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ORIGINAL PAPER

Theoretical prediction of the impact sensitivities of energetic C-nitro compounds

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Abstract

In order to design high-energetic and insensitive explosives, the frontier orbital energy gaps, surface electrostatic potentials, nitro group charges, bond dissociation energies (BDEs) of the C–NO_2 trigger bonds, and intermolecular interactions obtained by the M06-2X/6-311++G(2d,p) method were quantitatively correlated with the experimental drop hammer potential energies of 10 typical C-nitro explosives. The changes of several information-theoretic quantities (ITQs) in the density functional reactivity theory were discussed upon the formation of complexes. The BDEs in the explosives with six-membered ring are larger than those with five-membered ring. The frontier orbital energy gaps of the compounds with benzene ring are larger than those with *N*-heterocycle. The models involving the intermolecular interaction energies and the energy gaps could be used to predict the impact sensitivity of the C-nitro explosives, while those involving ΔS_S, ΔI_F, and ΔS_{GBP} are invalid. With the more and more ITQs, the further studies are needed to seek for a good correlation between impact sensitivity measurements and ITQs for the energetic C-nitro compounds. The origin of sensitivity was revealed by the reduced density gradient method.

Keywords C-nitro explosive · Impact sensitivity · M06-2X · RDG · Information-theoretic quantity

Introduction

The search of the new insensitive explosive has been one of the most popular topics in the field of energetic material in order to avoid the accidental explosion in use and cater to the military requirement [1–4]. Therefore, for a long time, much attention has been paid to the investigation into the relationship between the sensitivities and the X–NO_2 (X=C, N, and O) trigger-bond dissociation energies, frontier orbital energy gaps, nitro group charges or surface electrostatic potentials of the energetic compounds [5–12]. For example, Depluech et al. [13] believed that the shock wave sensitivity of nitro compounds was closely related to the electronic structure of molecules and some properties of the X–NO_2 trigger bonds, such as surface electrostatic potential, bond length, and bond strength. Mohammad et al. [14] established the relationship between structural parameters and the impact sensitivity of the nitrogen heterocyclic ring explosives. Zhu et al. [15] pointed out that the smaller the energy gap of high-energy crystals, the greater the sensitivity was.

In order to quantitatively evaluate the reactivity of molecules by the simple density functionals, in recent decades Liu et al. proposed density functional reactivity theory (DFRT) [16]. According to the Hohenberg-Kohn theorem of DFT, the exchange and correlation energies are closely related to the electron densities, and any chemical properties of the molecules in the ground state could be determined only by the electronic densities. Therefore, the molecular structures and chemical reaction activities should be attributed to only the electronic densities, which is the theoretical basis of DFRT. Thus, the different density functional forms could be directly used to quantitatively describe the reactivity of molecules in DFRT. Liu et al. have proved their practicability and effectiveness in quantifying regioselectivity, stereoselectivity, and other molecular reactivities so as to promote the development of the DFRT theory [16–22]. In combination with some quantities from the information-theoretic approach, Recently Rong et al. [23] reviewed the

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applications of DFRT to explain some chemical phenomena, such as the conformational stability, electrophilicity, nucleophilicity, covalent, and noncovalent interactions. These aroused our interest in whether the information-theoretic quantities (ITQs) can be used to evaluate and predict the sensitivity of explosives.

The C-nitro explosives are the most widely used energetic materials. The impact sensitivity is the most commonly used measure of the explosive sensitivities [1, 3]. There is always a serious contradiction between energy and impact sensitivity; i.e., the more the energy, the more the high impact sensitivity becomes [2]. In order to predict the impact sensitivity and design new high-energetic and insensitive C-nitro explosives, in this work, 10 typical C-nitro explosives (NTO, FOX-7, LLM-105, HNS, TATB, LLM-116, LLM-119, TNT, DNT, and ANPYO) were selected (see Fig. 1). The frontier orbital energy gaps, surface electrostatic potentials, nitro group charges, and bond dissociation energies (BDEs) of the X–NO_2 trigger bonds were quantitatively correlated with the drop hammer potential energies used to evaluate the impact sensitivities of explosives. As a new physical quantity developed in recent years, the changes of several ITQs in the density functional reactivity theory were discussed upon the formation of the complexes. The aim of this work is to find out a model suitable for the evaluation of the explosivesensitivity by comparing various models, and judge whether the ITQs could be used to evaluate and predict the sensitivity of explosives or not. These models will be used to evaluate and predict the impact sensitivity of C-nitro explosives. This theoretical investigation will be important for keeping, transporting, using, molecular design, and synthesis of the new and insensitive C-nitro explosives.

