

# Insight into shock-induced chemical reaction from the perspective of ring strain and rotation of chemical bonds

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**Abstract** Density functional theory BLYP/DNP and hyperhomodesmotic equations were employed to calculate ring strain energy, the bond dissociation energy of X–NO<sub>2</sub> (X=C, N) and the charges on the nitro groups of several four-membered and six-membered heterocycle compounds. BLYP/DNP and LST/QST + CG method were also applied to calculate bond rotational energy of X–NO<sub>2</sub> (X=C, N) of above mentioned compounds. It indicated that ring strain energy of four-membered heterocycle nitro compounds is apparently higher than that of six-membered heterocycle nitro compounds. Predictably, ring-opening reactions may preferentially occur for those compounds containing higher ring strain energy under shock. In addition, C–NO<sub>2</sub> bonds in these compounds may rotate easier than N–NO<sub>2</sub> bonds in response to the external shock. As for N–NO<sub>2</sub> bonds in these compounds, they also respond to the external shock by the rotation of N–NO<sub>2</sub> bonds, once to the saddle point of the rotational energy barrier, the whole molecule will become relaxed, N–NO<sub>2</sub> bond becomes weaker and eventually leads to the breakage. When one –C=O, –C=NH or –NH<sub>2</sub> group is introduced to the six-membered heterocycle, the charges on the nitro groups of the new compound decrease drastically, and ring strains increase remarkably. It can be predicted that the new

compounds will be more sensitive to shock, and the viewpoint is confirmed by the experimental results of shock sensitivity (small scale gap test) of several explosives.

**Keywords** Hyperhomodesmotic equations · Shock-induced reaction · Ring strain energy · Energy of bond rotation · Small scale gap test

## Introduction

Detonation of explosives initiated by shock wave involves a complicated physical and chemical process. Kuklja [1] argued that the energy gap is reduced with the compression caused by shock wave and eventually results in electron excitation and the breakage of a chemical bond. Fayer and Dlott [2] considered that the mechanical energy caused by shock wave is coupled to intramolecular vibrational modes by the way of phonon up pumping. Nanoshocks recommended by Dlott [3] are tiny but powerful laser-driven shock waves that can be used to produce large-amplitude compression in molecular materials on the picosecond time scale. When coupled with ultrafast molecular spectroscopy, the molecular response to nanoshocks can be probed in detail. Now nanoshocks are used to study shock-induced chemical reactions of energetic materials. Raman spectrum, an efficient measure to study shock-initiated chemistry, has been employed by McNesby and Coffey [4] to illustrate the relationship between shock sensitivity and molecular structures. A multidimensional reactive flow models of shock initiation and detonation of solid explosives was developed by Tarver [5]. It starts from the multiphonon up-pumping, early unimolecular reactions channel most of the available energy into excited vibrational states of intermediate product species. The intermediate products transfer some of their vibrational energy back into the transition

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states, accelerating the overall reaction rates. As the decomposition progresses, the highly vibrationally excited diatomic and triatomic molecules formed in very exothermic chain reactions are rapidly vibrationally equilibrated by “supercollisions”, which transfer large amounts of vibrational energy between these molecules. The induction period for the initial endothermic bond breaking reaction can be calculated using the high-pressure, high-temperature transition state theory. “Trinitrotoluene Route” was also proposed by Dubikhin [6] and experimentally was verified on thermal decomposition and detonation of TNT by Bulusu (by means of DKIE) [7]. Zeman and Varga [8] have verified this mechanism by means of mutual comparison of the results of 2,4,6-trinitrotoluene initiation by heat and by shock wave. Lowest singlet-triplet inter-system crossing in molecular nitromethane, nitramine, and nitric acid was performed according to *ab initio* complete active space self-consistent field (CAS SCF) wave functions by Manaa and Fried [9]. The lowest triplet state of these molecules exhibits a minimum equilibrium structure where the nitro group is no longer coplanar with the X (C, N, O) atom, in contrast to the equilibrium geometry of the ground-state singlets. CAS SCF and density functional theory (DFT) fully optimized triplet potential energy curves confirm that the triplets are adiabatically bound with respect to X–(NO<sub>2</sub>) bond dissociation pathway. Field, Dick and Gupta [10–12] considered that when a shock wave front passes through a molecular solid, a molecule will change its geometry to disperse this energy pulse.

