Review

Review of the establishment of nitro group charge method and its applications

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ABSTRACT

On the basis of our previous work, a new approach, nitro group charge method (NGCM) is established and applied to understand, evaluate and predict the properties of nitro compounds or explosives, including molecular stability, impact sensitivity and nitrating reaction. At first, the more negative nitro charges (Q_{Nitro}) correspond to the more stable nitro compounds. Secondly, for all nitro explosives in which the R—Nitro bond is the weakest, Q_{Nitro} can be regarded as a structural parameter to assess and predict the impact sensitivity. The more negative Q_{Nitro} means the higher H_{50}. Thirdly, the conditions, the velocities and the products' occurrence ratios of some nitrating reactions can be approximately evaluated and compared using NGCM: the more negative Q_{Nitro} corresponds to the easier and the faster reaction, and the higher occurrence ratio. Meanwhile, this idea of using charges on common atoms or groups to investigate related properties can be generalized to some other systems such as azide explosives.

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Contents

1. Introduction

Today, most extensively applied explosives are nitro compounds. Nitro groups make them active and explosive. Many investigations have showed that we could initiate the researches on the properties of nitro compounds from these nitro groups. On basis of many previous researches of nitro explosives such as syntheses, analyses, stabilities, detonation properties and other properties, we have studied some properties using these nitro groups, especially

charges on them, Q_{Nitro}. That is to say, some properties including molecular stabilities, nitrating reactions and impact sensitivities of nitro explosives have been related with Q_{Nitro} successfully [1–5]. This is the so-called *nitro group charge method* (NGCM). By NGCM, some complicated problems in nitro compounds can become simpler.

2. Nitro group charge method

2.1. Why to establish NGCM

As mentioned above, most widely used explosives containing C, H, O and N atoms are so far nitro compounds, such as the old
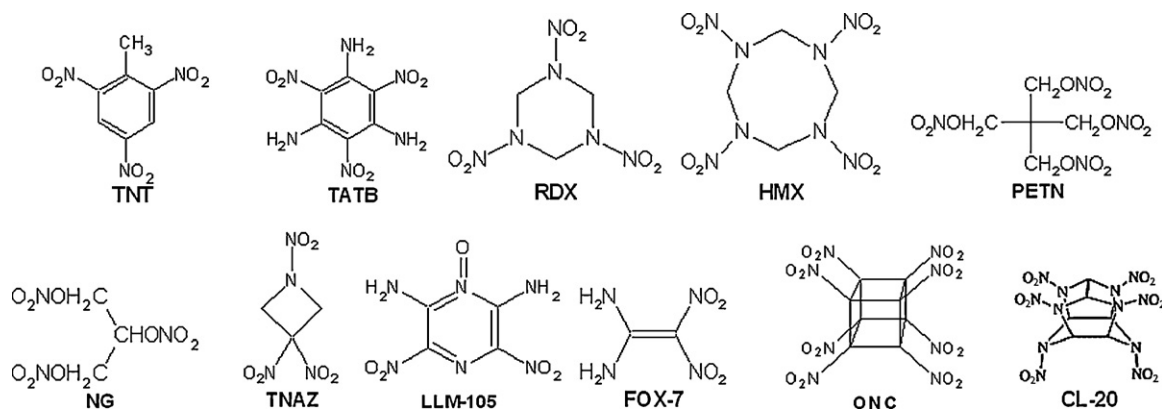
Fig. 1. Some nitro explosive molecules containing nitro groups.

2,4,6-trinitrotoluene (TNT), 1,3,5-triamino-2,4,6-trinitrobenzene (TATB), octahydro-1,3,5,7-trtranitro-1,3,5,7-tetrazocine (HMX), hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX), penta erythritol tetranitrate (PETN), nitrocellulose (NC) and nitroglycerin (NG), current hexaazaheanitriso wurtzitane (CL-20), 2,6-diamino-3,5-dinitropyrazine-1-oxide (LLM-105), 1,1-diamino-2,2-dinitroethylene (FOX-7) and 1,3,3-trinitroazetidine (TNAZ), and potential octnitrocubane (ONC) in Fig. 1 [6]. Nitro groups are their common parts and the root for their detonation properties. But all these nitro groups are completely same? Certainly not. For example, Q_{Nitro} is usually different from one another. In fact, the idea of NGCM is to look for the differences from these common parts, for example, to look for the charge differences from the common nitro groups, and then to investigate the correlation between these differences (e.g. charges) and properties (e.g. stability). As a matter of fact, the sign and quantity of Q_{Nitro} reflect the chemical environment of interested nitro group. Namely, the chemical environment of nitro group can be characterized by its charge. It is the physical basis of NGCM. And the reasons for establishing NGCM are as following. At first, high energy density materials (HEDMs) including nitro compounds are continuingly interested and required materials. NGCM is a useful approach to understand, evaluate and predict the properties of nitro compounds, particularly, the stabilities of nitro explosives. Secondly, owing to the improvement of algorithms and computer, and the easy obtainment of Q_{Nitro}, NGCM has a good operability. Thirdly, from the viewpoint of evaluating impact sensitivities of nitro explosives, NGCM has larger applicability than other existing methods. At last, the idea of the charges of common parts can be generalized to some other systems. Surely, our investigations have showed that to establish NGCM is feasible and necessary for HEDM researches.