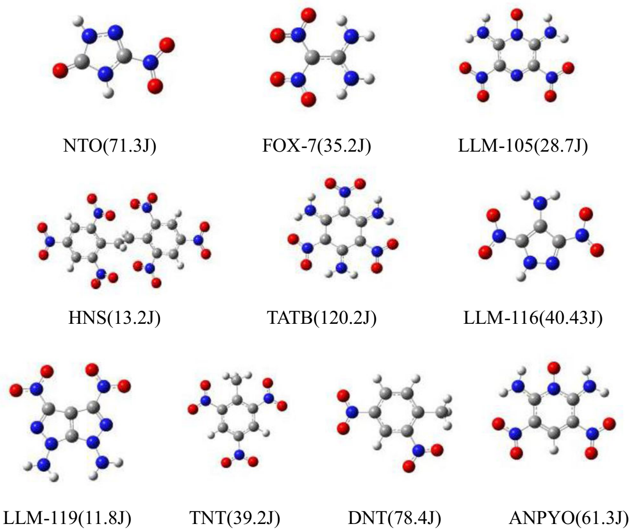

NTO(71.3J) FOX-7(35.2J) LLM-105(28.7J)
HNS(13.2J) TATB(120.2J) LLM-116(40.43J)
LLM-119(11.8J) TNT(39.2J) DNT(78.4J) ANPYO(61.3J)

Fig. 1 Molecular structure and impact sensitivity potential energy of ten C-nitro explosives

Computational details

All the monomers and complexes were fully optimized using the DFT-B3LYP/6-311++G(d,p) method, and the structures corresponding to the minimum energy points (NImag = 0) were obtained. The frontier orbital energy gaps, surface electrostatic potentials, nitro group charges, and BDEs were calculated with the MP2/6-311++G(2d,p) method. The plots of the RDG versus sign(λ_2)ρ were carried out at the MP2/6-311++G(2d,p) level. The experimental drop hammer potential energies of 10 C-nitro explosives came from the literatures [9, 11, 24]. All the calculations were completed by using the programs of Gaussian 09 [25]. The Multiwfn 3.4.1 program [26] and VMD [27] were utilized to calculate and analyze the ITQs by using the checkpoint file from the Gaussian calculations as the input file.

The interaction energies were calculated by evaluating the difference between the total energies of complex and monomer. The changes of the ITQs (signed as "ΔI_n") were calculated as follows:

$$\Delta I_n = (I_{\text{tot}} - nI_R)/n$$

where I_{tot} and I_R are the total information-theoretic quantity of the whole system and monomers, respectively. n is the number of molecules in the system.

Results and discussion

From Fig. 1, HNS, TATB, TNT, and DNT are high-energetic explosives with benzene ring structure, in which HNS has two benzene rings. Both TATB and TNT have a benzene ring structure and the same number of nitro groups, and the number of nitro groups in DNT is lower than that in TATB or TNT. NTO, LLM-105, LLM-116, LLM-119, and ANPYO have *N*-heterocyclic structure, among which LLM-105 and ANPYO are six-membered rings. LLM-116 and NTO is five-membered ring structure, and LLM-119 is composed of two five-membered rings juxtaposed. FOX-7 is made of carbon–carbon double bonds. Their structures and impact sensitivity potential energies ($E_{h_{50(\text{exp})}}$ see parentheses) are collected in Fig. 1.

Predictive models of the impact sensitivities

BDEs of the trigger bonds

The weakest bonds in high-energetic explosives, such as the trigger bonds C–NO_2, N–NO_2, and O–NO_2, are usually considered to be the important links in the explosive detonation. Therefore, the BDE of the weakest bond can be considered as the most direct criterion for the stability of explosives [10, 24, 28–31]. The BDE values of ten C-nitro explosives are shown in Table 1.

The BDE is fitted with the experimental impact sensitivity energy by the following functional relationship (1):

$$E_{h_{50}} = a \times \frac{\mathrm{BDE}}{b + \mathrm{BDE}} + \frac{c}{d + \mathrm{BDE}} + e \times \mathrm{BDE} \tag{1}$$

where $a = 15.45$, $b = -64.81$, $c = 1592.1$, $d = -166.7$, $e = 0.021$, and the correlation coefficient $R = 0.837$. The fitting results are shown in Fig. 2. The differences between the experimental $E_{\mathrm{h}_{50}}$ and predicted values by the relationship (1) are collected in Table 2. The RMS deviation of the results from experiment is up to 17.7 J. The differences between the experimental $E_{\mathrm{h}_{50}}$ and predicted values for NTO, FOX-7, LLM-105, HNS, TATB, and LLM-116 are small, no more than 5.0 J. However, the differences for LLM-119, TNT, DNT, and ANPYO are larger, more than 15.0 J, and even up to 42.8 for DNT. The DNT and ANPYO predictions are lower than the measured values, while those for LLM-119 and TNT are higher than the measured values.

Nitro charges

The more the negative charge on the nitro group, the greater the h_{50} of the nitro compounds and the lower the sensitivity [8–10]. Therefore, it is a good method to predict and evaluate the sensitivity of nitrogen-containing dynamites with nitro charge. The nitro charges Q_{nitro} are shown in Table 1.