A rational design strategy of high energy molecule is to build rings or cages. Ring opening or cage opening of a high energy molecule will release extra strain energy under the condition of shock wave, and the high performance is realized. But the performance and the stability could not be possessed simultaneously. Therefore, the purpose of this paper is to illustrate the response mechanism of high energy molecules from the view of strain energy and do something for the design of novel high energy molecules containing both high performance and low sensitivity to shock.

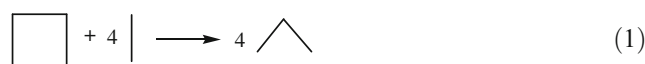
In this paper TNAZ (1,3,3-trinitroazetidine), DNAD (1,3-dinitro-1,3-diazetidine), and TNCB (1,1,3,3-tetranitrocyclobutane) were exemplified to study ring strain energy of four-membered energetic heterocycle derivatives and the rotational energy of C–NO<sub>2</sub> and N–NO<sub>2</sub> bonds, followed by the comparative studies of RDX (1,3,5-trinitro-1,3,5-triazacyclohexane), DNNC (1,3,5,5-tetranitrohexahydropyrimidine) and K6 (2-oxo-1,3,5-trinitro-1,3,5-triazacyclohexane) six-membered energetic heterocycle derivatives. This consideration is expected to reveal (i) the different responses to shock of four-membered and six-membered energetic heterocycle derivatives and the contribution to shock initiation by ring strain energy; (ii) the different responses to shock of nitramine and gem-dinitro energetic heterocycle derivatives in terms of the different rotational energy of N–NO<sub>2</sub> and C–

NO<sub>2</sub> bonds; and (iii) how the ring strain energy is influenced by the introduction of a carbonyl group or an imino group to the four-membered or six-membered heterocycle.

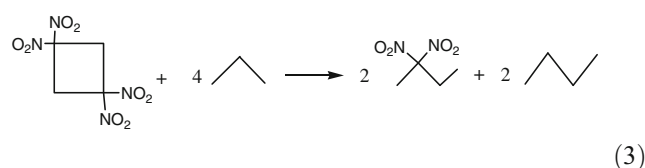
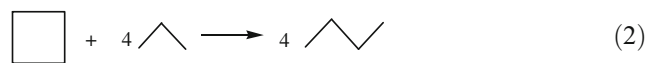
## Reaction design and discussion

All of the electronic structure calculations were performed using the DMol3 [13, 14] numerical-based density-functional computer software implemented in the Materials Studio Modeling 3.0 package [15] distributed by Accelrys, Inc. Geometrical optimizations were obtained by using the BLYP [16, 17] general-gradient potential approximation in conjunction with the double-numerical plus polarization basis set which was denoted as DNP. Although application of DFT methods to the study of initiation of energetic materials is very limited, and conclusions on the basis of conformation of isolated molecules neglect very important crystal-lattice effects that are vital in the determination of explosive properties; as papers of Vavra et al. [18, 19] show, approach on this base might be acceptable for relatively simple molecules, as are nitramines, also for compounds in our paper.