2.2. Origin of NGCM

The idea of NGCM comes from the investigation on the simplest compounds, hydrides. Atoms or groups will become electron acceptors or donors once compounds formed. Hydrogen atoms possess different quantities of the charges, due to the different chemical, i.e. or bonding environments in different hydrides (Fig. 2). So we can explore the molecular environment by the charges of hydrogen atoms. Obviously, the more positive charge the hydrogen atom (electron donor) possesses, the more stable the hydride becomes. For instance, the less positive hydrogen charges are well in agreement with the higher molecular decomposition percentages of hydrogen at 1273 K halides (HF: negligible, HCl: 0.0014, HBr: 0.5, and HI: 33) [7].

Table 1
Calculated results of nitro substitutes of methane

Compounds	H_3C-NO_2	$O_2N\diagdown NO_2$	$O_2N\diagdown^{NO_2}_{NO_2}$	$O_2N-\overset{NO_2}{\underset{NO_2}{\mid}}-NO_2$
Q_{Nitro} (e)	−0.285	−0.192	−0.152	−0.050
$R_{C-Nitro}$ (Å)	1.517	1.543	1.548	1.582

Nitro groups are usually electron acceptors in compounds owing to their strong electronegativity. From Table 1 we find that Q_{Nitro} can represent the molecular stability of nitro compounds, as hydrogen charges represent the stability of a hydride. For all nitro substitutes of methane, the decrease of negative Q_{Nitro} is consistent with the increase of C—Nitro bond length, i.e. the decrease of molecular stability.

2.3. Physical meaning and definition of NGCM

The so-call NGCM is the method of studying the properties of nitro compounds by Q_{Nitro}. Its physical meaning is that the more negative Q_{Nitro} (or electrons) corresponds to the higher molecular stability. Fig. 3 shows the orientation and size of electron

IIIA	IVA	VA	VIA	VIIA	
BH₃ -0.109 2.04 0.119 316	CH₄ 0.153 2.55 0.109 413	NH₃ 0.308 3.04 0.101 391	H₂O 0.352 3.44 0.096 453	HF 0.365 3.98 0.092 569	PII
	SiH₄ -0.090 1.90 0.143 316	PH₃ 0.055 2.19 0.142 331	H₂S 0.120 2.58 0.134 347	HCl 0.138 3.15 0.128 431	PIII
		AsH₃ -0.050 2.18 0.151 293	H₂Se 0.001 2.55 0.146 276	HBr 0.078 2.06 0.141 336	PIV
HₙR Charges of H χP of R R-H bond length, nm R-H bond energy, KJ/mol			H₂Te -0.122 2.10 0.166 238	HI 0.027 2.66 0.161 299	PV

Fig. 2. The charges of hydrogen atoms, Pauling electronegativities (χ_P) of non-hydrogen atoms (R), bond lengths, and bond energies in hydrides.
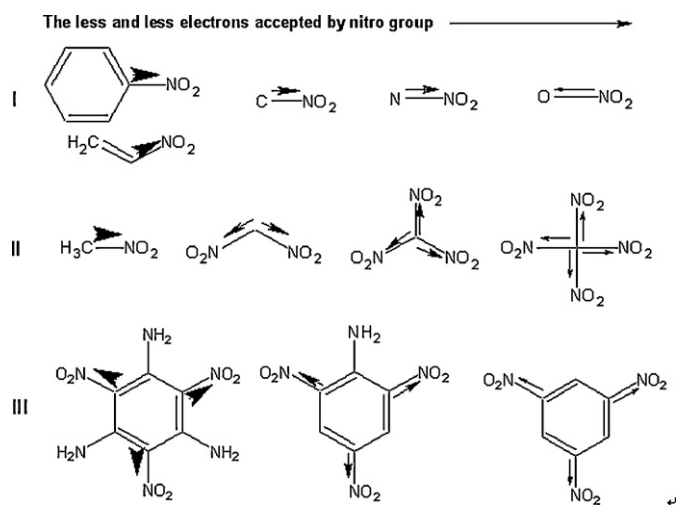
Fig. 3. Physical meaning of NGCM. The arrow points to the orientation of electron transfer, and the bigger arrowhead size corresponds to the more electrons transferred and the more molecular stability.