The relationship between the nitro charges and the experimental impact sensitivity energies is fitted by the following function (2).

$$E_{h_{50}} = a \times \frac{Q_{\mathrm{nitro}}}{b + Q_{\mathrm{nitro}}} + \frac{c}{d + Q_{\mathrm{nitro}}} + e \times Q_{\mathrm{nitro}} \tag{2}$$

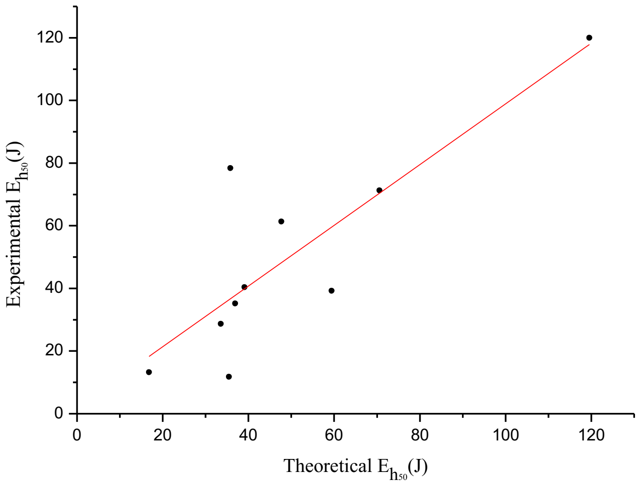


Fig. 2 The curve of theoretical impact sensitivity energy calculated by BDE and experimental impact sensitivity energy

where $a = -0.431$, $b = 0.251$, $c = 5.020$, $d = 0.412$, $e = 2.857$, and the correlation coefficient $R = 0.916$. The fitting results are shown in Fig. 3. The differences between the experimental and predicted impact sensitivity energies are collected in Table 2. The RMS deviation of the results from experiment is up to 13.1 J. For TATB, LLM-119, and DNT, the predicted values are very close to the experimental results, with the difference no more than 1.0 J. The largest deviations from experiment are the values for NTO and TNT, and the NTO prediction is lower than measured values by 22.7 J, while the prediction for TNT is too high by 18.1 J.

Table 1 The BDE (kJ/mol), Q_{nitro}(e), energy gap between HOMO and LUMO (ΔE, Hartree), maximum electrostatic potential of the C–NO_2 bond (kcal/mol) of ten C-nitro explosives

Compound	BDE	Q_{nitro}	ΔE	$V_{\max}$
NTO	78.77	− 0.315	0.139	33.103
FOX-7	315.06	− 0.316	0.129	23.763
LLM-105	577.61	− 0.288	0.143	28.713
HNS	105.02	− 0.219	0.114	36.444
TATB	183.79	− 0.371	0.158	26.541
LLM-116	288.81	− 0.325	0.133	27.699
LLM-119	341.32	− 0.257	0.130	21.686
TNT	1995.38	− 0.221	0.181	36.490
DNT	761.40	− 0.249	0.185	30.480
ANPYO	1417.77	− 0.306	0.121	29.660

Energy gaps

The smaller the energy gap of the compound, the greater the sensitivity, and the easier it is to initiate thermal decomposition and detonation [32–35]. The energies of HOMO and LUMO and energy gaps are shown in Table 1.

The energy gaps were fitted with the experimental value of the impact sensitivity energy, and the relationship between them was given by Eq. (3).

$$E_{h_{50}} = \mathrm{a} \times \frac{\Delta E}{\mathrm{b} + \Delta E} + \frac{c}{d + \Delta E} + e \times \Delta E \tag{3}$$

where $a = 0.503$, $b = -0.147$, $c = 0.067$, $d = -0.118$, $e = 306.0$, and the correlation coefficient $R = 0.922$. The fitting results are shown in Fig. 4. From Table 2, the RMS deviation of the results from experiment is lower than that from the model involving BDE or Q_{nitro}. Except for ANPYO and HNS, the differences between the experimental and predicted values are more than 5.0 J. The largest deviations from experiment are the values for FOX-7, TNT, and DNT. For FOX-7 and TNT, the predictions are higher than the measured values by 23.4 and 20.1 J, respectively, while the DNT prediction is lower than the measured values by 15.7 J.

Table 2 Differences between the predicted and experimental $E_{h_{50}}$ values (J) for the models involving the BDE, Q_{nitro}, energy gap between HOMO and LUMO (ΔE), maximum electrostatic potential of the C–NO$_2$ bond (V_{max}) of ten C-nitro explosives as well as the intermolecular interaction in their dimers ($E_{int.}$), and RMS deviation (J)

	Model (BDE)	Model (Q_{nitro})	Model (ΔE)	Model (V_{max})	Model ($E_{int.}$)
NTO	1.5	−22.7	−5.7	5.5	−24.8
FOX-7	3.5	15.3	23.4	−1.4	0.3
LLM-105	4.5	7.5	−7.4	19.9	16.5
HNS	4.3	15.3	4.3	11.5	-
TATB	−1.6	−0.6	−6.6	2.4	1.0
LLM-116	1.87	−11.73	−9.23	−15.13	10.87
LLM-119	23.4	0.8	5.4	19.4	0.2
TNT	21.0	18.1	20.1	8.3	9.0
DNT	−42.8	−0.8	−15.7	−26.1	0.9
ANPYO	−15.7	−14.5	1.0	−12.0	−12.0
RMS	17.7	13.1	12.1	14.4	11.1

Zhu et al. [15] only analyzed the energy gap as the criterion of impact sensitivity, but the quantitative relationship between energy gap and impact sensitivity was not given. Moreover, the quantitative relationship between impact sensitivity and energy gap of C-nitro explosives has not been established in previous studies.

