And the detonation properties including detonation velocities (D) and pressures (P) are employed to evaluate the energy densities and calculated using Kamlet–Jacobos

equation [34], in which a packing density (d) of an explosive reactant, a reaction representing the detonation, and the corresponding detonation heat are necessary. Firstly, d is predicted using the molar volume method with some modifications. The method predicts a molecule density from the molecular weight divided by the molar volume, yielded from the enclosed volume of molecular electron density. It is well known that d have a big influence on D and P , suggesting an accurate d is required. To keep the accuracy, we first confirm a cutoff isovalue of the electron density by comparing the predicted and experimental d of a group of analogues, and then use this cutoff isovalue to predict d of other interested compounds in the same group. That is, the cutoff isovalues for different groups of analogues can be different (see Supporting information). Secondly, we postulate a reaction denoting detonation as follows: all nitrogen atoms change to nitrogen gas; oxygen atoms form water if hydrogen atoms exist; carbon atoms convert to CO_2 in preference to CO if O atoms are surplus; the residual C atoms will exist in the solid state graphite if redundant; the

**Fig. 2** Plot showing the amination of RDX and TNT

remainder of O atoms will exist in gas state. Subsequently, the heat of detonation can be obtained according to HOF derived from semiempirical molecular orbital PM3 method calculations [35]. Note that the HOF of solid state should be used strictly. Because HOF influence is much lower on the detonation property than d , we have not made an effort in improving the accuracy of HOF.

Additionally, we summarize most explosives in Fig. 3 and find that the energy density denoted by D can be strongly related with d and OB : the larger d and the OB closer to zero leads to the larger D . The OB of an explosive $C_xH_yO_zN_r$ is calculated according to eq 1.

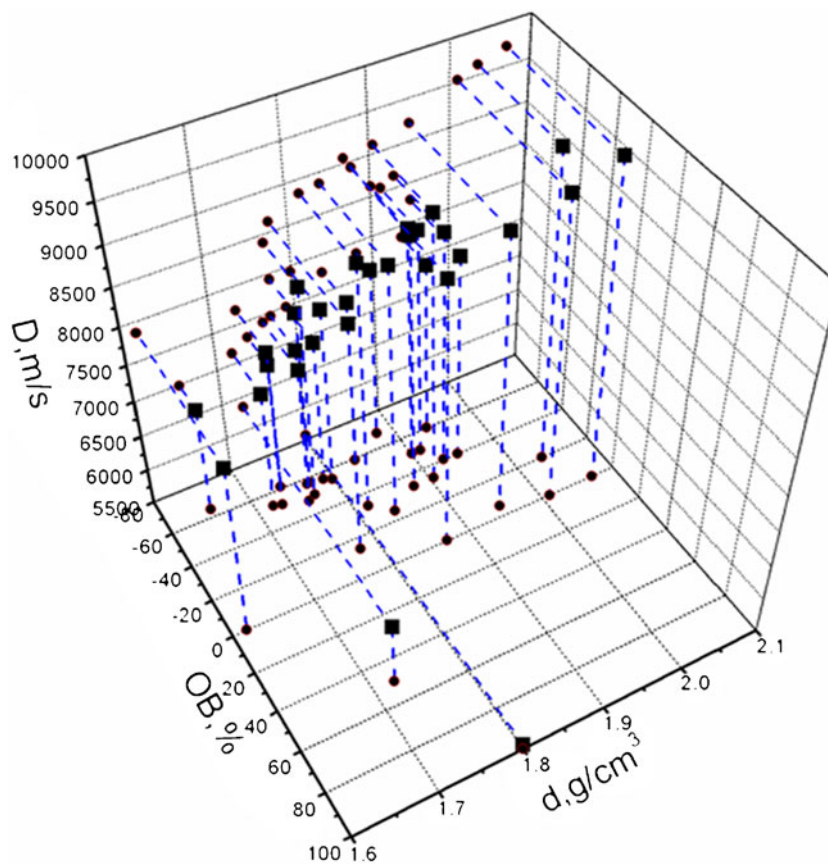
$$OB = \frac{z - (2x + 1/2y)}{2x + 1/2y} \times 100\% \quad (1)$$

All calculations on electronic structures and BDE were carried out utilizing the density functional theory (DFT) and general gradient approximation (GGA) methods with PBE functions and a double numeral adding polarization (DNP) basis set [36].

Results and discussion

The effects of amino groups are discussed according to the molecular skeletons as follows.