transfer. For Type I, atoms with different electronegativity have different abilities to donate electrons to nitro groups. Because of rich-electrons, the conjugated structure can easily offer the most electrons to nitro groups and lead to the most stable nitro compounds. For example, TATB belongs to this kind of structure and possesses very high decomposition temperature above 573 K relative to the common nitro compounds. The increasing electronegativity of C to N and O atoms results in the less and less electron transferred to nitro groups. And even electrons transfer from nitro group to O atom in O—Nitro bond. Consequently, compounds with O—Nitro bonds are usually unstable and nitric ether explosives such as NG and pentaerythritoltetranitrate (PETN)

are very sensitive and used as initiating charges. Type II indicates that the more nitro groups linked with the same C atom lead to the less negative Q_{Nitro} and the less molecular stability. Type III demonstrates electron donors' role in changing Q_{Nitro} and molecular stability. On benzene circle, the electron donor amino group on *ortho-* or *para*-position can effectively increase negative Q_{Nitro} and molecular stability. This result can also be obtained from the molecular electron density (Fig. 4). For two the most typical molecules, hexanitrobenzene (HNB) and TATB, can be distinguished using electron density slices along benzene circle, especially, the electron density of nitro group: the red areas of nitro groups of TATB are distinctly bigger than those of HNB. That is to say, TATB with a planar structure and a strong conjugated and delocalized effect $\prod_{18}^{24}$ has more negative Q_{Nitro} than HNB without any apparent delocalized effect; all nitro groups in HNB seriously deviate from the plane of benzene circle, and even benzene circle is no longer planar; therefore, TATB is more stable than HNB. The cases of other nitrobenzene are between HNB and TATB.

$$Q_{Nitro} = Q_N + Q_{O1} + Q_{O2} \tag{1}$$

$$\overline{Q}_{Nitro} = \frac{1}{n}\sum_{i=1}^{n} Q_{Nitro,i} \tag{2}$$

Q_{Nitro}, is the algebraic sum of charges of all three atoms on nitro group (Eq. (1)). The average Q_{Nitro} can be sometimes used for some purpose and calculated by Eq. (2). However, the atomic charges are defined quantities, not physical observables. There exist some defined atomic charges currently, such as Mulliken charges, ESP charges, Hirshfeld charges, natural charges, charges derivated from charge equilibration methods (QE), and other charges [8–13]. Mulliken charges were chosen to study after comparing these charges in all our work. And all calculations were performed by density functional theory (DFT) and the general gradient approximation (GGA) method with the Beck/LYP hybrid functional and the DNP basis set
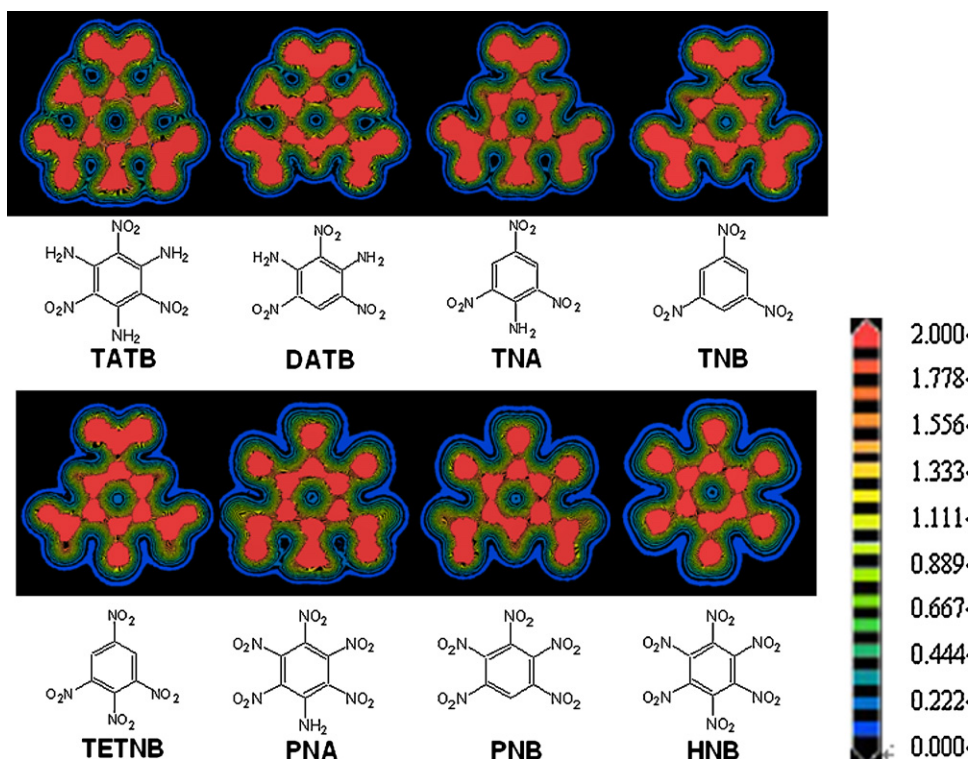

Fig. 4. Electron density slices along benzene circle of nitrobenzene (unit in e).

Table 2
Average of Q_{Nitro} (e) and total energies (E_t, hartree) of some nitro derivatives of benzene

I			
Q_{Nitro}	−0.399	−0.324	−0.365
E_t	−492.1898292	−492.1845731	−492.1893164
II			
Q_{Nitro}	−0.257	−0.279	−0.278
E_t	−641.38768198	−641.4033873	−641.4033789
III			
Q_{Nitro}	−0.226	−0.239	−0.252
E_t	−845.9586806	−845.9693607	−845.9836444

or local density approximation (LDA) method with PWC functional in Acceryls' code Dmol [3,14–16].