Surface electrostatic potentials

Electrostatic potential is a widely used method to study molecular properties. Politzer, Murray, and Rice [36] had shown that the surface electrostatic potential on the surface of the molecule had a certain relationship with the impact sensitivity of the explosives. With the increase of the positive surface electrostatic potential on the surface, the sensitivity of the explosives increases and the h_{50} decreases. Therefore, the impact sensitivity of explosive molecules has a certain quantitative relationship with surface electrostatic potential [37, 38].

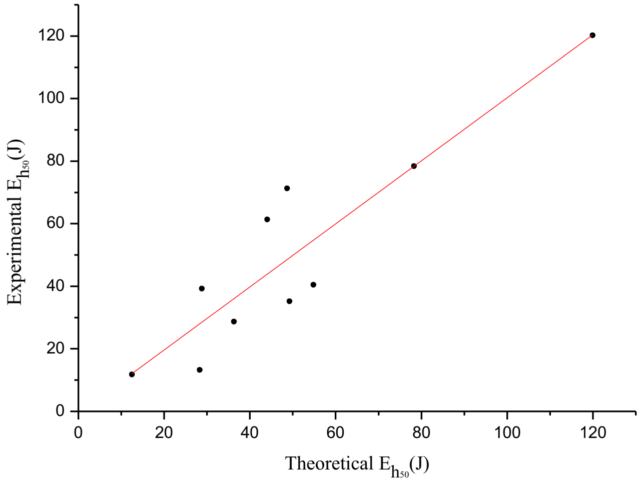


Fig. 3 The curve of theoretical impact sensitivity energy calculated by nitro charge and experimental impact sensitivity energy

Figure 5 illustrates the surface electrostatic potentials of ten C-nitro explosive molecules with 0.001 electron/bohr^3 isosurface of electron density. The colors range from −55.0 to 55.0 kcal mol^{-1}, with red denoting extremely electron deficient regions and blue denoting electron rich regions.

From Fig. 5, there are obvious blue region on the periphery of all the molecules, corresponding to the maximum value of the nitrogen negative surface electrostatic potential. Much of the red region is over the C–NO$_2$ bonds for each of the molecules, showing the electron deficient feature of the C–NO$_2$ bonds. It indicates that there is a maximum of positive surface electrostatic potential at the top of C–NO$_2$, which is consistent with the research of many previous investigations. That is, the larger the surface electrostatic potential value of the chemical bond, the weaker the chemical bond [39–41]. In the process of initiation, it is easy to break and thus becomes the triggering bond. The maximum surface electrostatic potentials are shown in Table 1.

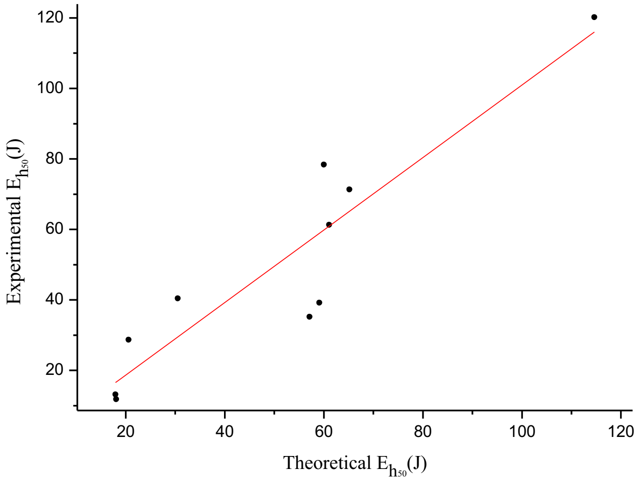


Fig. 4 The curve of theoretical impact sensitivity energy calculated by energy gaps and experimental impact sensitivity energy

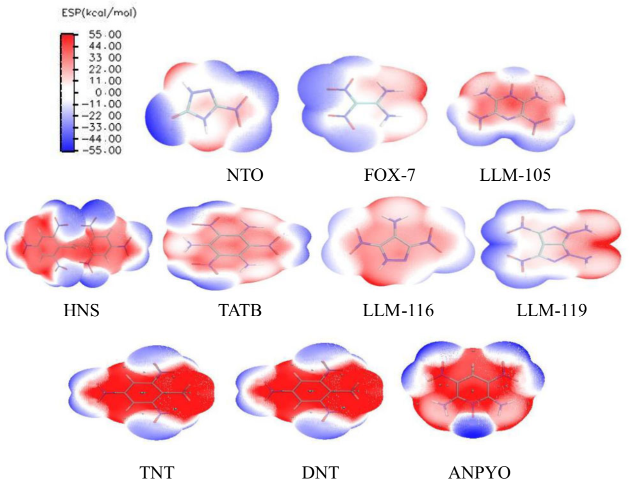


Fig. 5 The surface electrostatic potential and molecular structure of ten C-nitro explosives