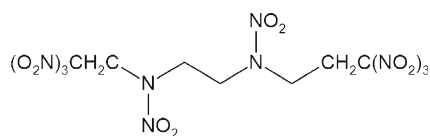
Fig. 3 Plot showing detonation velocities (D) related with packing densities (d) and oxygen balances (OB)



Acyclic hydrocarbon

Nitro, nitroamino and nitric ester derivatives of acyclic hydrocarbons are an important group of explosives, such as a modeling compound nitromethane, and applied FOX-7, pentaerythritoltetranitrate (PETN), nitroglycerin (NG), Bis (β, β, β -trinitroethyl-N-nitro) ethylene diamine (Scheme 1). Here, the amino-nitro derivatives of saturated ethane, and unsaturated ethene and ethyne are chosen for the discussion.

As shown in Fig. 4, all 19 derivatives can be divided into five groups according to the amount of nitro groups of compounds: Group I (1-6), group II (7-11), group III (12-17), group IV (18, 19) and group V (20). Firstly, we are concerned about the sensitivity after introducing amino groups. In all groups I-V, Q changes little, and BDE decreases and R increases obviously when the introduced amino groups increase, suggesting a decrease of the molecular stability. It is known that nitro groups are strong electron-acceptors usually attracting electrons from neighboring atoms or groups, and here is from carbon atoms. The amino groups in this case also show a great ability to attract electrons, attributed to the strong electronegativity of the nitrogen atoms of them and the lack of a resonant chemical environment for them denoting electrons. That is, both nitro and amino groups bonded with carbon atoms attract electrons from carbon atoms, causing the reduced molecular



Scheme 1 Molecular structure of Bis-(β,β,β-trinitroethyl-N-nitro) ethylene diamine

stability. In some cases as illustrated in the figure, amino groups can even show a stronger ability to decrease molecular stability than nitro groups, compared *BDE* and *R* of 11, 14 and 19 with 20: 15.1, 20.1 and 13.1 with 28.2 kcal mol⁻¹, and 1.740, 1.734 and 1.643 with 1.592 Å, respectively. Besides, *Q* in all cases changes slightly, possibly due to a combining effect on it: the hydrogen-bonding between amino and nitro groups makes *Q* more negative and the elongation of C-Nitro bonds caused by introducing amino groups makes negative *Q* lessened.

As to *d*, we find that the cases for all groups are different and the introduction of amino groups changes *d* a little as a whole. That is to say, the introduction in groups I and II increases slightly *d*, while that in groups III and IV decreases slightly *d*. This can be owing to two sides: one, including the displacement of hydrogen atoms by amino groups and the hydrogen-bonding between amino and nitro groups, is advantageous to increase *d*; and the other, the increased molecular volume induced by the stretched C-Nitro bonds, is disadvantageous to it. Also, the calculated

results show us that there are very few changes of detonation properties, attributed to the few changes of *d*. As illustrated in Fig. 4, the scope of the changed *D* and *P* of groups I to V are: 0, 0.3, 0.4 and 0.3 km/s, and 0.2, 1.9, 3.0 and 1.9 GPa, respectively.

Next, we pay attention to the effects of the introduction to nitro derivative of unsaturated ethene and ethyne. As indicated in Fig. 5, it seems that the effects of these cases are much different from those of the nitro derivatives of ethane. Comparing 21 with 22 and 23, we can find that *BDE*, *d* and *Q* increase distinctly from 60.6 to 66.4 and 68.8 kcal mol⁻¹, 1.752 to 1.768 and 1.889 g/cm³, and -0.19 to -0.27 and -0.33 e, respectively; *R* reduces from 1.484 to 1.465 and 1.439 Å; *P* increases from 33.6 to 36.9 and 35.7 GPa; while *D* changes very little in a range of 0.2 km/s. It seems that when amino groups are introduced to the *ortho*-positions relative to nitro groups in C=C, the molecular stability is improved obviously and the detonation properties are enhanced in terms of *d* and OB. That is, the OB closer to zero and higher *d* leads to a more enhanced *D* and *P*. We can also draw the same conclusion by comparing 27 with 28. However, when both an amino group and a nitro group are linked with the same carbon atom, some of the above mentioned effects can be abated. For instance, the molecular stability decreases as *B* reduces and *R* increases when an amino group is introduced to 24 to form 25. By the way, the displacement of the amino group in 25 by a nitro group to