3. Applications of NGCM

3.1. Evaluation of molecular stabilities of nitro compounds

It can be known from above discussion that the most important application of NGCM is to evaluate molecular stability usually measured by the total energy (for isomers), bond length, bond dissociation energy (BDE), and so forth. This paper just uses the correlation between Q_{Nitro} and these indexes to reveal that Q_{Nitro} is also a structural parameter to assess molecular stability.

Firstly, mono-, di- and trinitrobenzenes are taken as the interested objects. Here, the stabilities of conformers are compared by the well-known total energies. From Table 2, we can conclude that the more the negative average Q_{Nitro}, the lower the total energy, i.e. the more stable the molecule. It shows the molecule will become more stable when the nitro groups possess more negative charges. Thus, it may be a way to evaluate the molecular stabilities of nitro isomers using NGCM.

Secondly, the correlation between Q_{Nitro} and C—Nitro bond length is useful to evaluate the molecular stability using NGCM. Main insensitive explosives such as 1,3-diamino-2,4,6-trinitrobenzene (DATB), TATB, FOX-7, 2,6-diamino-3,5-dinitropyrazine (ANPZ) and LLM-105 not only contain nitro and amino groups, but also possess planar and conjugated molecular structures. In C—Nitro compounds, C—Nitro bonds are usually the weakest in the molecules and may be broken as the initial step in the molecular decomposition [17]. From the viewpoint of this, the strength of C—Nitro bond determines the molecular stability. In above insensitive explosive molecules, amino groups are helpful to decrease the C—Nitro bond length and increase its strength, and further strengthen the stability of the nitro compound. So, the correlation between Q_{Nitro} and C—Nitro bond lengths when introducing amino groups in planar and conjugated molecules has been investigated (Table 5). The planar and conjugated structures are of the analogues of the TATB, FOX-7, ANPZ, i.e. the amino-nitro derivatives of aromatic hydrocarbon, alkene and minor heterocyclic nitrogen compounds [5a].

In Table 3, fifteen fitted lines show there is a good linear relationship between Q_{Nitro} and $R_{C–Nitro}$ in any given group of compounds (the correlation coefficients are all above 0.96). In the investigation, we can find that Q_{Nitro} decreases as nitroben-

zene (−0.310 e) > dinitrobenzene (−0.279 e) > trinitrobenzene (−0.252 e). It indicates that the more the nitro groups, the less negative Q_{Nitro}, and the longer and weaker $R_{C–Nitro}$ under the same condition (for example, these molecules have the same quantities and positions of amino groups). In fact, the more nitro groups and the less amino groups the nitrobenzene has, the less stable it becomes. It shows that the more negative Q_{Nitro}, the shorter and stronger $R_{C–Nitro}$, and the more molecular stability. Additionally, Q_{Nitro} is more sensitive to molecular changes than $R_{C–Nitro}$. For example, $R_{C–Nitro}$ of nitrobenzene, 3-amino-nitrobenzene and 3,5-diamino-nitrobenzene are all 1.491 Å, but Q_{Nitro} of them are −0.310 e, −0.324 e and −0.334 e, respectively. Because Q_{Nitro} of them should be right according to the above-mentioned rule, it may be the advantage of Q_{Nitro} when it is used to evaluate the strength of the C—Nitro bond. Therefore, NGCM may be a more sensitive and effective approach to assess molecular stabilities due to the Q_{Nitro} and $R_{C–Nitro}$ correlation, and the advantage of Q_{Nitro}. Certainly, it should be emphasized that the linear relationship between Q_{Nitro} and $R_{C–Nitro}$ can only exist in separate groups of the nitro compounds.

Finally, the correlation between Q_{Nitro} and BDE also shows we can evaluate the molecular stability using NGCM. Analyzing the computational data of Q_{Nitro} and experimental data of BDE [18] in Table 4 [5b], we can obtain some results as below: (1) for all groups of nitro organic compounds, there are linear correlations between Q_{Nitro} and BDE, with correlation coefficients above 0.91; (2) the more negative Q_{Nitro} corresponds to the more BDE; (3) from the fitted correlation equations, we can find that different structures or substituted groups have different abilities to offer electrons to nitro groups. For example, conjugated structures, and C, N and O atoms linked with nitro groups are distinctly different from offering even attracting electrons to or from nitro groups.
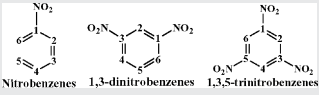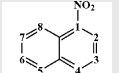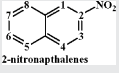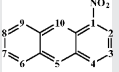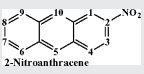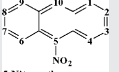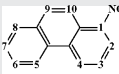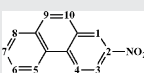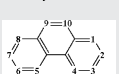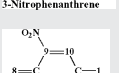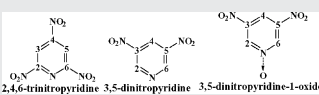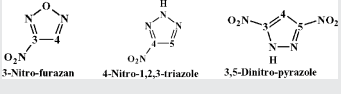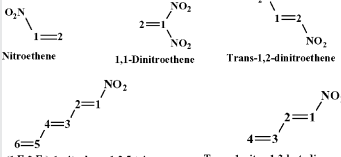
3.2. Evaluation of the impact sensitivities of nitro explosives