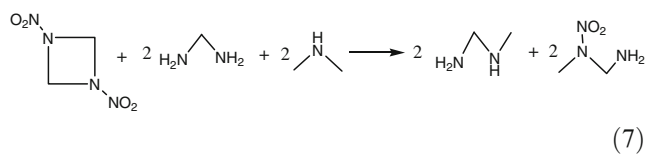
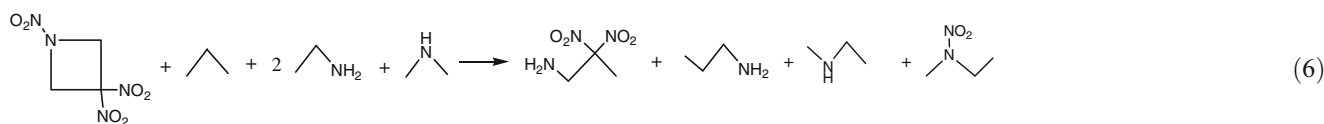
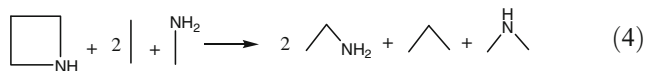
Homodesmotic and hyperhomodesmotic reactions [20–25] are usually applied to calculate ring strain energy, on each side of the equation both bond type and valence are kept the same, and this treatment may minimize systematic error. Firstly, the reliability of this kind of design should be verified. According to Eq. 1, ring strain energy can be calculated in terms of the difference of total energy on each side of the equation,  $E_S = \sum E_R - \sum E_P$ , where  $E_S$ ,  $E_R$  and  $E_P$  denotes strain energy, energy of reactant and energy of product in the homodesmotic or the hyperhomodesmotic reaction, respectively.



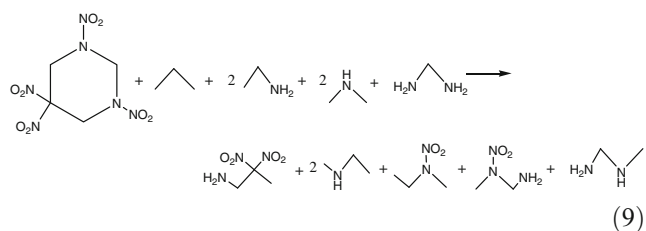
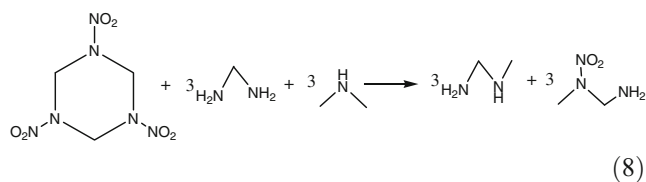
The calculated ring strain energy of cyclobutane in terms of homodesmotic reaction (1) is 153.0 kJ mol<sup>-1</sup>, higher than the reported value (110.8 kJ mol<sup>-1</sup>) [26]; A hyperhomodesmotic reaction (2) was then proposed to measure ring strain energy of cyclobutane, and the calculated result (107.9 kJ mol<sup>-1</sup>) is closed to the reported value. The similar reaction (3) was designed to calculate ring strain energy of TNCB, 123.6 kJ mol<sup>-1</sup>, 12.8 kJ mol<sup>-1</sup> higher than cyclobutane's.



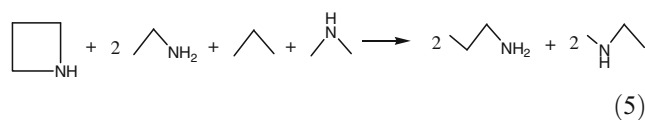
Homodesmotic reaction (4) and hyperhomodesmotic reactions (5) were put forward to compute the ring strain energy of azetidine firstly, the results indicated that the former is  $126.5 \text{ kJ mol}^{-1}$ ,  $21.2 \text{ kJ mol}^{-1}$  higher than the reported data, and the latter is  $101.3 \text{ kJ mol}^{-1}$ , closed to the reported value ( $105.3 \text{ kJ mol}^{-1}$ ) [22].



The above-mentioned designs and computations showed that hyperhomodesmotic reactions are reliable to calculate the ring strain energy, reactions (8) and (9) were also presented to investigate RDX and DNNC, their ring strain energy are  $88.2$  and  $79.8 \text{ kJ mol}^{-1}$ , respectively, much less than that of TNCB, TNAZ, and DNAD.