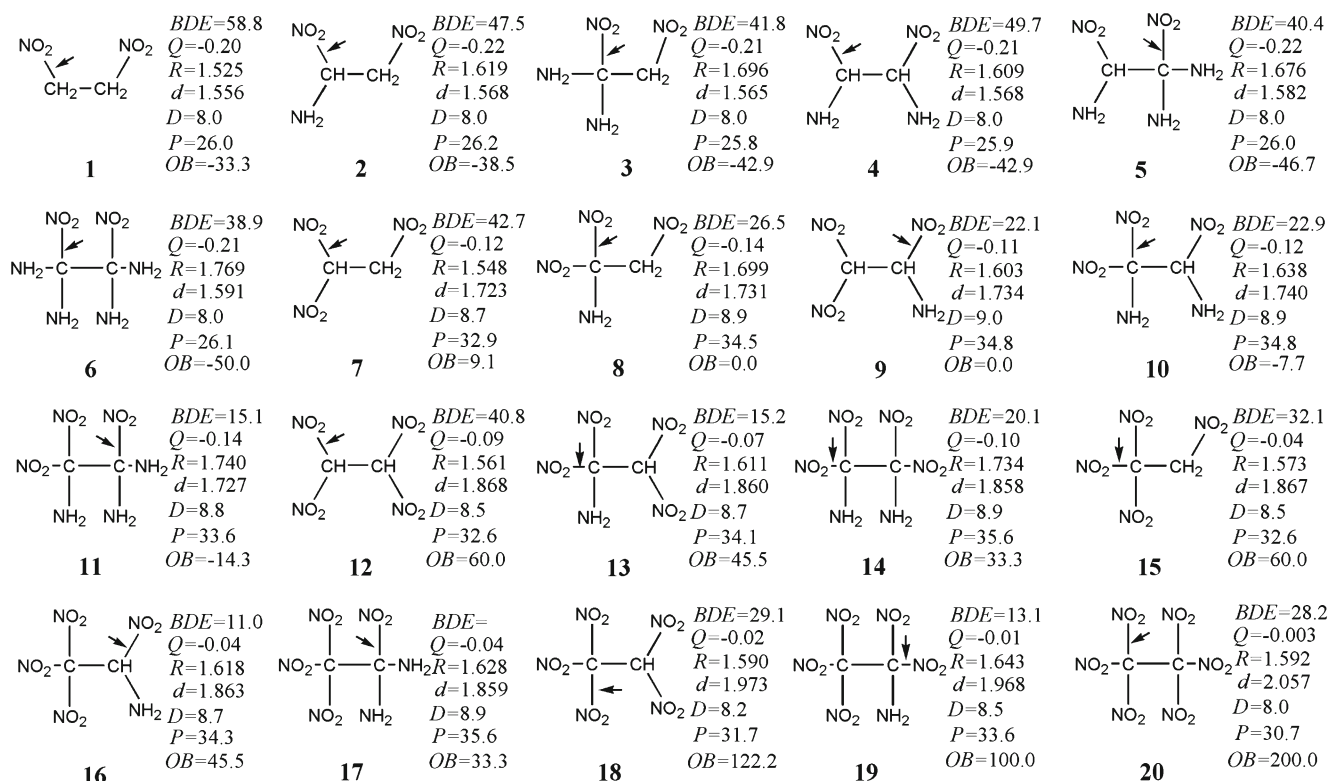
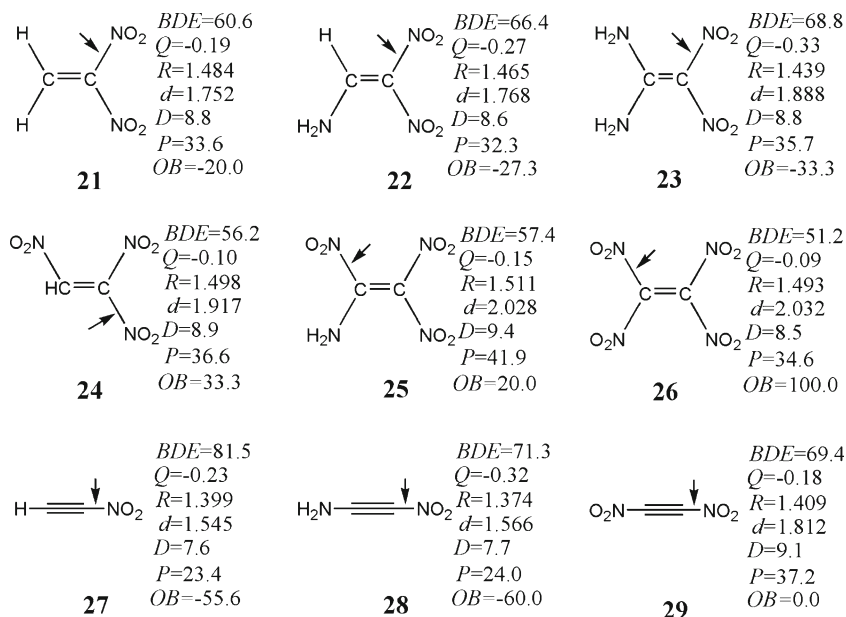


Fig. 4 Calculated properties of amino-nitro derivatives of ethane. The arrows point to the weakest bonds in molecules

Fig. 5 Calculated properties of amino-nitro derivatives of ethane (**21–25**) and ethyne (**27–29**). The arrows point to the weakest bonds in molecules



form 26 decreases the detonation properties, and conversely that in 28 to form 29 increases the detonation properties, attributed to the requirement of OB .