A continuing major concern in the area of energetic materials is their vulnerability to explosion caused by accidental external stimuli. Such stimuli can include impact, shock wave, friction, heat and electrostatic charges. The degree of vulnerability is commonly termed the 'sensitivity' of the material. One of them, the impact sensitivity is used to show the stability of the nitro compound and is measured by the height H_{50}, from where a given weight falling upon the compound gives a 50% probability of initiating an explosion. The shorter the drop height, the greater the impact sensitivity. There have been some investigations on molecular structure–sensitivity relationship, which are helpful to understand the factors determining sensitivity and develop a predictive capability, although the initiation of decomposition in an energetic compound involves a complex interplay of various element such as its molecular structure, crystal properties and physical state [16]. These representative investigations were finished by Delpuech and Cherville [19–21], Kamlet and Adolph [22], Politzer and Howard [23], Xiao [24], Owens and co-workers [25], and so forth. Currently, my work also offered a new method [26].

On the basis of the correlation between Q_{Nitro} and molecular stability, it may be more practically meaningful to explore the Q_{Nitro}/H_{50} relationship of nitro explosives. That is to say, this relationship is very useful to make computational results take positive roles i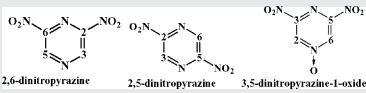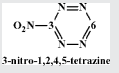n understanding, evaluating and predicting the properties of explosives. So, NGCM is helpful to design HEDMs with nitro groups.

The experimental H_{50} [27] and our computational Q_{Nitro} at the level of DMol3/LDA/PWC of 40 nitro explosives listed in Fig. 5 illustrates there is an approximate tendency between them: the more negative Q_{Nitro} and the more H_{50}. This approximation can be

Table 3
Linear correlation between Q_{Nitro}, and C—Nitro bond length $R_{C-Nitro}$

No.	Mother molecules	N	Fitted equation	R	Representatives of explosive
1	Nitrobenzenes 1,3-dinitrobenzenes 1,3,5-trinitrobenzenes	36	$y = 4.9258 - 3.1027x$	0.9723	TNB, DATB, TATB
2	1-nitronaphthalenes	7	$y = 3.7062 - 2.2404x$	0.9927	–
3	2-nitronapthalenes	8	$y = 4.4671 - 2.7843x$	0.9867	–
4	1-Nitroanthracene	9	$y = 3.6906 - 2.2279x$	0.9922	–
5	2-Nitroanthracene	10	$y = 4.3772 - 2.7231x$	0.9786	–
6	5-Nitroanthracene	5	$y = 3.7725 - 2.2557x$	0.9793	–
7	1-Phenanthrene	7	$y = 3.6188 - 2.1760x$	0.9900	–
8	2-Nitrophenanthrene	8	$y = 4.6743 + 2.9274x$	0.9982	–
9	3-Nitrophenanthrene	8	$y = 4.2872 - 2.6615x$	0.9784	–
10	9-Nitrophenanthrene	7	$y = 4.0190 - 2.4429x$	0.9961	–
11	2,4,6-trinitropyridine 3,5-dinitropyridine 3,5-dinitropyridine-1-oxide	29	$y = 4.7208 - 2.9370x$	0.9650	
12	2,6-dinitropyrazine 2,5-dinitropyrazine 3,5-dinitropyrazine-1-oxide	18	$y = 3.8184 - 2.3529x$	0.9690	ANPZ, LLM-105
13	3-nitro-1,2,4,5-tetrazine	3	$y = 3.4902 - 2.1537x$	0.9675	–
14	3-Nitro-furazan 4-Nitro-1,2,3-triazole 3,5-Dinitro-pyrazole	10	$y = 3.5271 - 2.2225x$	0.9649	DNF, ANTZ
15	Nitroethene 1,1-Dinitroethene Trans-1,2-dinitroethene (1E,3E)-1-nitrohexa-1,3,5-triene Trans-1-nitro-1,3-butadiene	35	$y = 5.5201 - 3.5598x$	0.9949	FOX-7

Mother molecules are the initial molecules before introducing amino groups. In fitted equations, y and x are the quantity of Q_{Nitro} (e) and $R_{C-Nitro}$ (Å), respectively. N is the number of samples. R is the linear correlation coefficient.