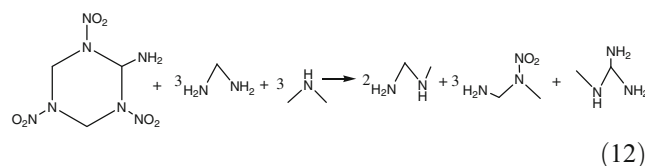
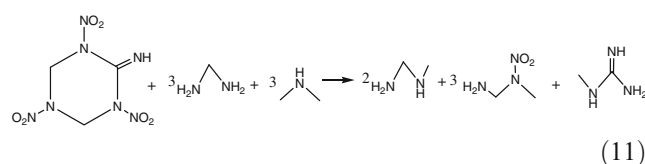
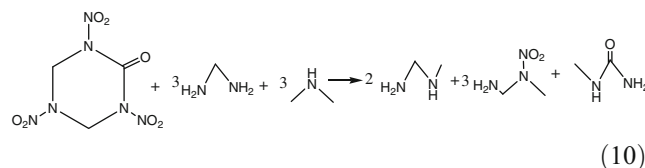


Modification of an existing high energy molecule is also a promising route for the design of novel energetic materials. Introducing a carbonyl group, or an imino group, or an amino group to a methylene of RDX, the change of ring strain energy may be studied according to the hyperhomodesmotic reactions (10)~(12). When a carbonyl group is



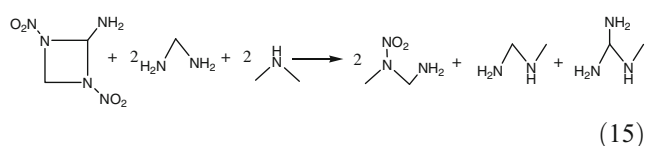
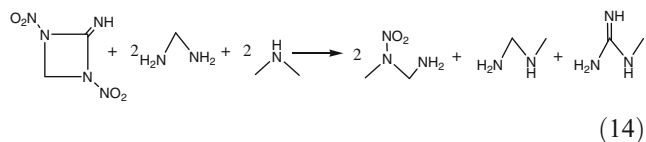
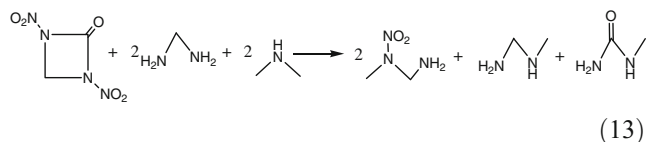
Hyperhomodesmotic reactions (6) and (7) were designed to compute the ring strain energy of TNAZ and DNAD,  $123.1$  and  $126.8 \text{ kJ mol}^{-1}$ , respectively. DNAD is hard to experimentally synthesize, this is more or less relevant to the ring strain energy. It was reported 1,3-diazetidine was synthesized by the means of photochemical method [27].

introduced to heterocycle of RDX, the new molecule is called K6 (keto-RDX), and the ring strain energy is  $223.9 \text{ kJ mol}^{-1}$ , far greater than that of RDX ( $88.2 \text{ kJ mol}^{-1}$ ); The introduction of an imino group also causes a drastic increase of ring strain energy (relative to RDX),  $106.1 \text{ kJ mol}^{-1}$ ; Only the introduction of an amino group leads to a slight increase,  $27.4 \text{ kJ mol}^{-1}$ .



Introducing a carbonyl group, or an imino group, or an amino group to replace a methylene of four-membered heterocycle DNAD, the ring strain energy may be calculated in terms of hyperhomodesmotic reactions (13)~(15). Similarly, the introduction of a carbonyl group, or an imino group may create an increase of  $103.8 \text{ kJ mol}^{-1}$  and  $71.0 \text{ kJ mol}^{-1}$

(relative to DNAD,  $126.8 \text{ kJ mol}^{-1}$ ), respectively. An interesting result is the introduction of an amino group, on the contrary, the ring strain energy ( $117.6 \text{ kJ mol}^{-1}$ ) decreases  $9.2 \text{ kJ mol}^{-1}$ .