From the above discussion, we find that the introduction of amino groups to neighboring nitro groups in derivatives of acyclic saturated hydrocarbons can usually decrease their molecular stability and changes a bit their energy densities; while the introduction on the *ortho*-positions relative to nitro groups of derivatives of unsaturated hydrocarbons can improve their sensitivity distinctly and detonation properties conditionally.

Aliphatic heterocycle

The extensively applied HMX, RDX and TNAZ are of nitro derivatives of aliphatic nitrogen heterocycles. We introduce amino groups to them to form new compounds as illustrated in Fig. 6, which can be divided into three groups according to the molecular skeletons: group I including 30–32, group II including 33–36, and group III including 37–41.

For group I, we first examine the weakest bonds because of a very big strain among the four numbered ring, by comparing B of C–C, C–N and N–N bonds. As a result, as shown in Fig. 6, the C–Nitro bond labeled as 1 is the weakest in each molecule of group I, and it is weakened more and more as the introduced amino groups increase, i.e., BDE_2 decreases too and R_2 increases from 30 to 32. Because the stability of a whole molecule is determined by the strength of its weakest linkage, the more and more introduction of amino groups to TNAZ leads to less and less stability, in spite of the increasingly strengthening of C–Nitro bonds from 30 to 32 whose break are usually regarded as the initial step for explosive decomposition. As for detonation properties, we find no improvement after the introduction due to the reduced d and worsened OB .

For analogues of RDX, we confirm that the weakest bonds are the C–Nitro bond labeled as 1 rather than the C–N bond labeled as 2, with the increasing of introduced amino groups in 33 to 36. Comparing the lowest BDE of 33 to 36, 44.5, 39.4, 39.8 and 41.0 kcal mol⁻¹, respectively, we find a disordered change of them and a decrease of molecular stability after the introduction. In addition, the calculated results show almost no change even a little decrease of detonation properties after the introduction, similarly attributed to no improved d and OB .

As to group III, it is interesting that both C–Nitro bonds (labeled as 1) and C–N bonds (labeled as 2) on the ring are weakened as the introduced amino groups increase, and the weakest linkage is always the C–Nitro bonds. Similar to the cases of groups I and II, the introduction does not improve the detonation properties and even abates them.

From the above discussion on the derivatives of the three kinds of aliphatic heterocycles, we can draw a conclusion that the introduction of amino groups on these cycles will decrease molecular stability, and will not enhance and even reduce detonation properties.

Cage

The cage structures are advantageous to increase d , as well as HOF due to the strain energy stored in them. The existing CL-20 and ONC with cages possess high energy densities but also high sensitivities. Ghule et al. [37] predicted that the amino displacement of nitro groups in CL-20 can increase molecular stability but decrease detonation properties. For this case, we select 1,3,5,7-tetranitrocubane (TNC) to displace its hydrogen atoms by different amount of amino groups to study the effect of the introduction. As shown in