The maximum surface electrostatic potential of the C–NO_2 bonds was fitted with the experimental value of impact sensitivity energy, and the relationship between them was given by Eq. (4).

$$E_{h_{50}} = a \times \frac{V_{\max}}{b + V_{\max}} + \frac{c}{d + V_{\max}} + e \times V_{\max} \tag{4}$$

where $a = -1.299$, $b = -34.58$, $c = 4.311$, $d = -26.49$, $e = 1.367$, and the correlation coefficient $R = 0.901$. The fitting results are shown in Fig. 6. The RMS deviation is lower than that from the model involving BDE while higher than that involving Q_{nitro} or ΔE (see Table 2). Except for FOX-7 and TATB, the differences between the experimental and predicted values are more than 5.5 J. The largest deviations from experiment are the values for DNT, LLM-105 and LLM-119. For DNT, the predictions are lower than the measured values by 26.1 J., while for LLM-105 and LLM-119, the predictions are higher than the measured values by about 19.0 J.

The quantitative relationship between impact sensitivities and maximum surface surface electrostatic potentials established by Rice et al. is unreliable because of their small correlation coefficient (0.80) [12].

Intermolecular interaction energies

The intermolecular interaction energies of the system can be used to analyze and explain the interactions between the systems and serve as a criterion for intermolecular stability. The smaller the intermolecular interaction energy, the more stable the structure, the lower the sensitivity, and the larger the h_{50} of the compounds. Here, we establish the model involving the intermolecular interaction energies with BSSE.

The intermolecular interaction energies and the experimental impact sensitivity energies are fitted by the following functional relationship (5):

$$E_{h_{50}} = a \times \frac{E_{\mathrm{int}}}{b + E_{\mathrm{int}}} + \frac{c}{d + E_{\mathrm{int}}} + e \times E_{\mathrm{int}} \tag{5}$$

where $a = 53.91$, $b = -4.14$, $c = 1.65$, $\mathrm{d} = -65.90$, $e = -0.52$, and the correlation coefficient $R = 0.924$. The fitting results are shown in Fig. 7. From Table 2, the RMS deviation is lowest, only 11.1 J. Furthermore, for FOX-7, TATB, LLM-119, and DNT, the experimental $E_{h_{50}}$ and predicted values are very close to each other, with the difference no more than 1.0 J. The largest deviations from experiment are the values for NTO and LLM-105, and the NTO prediction is lower than measured values by 24.8 J, while the prediction for TNT is too high by 16.5 J.

From Table 1, the order of BDEs of ten high-energetic explosives is TATB > ANPYO > LLM-119 > DNT > LLM-

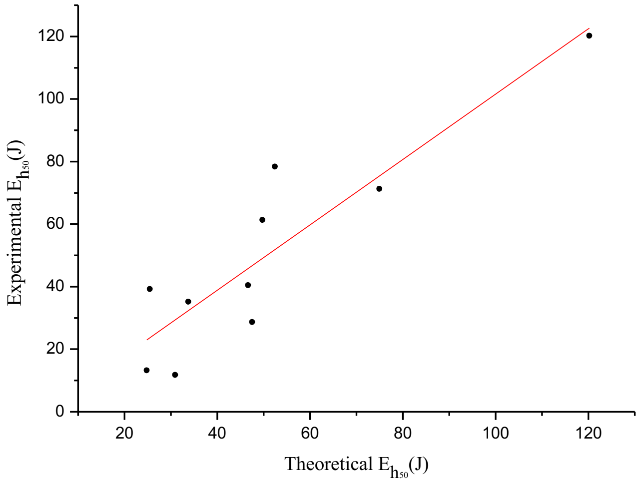


Fig. 6 The curve of theoretical impact sensitivity energy calculated by maximum surface electrostatic potential and experimental impact sensitivity energy

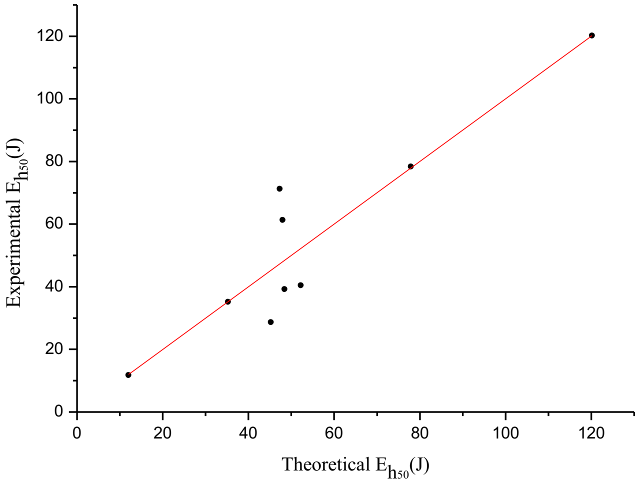


Fig. 7 The curve of theoretical impact sensitivity energy calculated by intermolecular interaction energy and experimental impact sensitivity energy