Table 4
Q_{Nitro} and BDE (in bracket) of nitro organic compounds

R—Nitro	Q_{Nitro} (e) and BDE (kJ/mol)
C—Nitro	(1) CH_3—NO_2 $-0.284(260.7 \pm 2.1)$, C_2H_5—NO_2 $-0.281(254.4)$, nC_3H_7—NO_2 $-0.283(256.5)$, nC_4H_9—NO_2 $-0.286(256.0)$, nC_5H_{11}—NO_2 $-0.286(252.7 \pm 6.3)$, nC_6H_{13}—NO_2 $-0.282(251.9)$; (2) $cyclo$-C_3H_5—NO_2 $-0.286(295.4)$, $cyclo$-C_6H_{11}—NO_2 $-0.280(267.8 \pm 6.3)$; $(NO_2)CH_2$—NO_2 $-0.200(218.4)$, $(CH_3)CH(NO_2)$—NO_2 $-0.196(211.3)$, $(C_2H_5)CH(NO_2)$—NO_2 $-0.190(208.8)$, $(C_3H_7)CH(NO_2)$—NO_2 $-0.192(211.3)$; $(NO_2)_2CH$—NO_2 $-0.122(188.7)$, $(CH_3)(NO_2)_2C$—NO_2 $-0.121(178.7)$, $(C_2H_5)(NO_2)_2C$—NO_2 $-0.117(175.3)$, $(C_3H_7)(NO_2)_2C$—NO_2 $-0.116(173.6)$, $(C_4H_9)(NO_2)_2C$—NO_2 $-0.115(170.3)$, $(NO_2)_3C(NO_2)_2C$—NO_2 $-0.035(149.8)$; $(NO_2)_3C$—NO_2 $-0.050(169.5 \pm 4.2)$. BDE $= 127.17 - 466.38Q_{Nitro}$, $R = 0.964$ (2) ph-NO_2 $-0.310(295.8 \pm 4.2)$, 1,3-dinitrobenzene $-0.278(278.2)$, 1,4-dinitrobenzene $-0.279(280.3)$, 1,3,5-trinitrobenzene $-0.252(276.1)$, 2-methyl-nitrobenzene $-0.334(293.7 \pm 10.0)$. BDE $= 207.85 - 264.85Q_{Nitro}$, $R = 0.9138$
N—Nitro	(3) CH_3NH—NO_2 -0.208 (209.2), $((NO_2)_3CCH_2)_2N$—NO_2 $-0.100(167.4)$, $(H(NO_2)_2CCH_2)_2N$—NO_2 -0.113 (190.4), $CH_3N(NO_2)$—NO_2 $-0.031(118.4)$, $C_2H_5N(NO_2)$—NO_2 $-0.024(118.4)$, $C_3H_7N(NO_2)$—NO_2 $-0.033(129.7)$. BDE $= 111.07 - 524.71Q_{Nitro}$, $R = 0.9571$
O—Nitro	(4) CH_3O—NO_2 $0.028(174.1 \pm 4.2)$, C_2H_5O—NO_2 $0.020(172.8 \pm 4.2)$, C_3H_7O—NO_2 $0.018(177.0 \pm 4.2)$, HOO—NO_2 $0.097(100.0 \pm 2.9)$, CH_3OO—NO_2 $0.103(86.6 \pm 8.4)$. BDE $= 197.37 - 1038.94Q_{Nitro}$, $R = 0.995$

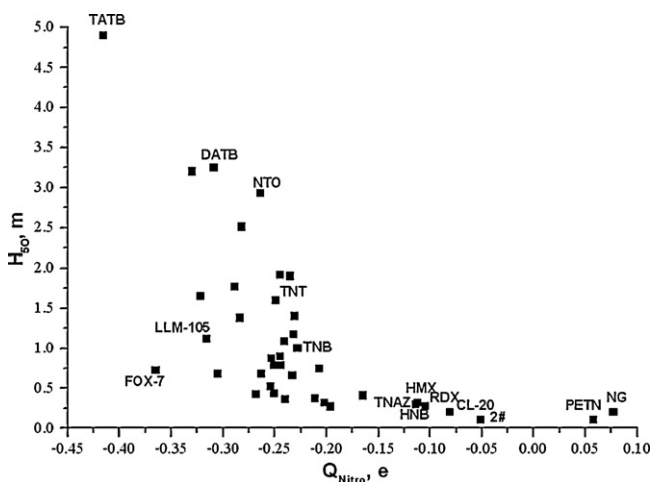In fitted equations, R is the linear correlation coefficient.

Fig. 5. Dependence of Q_{Nitro} versus H_{50} in nitro explosives. Q_{Nitro} is calculated at the level of DFT/LDA/PWC. Only famous explosives are labeled.

described as Eq. (3).

$$\frac{1}{H_{50}} = 5.88 + 17.22Q_{Nitro} \quad (R = 0.83) \tag{3}$$

It is no surprising of this not too good relation coefficient in Eq. (3) due to Q_{Nitro} only related with molecular stability, but H_{50} influenced by many factors such as molecular structures, crystal structures, chemical and physical properties, surface and interface properties of explosive components, and test conditions. However, molecular structure possibly represented by Q_{Nitro} is in fact one of the most essential factors influencing H_{50}.