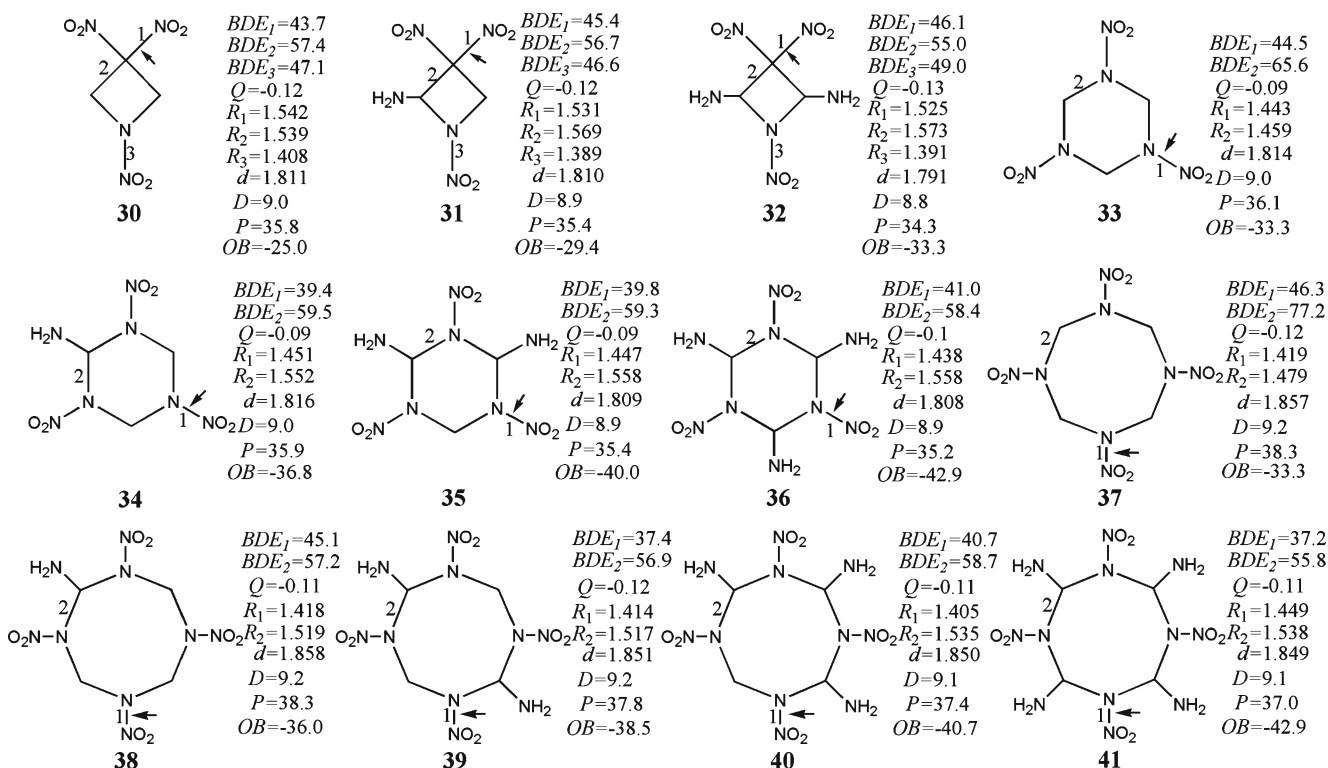


Fig. 6 Calculated properties of amino-nitro analogues of TNAZ (30–32), RDX (33–36) and HMX (37–41). The arrows point to the weakest linkage in molecules. BDE_1 and R_1 , and BDE_2 and R_2 , are of bonds labeled 1 and 2, respectively

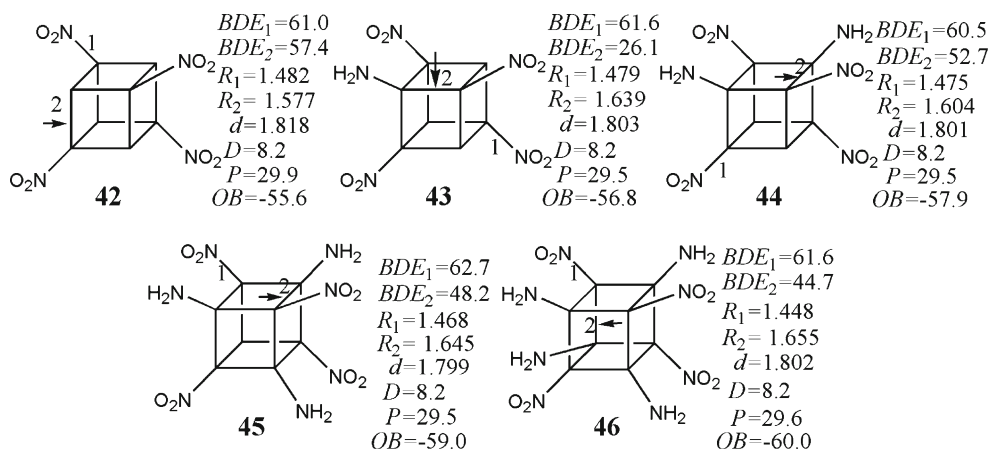
Fig. 7, the weakest linkage of this group of molecules is the C-C bonds labeled as 2 on the rings, rather than C-Nitro bonds strengthened after the introduction. The linkage is weakened after introducing amino groups as BDE_2 decreases and R_2 increases, suggesting the increased sensitivity. It can even be found that 46 is much more unstable than ONC by comparing their BDE and R of the weakest C-C bonds, 44.7 vs. 59.5 kcal mol⁻¹ and 1.655 vs. 1.569 Å. Also, we cannot find any enhanced detonation property after the displacement because of no obvious improvement of d and worsened OB . It can be accordingly concluded that it is unwise to

displace hydrogen atoms on a cage by amino groups to improve the sensitivity and D of explosives.