105 > HNS > FOX-7 > TNT > LLM-116 > NTO. It indicates that the BDEs in the C–NO_2 explosives with the six-membered ring are larger than those with five-membered ring in most cases. The values of nitro charges follow the order of TATB > LLM-116 > FOX-7 > NTO > ANPYO > LLM-105 > LLM-119 > DNT > TNT > HNS. It is shown that the nitro charges of N-heterocyclic ring are usually larger than that of benzene ring, but TATB is an exception. The order of the values of frontier orbital energy gaps is DNT > TNT > TATB > LLM-105 > NTO > LLM-116 > LLM-119 > FOX-7 > ANPYO > HNS. It indicates that the frontier orbital energy gaps of the C-nitro compounds with benzene ring are larger than those with *N*-heterocycle, followed by FOX-7, and the more the number of the nitro groups, the smaller the frontier orbital energy gaps are. According to the data of maximum surface electrostatic potentials, it is shown that the more the number of the nitro groups and, simultaneous, the less the number of the NH_2 groups, the lager the maximum surface electrostatic potentials become.

From models 1~5, the correlation coefficient in the model involving the intermolecular interaction energies is the largest, followed by the model involving the energy gaps. Thus, the models involving the intermolecular interaction energies and the energy gaps could be used to predict the impact sensitivity of C-nitro explosives. In fact, it has been shown many investigations that the intermolecular interaction influenced greatly the sensitivity of highly energetic compounds [42]. It is worth mentioning that and the frontier orbital energy gap reflects the global property of the energetic C-nitro compounds, while the trigger-bond dissociation energy, nitro group charge, and the maximum surface electrostatic potential of the C–NO_2 bond represent only the local property. Therefore, the sensitivity of the C–NO_2 explosive should be attributed to the intermolecular interaction and global property of the molecule. Politzer et al. have found that the global properties, such as the molecular surface electrostatic potentials, are one of the important factors that affect the sensitivities of energetic materials [6]. It is worth mentioning that although the plots of the computed versus experimental impact sensitivities are useful, the correlation does not imply causation. As mentioned by Brill, James [43], and Rice [12], the correlation studies should not be used for the interpretation of mechanistic details. Rather, the correlation studies should be used to identify the molecular properties that indicated the sensitivity to impact.

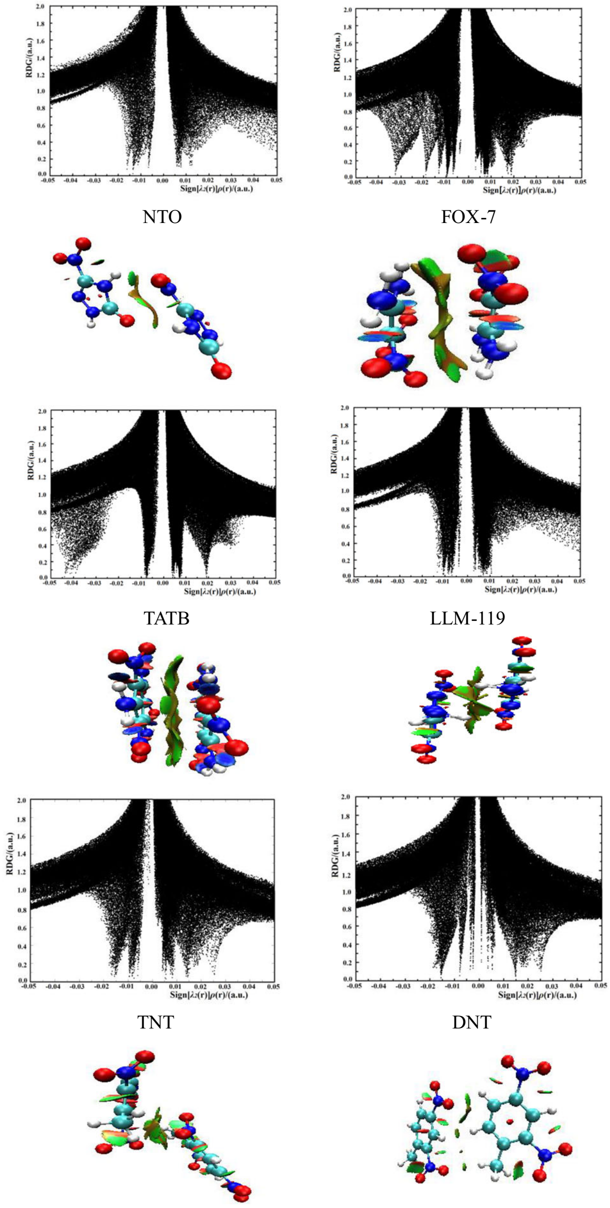
RDG analysis

In order to further reveal the nature of the effect of the intermolecular interaction on the explosive sensitivity, the reduced density gradient (RDG) [44] was analyzed. RDG can be used to explore the features associated with the intramolecular interactions in real space based on the electron density. It is defined as Eq. (6):

$$\mathrm{RDG} = \frac{1}{2(3\pi^2)^{1/3}} \frac{|\nabla\rho(r)|}{\rho(r)^{4/3}} \tag{6}$$

Figure 8 depicts the plots of RDG versus sign($\lambda_2(r)\rho$(r)) for the NTO, FO7, TATB, LLM-119, TNT, and DNT dimer complexes calculated and plotted by the Multiwfn suite and VMD programs.