In contrast to other parameters related with H_{50} such as oxygen balance, molecular electrostatic potential, bond length, and BDE, NGCM has more applicability in nitro explosives. As a matter of fact, Fig. 5 contains all kind of nitro explosives and embodies the stability order depicted in Fig. 3, i.e. the impact sensitivity decreases from conjugated C—Nitro explosives (e.g. TATB, DATB, NTO, FOX-7, TNT, LLM-105, and TNB) to nonconjugated C—Nitro explosive (e.g. TNAZ), nitroamino explosive (e.g. HMX, RDX and CL-20), and nitric ether explosive (e.g. NG and PETN). It should be emphasized that this rule works well only when R—Nitro bond is the weakest in the nitro compound since it can determine the molecular stability. It is the limitation.

In a word, by NGCM, Q_{Nitro} can be regarded as a structural parameter used to assess the impact sensitivity. The compound will have a high H_{50} when it has a high $-Q_{Nitro}$. According to the data in this paper, the compound may have $H_{50} < 0.4$ m when its nitro group has lower negative Mullkiken charges than about 0.23 e.

3.3. Evaluation of nitrating reactions

Nitrating reaction is one of the most important ways to synthesize nitro compound. From Fig. 6, we can find that Q_{Nitro} can be related with some characteristics of nitrating reaction. At first, the quantity of negative Q_{Nitro} of products determines the degree of difficulty of nitrating. From reaction I to IV, the negative Q_{Nitro} of products becomes the less and less, and the reaction becomes the more and more difficult. The negative Q_{Nitro} of HNB is so few that it cannot be obtained by directly nitrating benzene, mononitrobenzene, dinitrobenzene or trinitrobenzene. Relative to nitrobenzenes, nitrotoluenes and nitrophenols have more negative Q_{Nitro}. So, the corresponding nitrating reactions are easier. In other words, Q_{Nitro} can predict the nitrating velocity: the more negative Q_{Nitro} and the faster nitrating reaction. For example, the increasing Q_{Nitro} order of nitrobenzene, 2-nitronaphthalene, 1-nitronaphthalene and 5-nitroanthracene with -0.310 e, -0.322 e, -0.345 e and -0.399 e, respectively, is well consistent with the nitrating results of below reactions, i.e. it is more and more easily to form these nitro compounds or it is more and more reactive on the corresponding sites on these aromatics denoted by asterisks in Fig. 6. Anthracene is actually the most reactive among these aromatics, especially on 5- and 10-position. And the corresponding nitrating products are mainly the substitutes of 5- and 10-position. Reaction X and IX are 750 and 50 times faster than reaction I [8]. At last, for naphthalene, anthracene and phenanthrene, Q_{Nitro} has relation on the occurrence ratio of nitrating products. For naphthalene, the nitrating reaction mainly takes place on α-position, where the negative Q_{Nitro} is the most. The main nitrating sites of anthracene and phenanthrene are also very consistent with the places where the negative Q_{Nitro} is the most.

3.4. Generalization of NGCM

In fact, this method of predicting the properties of covalent compounds by the charges of common atoms or common groups can be generalized to other system besides hydrides and nitro compounds, such as oxides and alkyl radicals [1]. Table 5 also indicates that there is an obvious tendency of azide group charges versus impact sensitivities of metal-azide compounds: the more negative the azide group charges (cited from Ref. [28]) imply the more impact work, the heavier drop weight, the higher upper limit, or the higher lower limit, that is, the lower the impact sensitivity of metal-azide explosive. Azide groups are electro-acceptors and metal-azides will become stable when they accept adequate electrons from metal atoms, like nitro groups in nitro compounds. It can be seen as a generalization of group charge method. Similarly, this tendency is not monotonic in that some other factors influencing impact sensitivity are overlooked.
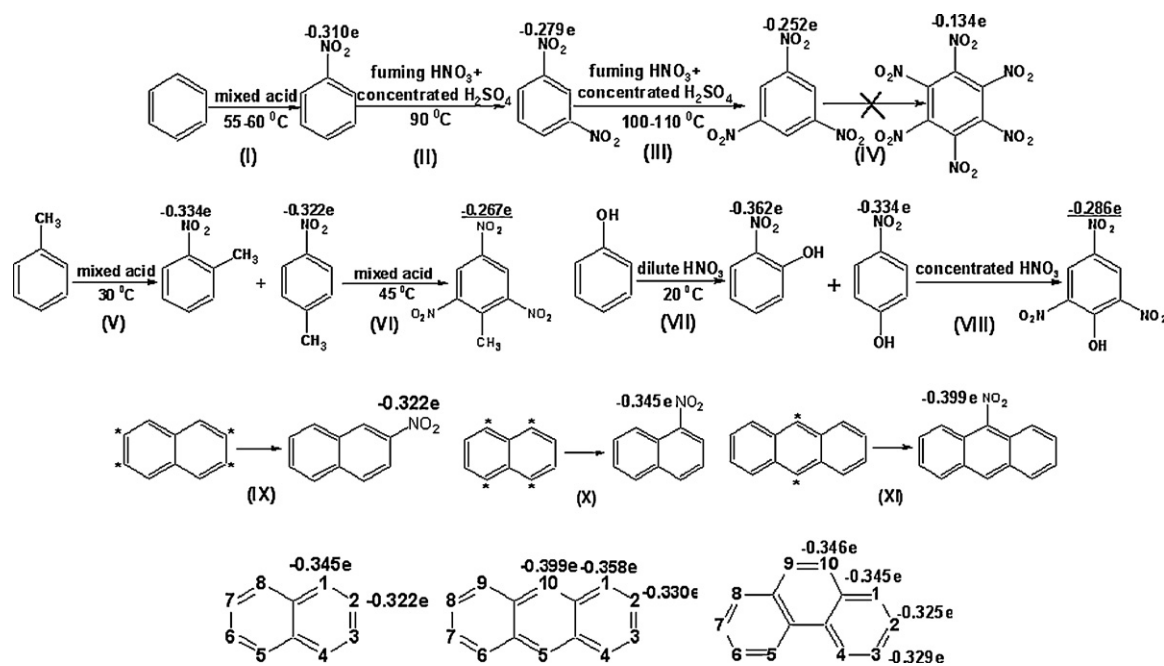
Fig. 6. Q_{Nitro} of nitrating products and the reactivity of aromatic hydrocarbons.