Aromatic cycle

It has been confirmed theoretically and experimentally that the *ortho*- or *para*-sited amino groups to nitro groups on a benzene ring can strengthen molecular stability [9–11] and increase d [4]. Here, we choose another aromatic cycle, 1,4-pyrazine-1-oxide, as a skeleton to build amino-nitro compounds to expose the effect in an aromatic environment, in which the applied

Fig. 7 Calculated properties of amino-nitro derivatives of ONC. The arrows point to the weakest linkage in molecules. B_1 and R_1 , and B_2 and R_2 , are of bonds labeled 1 and 2, respectively



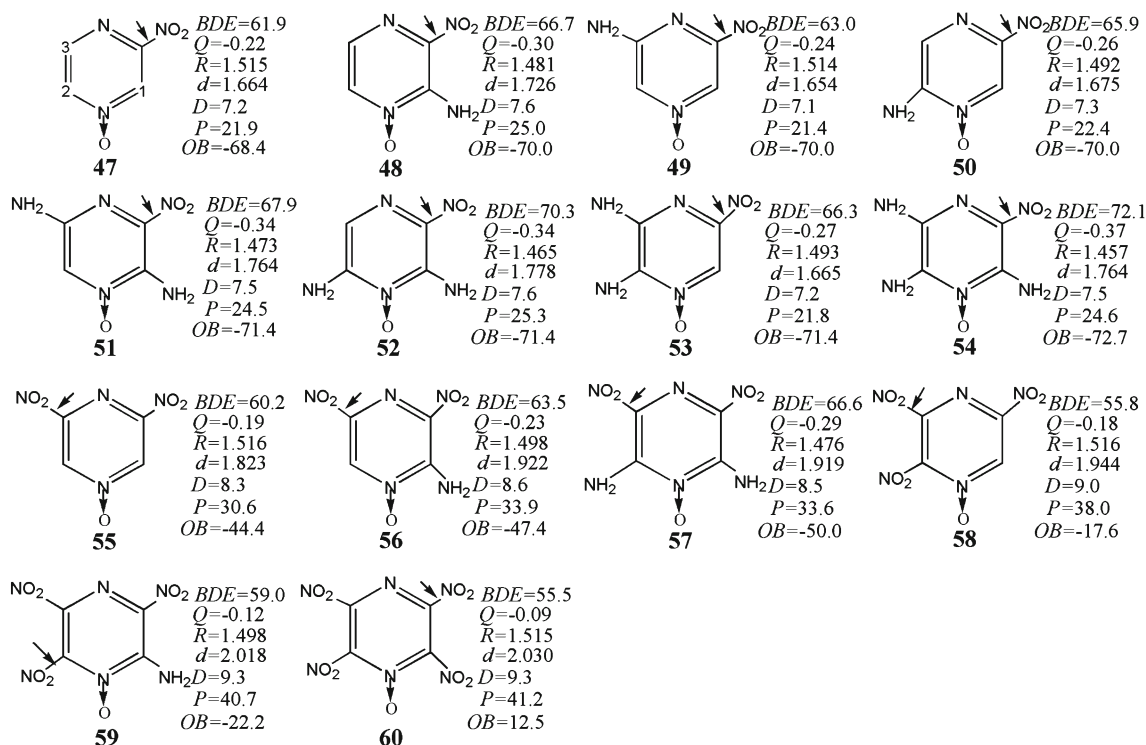


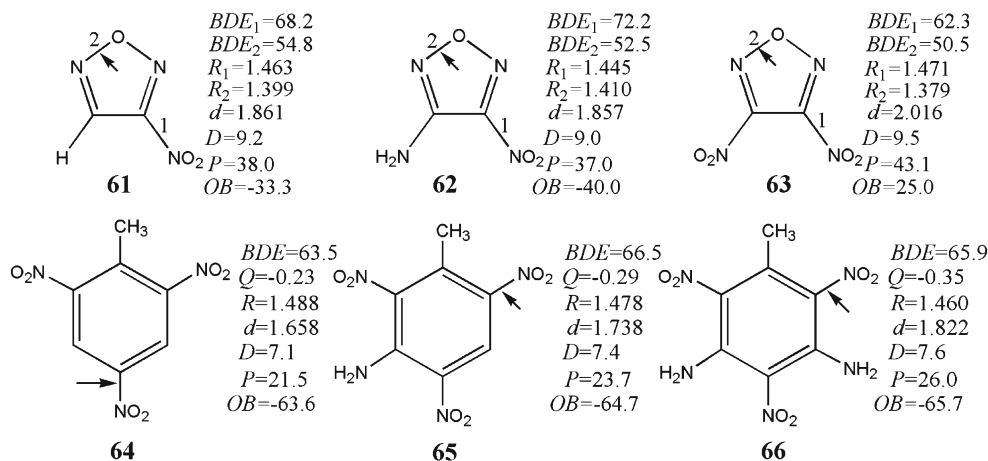
Fig. 8 Calculated properties of amino-nitro derivatives of 1,4-pyrazine-1-oxide. The arrows point to the weakest linkage in molecules