As can be seen from Fig. 8, the plot includes two parts: left ($\lambda_2 < 0$) and right ($\lambda_2 > 0$). The top left-side and right-side points (small density and large reduced gradient) correspond to the exponentially decaying tail regions of the density, i.e., far from the nuclei.



NTO FOX-7

TATB LLM-119

TNT DNT

Fig. 8 RDG diagrams of six dimer molecules and corresponding RDG isosurface diagrams

Table 3 The changes of the information-theoretic quantities, i.e., Shannon entropy S_S, Fisher information I_F, and Ghosh–Berkowitz–Parr entropy S_{GBP} (in a.u.) in the dimers (in plain) and trimers (in italics)

	S_S		I_F		S_{GBP}	
NTO	− 0.23319	*− 0.27408*	− 1.49774	*− 1.83355*	− 0.19208	*− 0.24166*
FOX-7	− 0.38731	*− 0.37485*	− 2.33706	*− 2.41353*	− 0.38257	*− 0.37323*
LLM-105	− 0.13986	*− 0.18227*	− 1.08432	*− 1.41789*	− 0.14139	*− 0.18517*
TATB	−0.58138	*− 0.58809*	− 3.62587	*− 3.73551*	− 0.58581	*− 0.57461*
LLM-116	− 0.13491	*− 0.21414*	− 1.01884	*− 1.59734*	− 0.13306	*− 0.20588*
LLM-119	− 0.52364	*− 0.69226*	− 3.40182	*− 4.35965*	− 0.52307	*− 0.67562*
TNT	− 0.21852	*− 0.65595*	− 1.34611	*− 3.99511*	− 0.20537	*− 0.66149*
DNT	− 0.45381	*− 0.5545*	− 2.59414	*− 3.25972*	− 0.42486	*− 0.52554*
ANPYO	− 0.13337	*− 0.18257*	− 1.01451	*− 1.39527*	− 0.13245	*− 0.18219*

According to Johnson et al. [44], $\lambda_2 < 0$ and $\lambda_2 > 0$ mean the bonded and non-bonded interactions, respectively. The negative and positive values of sign(λ_2)ρ for the spikes are the indicatives of attractive and repulsive interactions, respectively. Most important for our present consideration is the region in low density and low gradient. For the left-side, several spikes lying at negative value are found in the low density and low gradient region, a signature of noncovalent interactions between dimer molecules. The strong intramolecular interactions between nitro-group and amine-group of FOX-7 and TATB dimer molecules correspond to the region of − 0.035 ~ −0.030 a.u. and − 0.050 ~ − 0.035 a.u. respectively. So the impact sensitivity of the TATB is the lowest. The repulsion and steric effect of FOX-7 are stronger than that of TATB, so the impact sensitivity of FOX-7 is higher than TATB. The other dimer molecules have no strong intramolecular interactions. The intermolecular H-bonding interactions correspond to the density values of − 0.020 ~ − 0.010 a.u. (NTO), − 0.020 ~ − 0.010 a.u. (FOX-7), − 0.015 ~ − 0.010 a.u. (LLM-119), − 0.020 ~ − 0.015 a.u. (TNT), and − 0.020 ~ − 0.015 a.u. (DNT), respectively. The TATB dimer molecule has very strong intermolecular H-bonding interaction, so its density values between − 0.050 and − 0.035 a.u. The moderate density values indicate that the intermolecular H-bonding interactions between nitro-groups and amine-groups of different single molecule are not strong. LLM-119 dimer molecule has the weakest intermolecular H-bonding interaction and strong repulsion and steric effect, so the impact sensitivity of LLM-119 explosive is the highest. The density values between − 0.010 a.u. and − 0.005 a.u. (low reduced gradient) for all dimer molecules show the van der Waals interactions. The points on the bottom right side (density values of 0.050~0.025 a.u. and low reduced gradient) correspond to the covalent bonds, the repulsion, or steric effect in dimer molecules for all dimer molecules. For TNT and DNT, their intramolecular and intermolecular H-bonding interactions are equivalent, but the repulsion and steric effect of TNT are stronger than DNT, which reflects that the impact sensitivity of TNT is higher than DNT. Therefore, the RDG analysis of C-nitro explosives dimer molecules can theoretically evaluate the impact sensitivity of C-nitro explosives.

For the RDG isosurfaces, the red shows the repulsions and steric effects in the rings or among the groups or chemical bonds, while the blue and green isosurface corresponds to the attractive intermolecular or intramolecular interactions. From Fig. 8, the weak intermolecular H-bonding and vdW interactions are dominant in all the dimers. In FOX-7 and TATB dimers, except for the weak interactions, the intermolecular strong H-bonds are found.