Table 5
Dependence of azide group charges and impact sensitivities in azide compounds

Azide	Q_{N_3} (e)	Impact sensitivity			
		Work (kg m cm^{-2})	Drop weight (mg)	Upper limit (cm)	Lower limit (cm)
Cu(N$_3$)$_2$	−0.628	Most sensitive	600	70	70
Hg(N$_3$)$_2$	−0.826		600	80	70
CuN$_3$	−0.914	2.66	600	125	70
Pb(N$_3$)$_2$	−0.956	4.76	975	235	65–70
Ba(N$_3$)$_2$	−0.981	7.70			
Sr(N$_3$)$_2$	−0.990	9.10			
AgN$_3$	−0.985	13.97	914	245	150
TlN$_3$	−1.057	16.18			
LiN$_3$	−0.995	No detonation			

3.5. Some limitations of NGCM

There are still some limitations for NGCM even though it has been proved to be a simple but effect tool to evaluate the nitro compounds' stability. These limitations can be summarized as following: (1) NGCM is applicable to the nitro compounds, of which stability are determined by chemical bonds linking nitro groups. Namely, NGCM is ineffective when the bond linking nitro group is not the weakest one in compound [1]; (2) for its application to the impact sensitivity of nitro explosives, it only considers explosive molecular structures, but overlooks the other characteristics still influencing impact sensitivity such as crystal, surface and interfacial structures, and so forth. In other words, the Q_{Nitro}–H_{50} correlation is rather rough; (3) because Q_{Nitro} is very sensitive to cal-

culation methods, any intertion of evaluation or comparison should be carried out using a same method.

4. Conclusions

The nitro group charge method, NGCM was established and applied to investigate the properties of nitro compounds including molecular stability, impact sensitivity and nitrating reaction. At first, for a given class of nitro compounds, the more negative Q_{Nitro} it has, and the stronger the C—Nitro bond becomes. Secondly, for all nitro explosives in which the R—Nitro bond is the weakest, the nitro group charges can be regarded as a structural parameter used to assess the impact sensitivity. The more negative Q_{Nitro} corresponds to the higher H_{50}. Thirdly, the conditions, the velocities

Table 6
Comparison of NGCM and other methods employed in explosive structure–sensitivity correlation researches

Method	Proposer	Applicability	Characteristics
Electrostatic potential	Politzer	According to group	Easy to calculate
Bond energy/length/order	Depluech and Cherville	According to group	Easy to calculate
Ability to donate electron	Bates	According to group	Easy to calculate
Ability to attract electron	Us	According to group	Easy to calculate
Oxygen balance	Kamlet and Adolph	According to group	Easy to calculate, but no consideration of molecular structure
Decomposition mechanism	–	Almost all nitro explosives	Difficult to calculate
Nitro group charge method (NGCM)	Zhang	Almost all nitro explosives	Easy to calculate

and the products' occurrence ratios of some nitrating reactions can be approximately evaluated using NGCM: the more negative Q_{Nitro} corresponds to the easier and faster the reaction, and the higher occurrence ratio. Meanwhile, this idea of charges on common atoms or groups can be extended to treat other covalent systems. In a word, NGCM is a simple but effective approach to understand, evaluate and predict some properties of nitro compounds even though there exit some limitations of it. A simple comparison of NGCM and other methods employed in the structure–sensitivity correlation researches on explosives are listed in Table 6.

Acknowledgement

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