LLM-105 is involved. The compounds in Fig. 8 can be classified into four groups according to the amount of nitro groups contained. From group I including 47-54, we can find that the *ortho*- or *para*-sited amino groups to nitro groups on the pyrazine ring can strengthen the C-Nitro bond by shortening its R and increasing its BDE . Comparing the R and BDE of 47 and 49, and 50 and 53, respectively, it can be found that the *meta*-sited amino groups do not possess similar effects as *ortho*- or *para*-sited amino groups. In group II containing 55-57 and group II containing 58 and 59, the mentioned effects of *ortho*- and *para*-sited amino groups can also be verified. Meanwhile, it can be seen from the data of d , D and P in Fig. 8, that the

introduction of amino groups on the *ortho*- or/and *para* sites to nitro groups can more or less improve detonation properties, owing to the distinct increases of d despite a little worsened OB . Therefore, it seems that there is an effect of killing two birds with one stone of the introduction: to improve not only sensitivities but also D .

At the same time, the effect on the furazan ring and toluene is considered. Furazan is the skeleton of another important group of explosives [38]. As shown in Fig. 9, when an amino group displaces the hydrogen atom on the ring, the C-Nitro bond is strengthened but the N-O bond on the ring is weakened, and the detonation properties are increased as a result of the increased d and a little worsened OB .

Fig. 9 Calculated properties of amino-nitro derivatives of furazan and toluene



Conclusions

The reason that applied amino group contained explosives are very limited is made clear by discussing the effects of displacement of hydrogen atoms or nitro groups by amino groups on molecular stability and detonation properties, considering four groups of molecular skeletons involved in most of applied explosives including acyclic hydrocarbon, aliphatic heterocycle, cage and aromatic ring. As a result, the resonant displacements to a nitro group in a conjugated system like ethene, ethyne and aromatic rings can make safety enhanced distinctly and the detonation properties increased in terms of oxygen balance; while these displacements in nonconjugated systems can make decreased molecular stability and the almost changeless detonation properties.

All applied amino group contained explosives including FOX-7, LLM-105, TNA, DATB, TATB and NQ possess conjugate molecular skeletons, consistent with the above conclusion. Therefore we can conclude that amino groups are conditionally advantageous to IHEs. That is, the condition is that the amino groups are introduced resonantly to the nitro groups in a conjugated system and the introduction improves *OB*.

Acknowledgments Authors greatly appreciate the financial support from the Science and Technology Fund of CAEP (2011A0302014), the National Natural Science Foundation of China (11072225 and 21173199) and the Personal Innovation Project of Chongqing University (CDJXS10220001).