It can be speculated that the introduction of a carbonyl group or an imino group to the azaheterocycle will lead to a drastic increase of ring strain energy and a ring-opening reaction under shock. However, the import of an amino group may decrease ring strain energy and increase the density of crystalline derivative, so the new derivative is expected to be an ideal energetic compound.

On the one hand, ring strain energy will contribute to the explosion heat of an energetic compound, because the decomposition of an energetic compound will release extra ring strain energy; On the other hand, high ring strain energy may result in high shock sensitivity, it is more easily to open the strained ring for the molecule with higher ring strain energy under shock. Therefore, evaluating ring strain energy may be helpful for the investigation of rational design, effective synthesis, even for the prediction of performance of novel energetic molecule.

C–NO<sub>2</sub> bond or N–NO<sub>2</sub> bond is often the weakest bond in aforementioned nitro compounds. These two chemical bonds will firstly respond to stimuli of shock, rotation round C–N or N–N bond may be the most specific reponse. The rotational bond with lower energy barrier will buffer impact energy and restore the relaxed molecule, but it is hard to restore for the one with higher energy barrier and it will lead to decomposition under shock.

### The energy barrier of bond rotation and Mulliken charges of nitro group

The idea that free rotation diminishes sensitivity was introduced by Kamlet [28] quite some time ago. Density

functional theory BLYP/DNP combined with LST/QST + CG [29] (Linear Synchronous Transition/Quadratic Synchronous Transition + Conjugate Gradient) was applied to compute bond rotational energy; Expression  $\text{BDE} = E_{\text{RX}} + E_{\cdot\text{NO}_2} - E_{\text{RXNO}_2}$  was employed to calculate bond dissociation energy (BDE) of RX–NO<sub>2</sub> (X=C or N), where  $E_{\text{RX}}$ ,  $E_{\cdot\text{NO}_2}$ , and  $E_{\text{RXNO}_2}$  denote the total energy of the radicals RX·, ·NO<sub>2</sub> and molecule RXNO<sub>2</sub>, respectively; Expression  $q_{\text{NO}_2} = q_{\text{N}} + q_{\text{O}} + q_{\text{O}'}$  (in terms of BLYP/DNP) was also used to compute Mulliken charges of nitro group. The results were showed in Table 1.

Table 1 shows that rotational energy barriers of N–NO<sub>2</sub> and C–NO<sub>2</sub> bond (in gem-dinitro) bond in aforementioned compounds range from 49.2 to 59.8  $\text{kJ mol}^{-1}$  and 6.5 to 23.1  $\text{kJ mol}^{-1}$ , respectively, that is, rotational energy barrier of a C–NO<sub>2</sub> bond (in gem-dinitro) is much lower than that of a N–NO<sub>2</sub> bond. It is worthy of note that the rotational energy barrier of N–NO<sub>2</sub> bonds located to *ortho*-position of carbonyl of K6 is 27.7  $\text{kJ mol}^{-1}$ , about half of the *para*-position N–NO<sub>2</sub> bonds'.

The calculation also indicates that the bond dissociation energy of N–NO<sub>2</sub> (or C–NO<sub>2</sub>) bonds reduces when the N–NO<sub>2</sub> (or C–NO<sub>2</sub>) bond revolves to the site of rotational energy barrier (energy maximum), which fits the expression  $\text{BDE} = \text{BDE}' + E_{\text{b}}$  (BDE' denotes bond dissociation energy of N–NO<sub>2</sub> (or C–NO<sub>2</sub>) involving in the state of energy maximum,  $E_{\text{b}}$  is rotational energy barrier). A high rotational energy barrier of N–NO<sub>2</sub> bond will lead to the breakage when the rotation of N–NO<sub>2</sub> bond occurs and it is hard to restore to state of the lowest energy, so the rotation of N–NO<sub>2</sub> bond

**Table 1** Rotational energy barriers of nitramines, bond dissociation energy of RX–NO<sub>2</sub> (X=C or N) and Mulliken charge changes of nitro groups