Analysis of ITQs

Upon the formation of the complexes, the changes of the ITQs, i.e., Shannon entropy S_S, Fisher information I_F, and Ghosh–Berkowitz–Parr entropy S_{GBP}, are collected in Table 3. All the values are negative, indicating that the ITQs are increased. Shannon entropy is a measure of electron density delocalization, and Fisher information is a descriptor of the electron density localization [19, 45–48]. Therefore, both the electron density delocalization and localization are enhanced upon the formation of the complexes of the energetic C-nitro compounds. S_{GBP} is closely related to $t(r,\rho)$ and $t_{TF}(r,\rho)$. According to Liu et al. [19, 24, 47, 48], $t(r,\rho)$ is the kinetic energy density, which is related to the total kinetic energy, and $t_{TF}(r,\rho)$ is the Thomas-Fermi kinetic energy density without any external force. The larger the value of $t(r,\rho)$ and simultaneously the smaller the value of $t_{TF}(r,\rho)$, the larger the value of S_{GBP} becomes. Therefore, upon the formation of the complexes of the energetic C-nitro compounds, the kinetic energy densities might be increased while the Thomas-Fermi kinetic energy densities might be decreased. From Table 3, the values of ΔS_S, ΔI_F, and ΔS_{GBP} in the trimers are larger than those in the dimers of the energetic C-nitro compounds. These results show that in comparison with the dimers, for the trimers, both the electron density delocalization and localization of $(TNT)_{12}$ are more notable, and the kinetic energy densities are larger while the Thomas-Fermi kinetic energy densities are lower.

The change of the electron density has a great influence on the stability of molecules. Therefore, the sensitivities of the energetic C-nitro compounds should be closely related to the ITQs ΔS_S, ΔI_F, and ΔS_{GBP}. Unfortunately, however, the correlation coefficients of all the relationships between the impact sensitivities and ΔS_S, ΔI_F, and ΔS_{GBP} are very small; only 0.62, 0.58, and 0.67 for the dimers; and 0.36, 0.69, and 0.43 for the trimers, respectively. These models did not adequately predict impact sensitivities of the energetic C-nitro compounds. With the more and more experimental data of h_{50} and the more and more ITQs, the further studies are needed to seek for and establish a better correlation between impact sensitivity measurements and ITQs for the energetic C-nitro compounds. In fact, up to now, only three kinds of models are considered feasible to predict impact sensitivities of the explosives: one is the molecular surface electrostatic potential (global property), two others being the free space of per molecule in the crystal lattice, and the maximum available heat of detonation [49, 50].

Conclusions

In order to predict the impact sensitivity and design new high-energetic and insensitive C-nitro explosives, in this work, 10 typical C-nitro explosives (NTO, FOX-7, LLM-105, HNS, TATB, LLM-116, LLM-119, TNT, DNT, and ANPYO) were selected. The frontier orbital energy gaps, surface electrostatic potentials, nitro group charges, BDEs of the X–NO_2 trigger bonds, and intermolecular interactions were quantitatively correlated with the drop hammer potential energies used to evaluate the impact sensitivities of explosives. As a new physical quantity developed in recent years, the changes of several ITQs in the density functional reactivity theory were discussed upon the formation of the complexes.

In most cases, the C-NO_2 BDEs in the explosives with the six-membered ring are larger than those with five-membered ring.

The frontier orbital energy gaps of the C-nitro compounds with benzene ring are larger than those with N-heterocycle, followed by FOX-7, and the more the number of the nitro groups, the smaller the frontier orbital energy gaps are.

The values of nitro group charges follow the order of TATB > LLM-116 > FOX-7 > NTO > ANPYO > LLM-105 > LLM-119 > DNT > TNT > HNS.

The more the number of the nitro groups and, simultaneous, the less the number of the NH_2 groups, the larger the maximum surface electrostatic potentials become.

Several good quantitative relationships between the frontier orbital energy gaps, nitro group charges, BDEs, maximum surface electrostatic potentials, intermolecular interaction energies, and the impact sensitivities h_{50} were obtained. The fitting effect of impact sensitivity energy and intermolecular interaction energy is the best ($R = 0.924$), followed by the frontier orbital energy gap ($R = 0.922$).

The models involving the intermolecular interaction energies and the energy gaps could be used to predict the impact sensitivity of the C-nitro explosives, while those involving ΔS_S, ΔI_F, and ΔS_{GBP} are invalid. With the more and more ITQs, the further studies are needed to seek for a good correlation between impact sensitivity measurements and ITQs for the energetic C-nitro compounds. The origin of sensitivity was revealed by the reduced density gradient method.

Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest.

Ethics statement We allow the journal to review all the data, and we confirm the validity of results. There is none of the financial relationships. This work was not published previously, and it is not submitted to more than one journal. It is also not split up into several parts to submit. No data have been fabricated or manipulated.

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