References

- Teipel U (2005) Energetic materials. Wiley-VCH, Weinheim
- Sikder AK, Sikder N (2004) A review of advanced high performance, insensitive and thermally stable energetic materials emerging for military and space applications. *J Hazard Mater A* 112:1–15
- Zhang C, Peng Q, Wang L, Wang X (2010) Thermal sensitivity of HMX crystals and HMX-based explosives treated under various conditions. *Propel Explos Pyrotech* 35:561–566, and references there in
- Dong H, Zhou F (1989) (ed) Properties of high energetic explosives and relatives. Science Press, Beijing
- Murray JS, Concha MC, Politzer P (2009) Links between surface electrostatic potentials of energetic molecules, impact sensitivities and C-NO₂/N-NO₂ bond dissociation energies. *Mol Phys* 107:89–97
- Pospíšil M, Vávra P, Concha MC, Murray JS, Politzer P (2010) A possible crystal volume factor in the impact sensitivities of some energetic compounds. *J Mol Model* 16:895–901
- Pospíšil M, Vávra P, Concha MC, Murray JS, Politzer P (2011) Sensitivity and the available free space per molecule in the unit cell. *J Mol Model* 17:2569–2574
- Murray JS, Lane P, Politzer P (1998) Effects of strongly electron-attracting components on molecular surface electrostatic potentials: application to predicting impact sensitivities of energetic molecules. *Mol Phys* 93:187–194
- Zhang C (2006) Investigations of correlation between nitro group charges and C-nitro bond strength, and amino group effects on C-nitro bonds in planar conjugated molecules. *Chem Phys* 324:547–555
- Zhang C (2008) Investigation of the correlations between nitro group charges and some properties of nitro organic compounds. *Propel Explos Pyrotech* 33:139–145
- Zhang C, Wang X, Huang H (2008) π -stacked interactions in explosive crystals: buffers against external mechanical stimuli. *J Am Chem Soc* 130:8359–8365
- Politzer P, Murray JS (2011) Some perspectives on estimating detonation properties of C, H, N, O compounds. *Central Europ J Energet Mater* 8:209–220
- Tao W, Zhu W, Zhang X, Li Y, Xiao H (2009) Molecular design of 1,2,4,5-tetrazine-based high-energy density materials. *J Phys Chem A* 113:9404–9412
- Qiu L, Gong X, Wang G, Zheng J, Xiao H (2009) Looking for high energy density compounds among 1,3-bis-homopentaprismene derivatives with CN, NC, and ONO₂ Groups. *J Phys Chem A* 113:2607–2614
- Kamlet MJ, Adolph HG (1979) The relationship of impact sensitivity with structure of organic high explosives. II. Polynitroaromatic explosives. *Propellants Explos Pyrotech* 4:30–34
- Rice BM, Sahu S, Owens FJ (2002) Density functional calculations of bond dissociation energies for NO₂ scission in some nitroaromatic molecules. *J Mol Struct THEOCHEM* 583:69–72
- Zhang C (2009) Review of the establishment of nitro group charge method and its applications. *J Hazard Mater* 161:21–28
- Zhang C, Shu Y, Wang X, Zhao X, Tan B, Peng R (2005) A new method to evaluate the stability of the covalent compound: By the charges on the common atom or group. *J Phys Chem A* 109:6592–6596
- Zhang C (2006) Investigation on the correlation between the interaction energies of all substituted groups and the molecular stabilities of nitro compounds. *J Phys Chem A* 110:14029–14035
- Zhou Z, Parr RG (1990) Activation hardness: New index for describing the orientation of electrophilic aromatic substitution. *J Am Chem Soc* 112:5720–5724
- Pearson RG (1989) Absolute electronegativity and hardness: Application to organic chemistry. *J Org Chem* 54:1423–1430
- Murray JS, Lane P, Politzer P, Bulduc PR (1990) A relationship between impact sensitivity and the electrostatic potentials at the midpoints of C-NO₂ bonds in nitroaromatics. *Chem Phys Lett* 168:135–139
- Tarver CM (1979) Density estimations for explosives and related compounds using the group additivity approach. *J Chem Eng Data* 24:136–145
- Stine JR (1981) Predictions of crystal densities of organic explosives by group additivity; Report LA-8920; Los Alamos National Laboratory. Los Alamos, NM
- Ammon HL, Mitchell S (1998) A new atom-functional group volume additivity data base for the calculation of the crystal densities of C, H, N, O and F-containing compounds. *Propellants Explos Pyrotech* 23:260–265
- Ammon HL (2001) New atom/ functional group volume additivity data bases for the calculation of the crystal densities of C-, H-, N-, O-, F-, S-, P-, Cl-, and Br-containing compounds. *Struct Chem* 12:205–212
- Karfunkel HR, Gdanitz RJ (1992) *Ab initio* prediction of possible crystal structures for general organic molecules. *J Comput Chem* 13:1171–1183
- Murray JS, Brinck T, Politzer P (1996) Relationships of molecular surface electrostatic potentials to some macroscopic properties. *Chem Phys* 204:289–295
- Kim CK, Lee KA, Hyun KH, Park HJ, Kwack IY, Kim CK, Lee HW, Lee B-S (2004) Prediction of physicochemical properties of organic molecules using van der Waals surface electrostatic potentials. *J Comput Chem* 25:2073–2079

30. Kim CK, Cho SG, Kim CK, Park H-Y, Zhang H, Lee HW (2008) Prediction of densities for solid energetic molecules with molecular surface electrostatic potentials. *J Comput Chem* 29:1818–1824
31. Xiao H (ed) (2008) *Theoretical Design of High Energy Density Materials*. Science Press, Beijing and references there in
32. Zhang C, Shu Y, Huang Y, Zhao X, Dong H (2005) Investigation of correlation between impact sensitivities and nitro group charges in nitro compounds. *J Phys Chem B* 109:8978–8982
33. Li J (2010) Relationships for the impact sensitivities of energetic C-nitro compounds based on bond dissociation energy. *J Phys Chem B* 114:2198–2202
34. Kamlet MJ, Jacobs SJ (1968) Chemistry of detonation. I. A simple method for calculating the detonation properties of C-H-N-O explosives. *J Chem Phys* 48:23–25
35. Stewart JJP (1989) Optimization of parameters for semiempirical methods I. Method *J Comput Chem* 10:209–212
36. Material Studio 5.5 (2010) Accelrys Inc, San Diego, CA
37. Ghule VD, Jadhav PM, Patil RS, Radhakrishnan S, Soman T (2010) Quantum-chemical studies on hexaazaisowurtzitanes. *J Phys Chem A* 114:498–503
38. Zhang C (2006) Computational investigation of the detonation properties of furazans and furoxans. *J Mol Struct THEOCHEM* 765:77–83, and references there in