Name	Rotational bond	Rotational energy barrier (kJ/mol)	BDE (kJ/mol)	$q_{\text{NO}_2}$ (a.u)
DNAD	N–NO <sub>2</sub>	50.5	202.7	–0.137(–0.049)
TNAZ	N–NO <sub>2</sub>	49.2	178.0	–0.131(–0.039)
	C–NO <sub>2</sub>	6.5	194.5	–0.182(–0.176)
TNCB	C–NO <sub>2</sub>	9.9	204.4	–0.183(–0.181)
RDX	N–NO <sub>2</sub>	59.8	170.1	–0.104(–0.095)
DNNC	N–NO <sub>2</sub>	58.7	169.3	–0.102(–0.034)
	C–NO <sub>2</sub>	23.1	192.4	–0.163(–0.138)
K6	N–NO <sub>2</sub> ( <i>o</i> -)	27.7	151.1	–0.029(–0.049)
	N–NO <sub>2</sub> ( <i>p</i> -)	55.3	169.4	–0.062(–0.065)

*o*- and *p*- denotes the *ortho*-position and *para*-position of carbonyl group, respectively; The values in brackets of the Mulliken charges of nitro group column denote the Mulliken charges of nitro group when a N–NO<sub>2</sub> or a C–NO<sub>2</sub> bond revolves to the site of rotational energy barrier (energy maximum)

may contribute to the activation of N–NO<sub>2</sub> bond and the rotational energy barrier may be part of dissociation energy of N–NO<sub>2</sub> bond. As for C–NO<sub>2</sub> bond, its low rotational energy barrier makes it easier to restore to the stablest state when the bond rotation occurs and its high dissociation energy makes it harder to rupture than N–NO<sub>2</sub> bond.

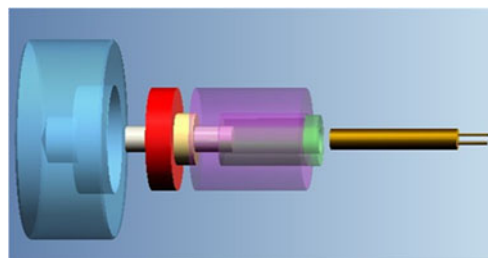
Usually Mulliken charge of nitro group in a gem-dinitro molecule is more negative than that of a nitroamine molecule, according to Zhang's [30] viewpoint and our recent work [31], it can be speculated that shock sensitivity of N–NO<sub>2</sub> is higher than gem-dinitro group. Mulliken charge of nitro group becomes more positive when the N–NO<sub>2</sub> (or C–NO<sub>2</sub>) bond rotates to the state of maximum energy. Charge transfer is actually one form of energy transfer.

After the revelation of bond rotational energy, ring strain energy, and bond dissociation energy, it can be predicted some responses of a specific molecule under shock. Take TNAZ as an example, which contains both N–NO<sub>2</sub> group and gem-dinitro groups. Rotational energy barriers of the N–NO<sub>2</sub> bond and C–NO<sub>2</sub> bond are 49.2 kJ mol<sup>-1</sup> and 6.5 kJ mol<sup>-1</sup>, respectively; Bond dissociation energy of the N–NO<sub>2</sub> bond and C–NO<sub>2</sub> bond are 178.0 kJ mol<sup>-1</sup> and 194.5 kJ mol<sup>-1</sup>, respectively; and its ring strain energy is 123.1 kJ mol<sup>-1</sup>. On comparison of these energy, the rotation of C–NO<sub>2</sub> bond may be the first response to shock, the rotation of N–NO<sub>2</sub> bond follows, the moment that the rotational energy barrier site ( $E_b=49.2$  kJ mol<sup>-1</sup>) arrives, the N–NO<sub>2</sub> bond is activated and the dissociation energy reduces 49.2 kJ mol<sup>-1</sup> ( $BDE'=128.8$  kJ mol<sup>-1</sup>), and this energy is at the same level of the ring strain energy (123.1 kJ mol<sup>-1</sup>). It is reasonable to assume both the rupture of N–NO<sub>2</sub> bond and ring opening may occur under shock, and this assumption is in agreement with the shock tube test of TNAZ [32].

### Small scale gap test

Small scale gap test is an experimental method which shock wave created via explosive detonation acts on the gap (here aluminium plate was employed), then the attenuated plane wave acts on a acceptor explosive pillar. The higher the shock-initiated pressure, the lower the shock sensitivity. The mechanical energy generated by shock wave transfers to explosive molecule and a stress-strain occurs, it will become relaxed and eventually lead to detonation. Small scale gap test was recently applied to test TNAZ, RDX and K6, and the specific schematic diagram is shown in Fig. 1.

The valid number of experiment is determined by “go” or “no go” showed in the steel witness plate, thickness (tunable)



**Fig. 1** Schematic diagram of small scale gap test. The order from top to bottom is 8<sup>#</sup> detonator, polyvinyl chloride internal holder and external holder, RDX donor explosives ( $\varphi 10 \times 10$ , two pillars), aluminium gap, receptor explosive pillar ( $\varphi 10 \times 10$ ), 45<sup>#</sup> steel witness plate, and 45<sup>#</sup> steel support, respectively

of aluminium gap is employed to determine shock-initiated pressure of the acceptor explosive pillar. A Mn–Cu manometer is applied to measure output pressure percolated through different thickness of aluminium gap, produced by  $\phi 10 \times 10$  90 % TMD (theoretical maximum density) RDX donor explosives pillars. Thickness of aluminium gap and calibrated shock-initiated pressure may be applied to measure shock sensitivity of various receptor explosive pillars.

Application of donor explosive two pillars is for the consideration of the steadily propagation of shock wave. Mn–Cu manometer, MH4E constant current source (BIT620), Tektronix TDS 540D /500 Hz/ 2GS/s oscilloscope were employed in this experiment to measure and calibrate shock-initiated pressure, and an expression  $\ln p = 3.497 - 0.159t$  was obtained,  $p$  and  $t$  denote shock-initiated pressure (GPa) and thickness of aluminium gap (mm). The experimental results of three receptor explosives TNAZ, RDX and K6 were shown in Table 2.

The aforementioned three explosive pillars were directly compressed without any binders, and the charge density was 90 % TMD (theoretical maximum density), higher charge density is hard to guarantee perfect pillars. With the comparison of RDX and K6, the ring strain energy of K6 (223.9 kJ mol<sup>-1</sup>) is much higher than RDX (88.2 kJ mol<sup>-1</sup>), in agreement with the order of shock-initiated pressure; With respect to RDX and TNAZ, ring strain energy of TNAZ (123.1 kJ mol<sup>-1</sup>) is also higher than RDX (88.2 kJ mol<sup>-1</sup>), it is evident that ring strain energy may play a dominant role in the contribution of the shock sensitivity.

**Table 2** The experimental results of three receptor explosives TNAZ, RDX and K6.  $\rho$ ,  $p$ ,  $t$  and RSE denote density, shock-initiated pressure, thickness of aluminium gap and ring strain energy, respectively

Explosive	$\rho$ (g/cm <sup>3</sup> )	$t$ (mm)	$p$ (GPa)	$E_s$ (kJ/mol)
TNAZ	1.575~1.579	15.0~15.5	2.81~3.04	123.1
K6	1.758~1.759	16.0~16.5	2.40~2.60	223.9
RDX	1.646~1.647	12.0~12.5	4.52~4.90	88.2



## Conclusions

Density functional theory BLYP/DNP and hyperhomodesmotic reactions were employed to compute ring strain energy, bond rotational energy, bond dissociation energy, and charges of nitro groups of several four-membered and six-membered azaheterocycles explosives with high energy. It indicated that ring strain energy of four-membered azaheterocycle derivatives is evidently higher than six-membered azaheterocycle derivatives, and the former will preferentially open the strained ring than the latter in the case of shock. In these azaheterocycle derivatives the rotational energy barrier of N–NO<sub>2</sub> bond is much higher than that of C–NO<sub>2</sub> bond. Low rotational energy barrier of C–NO<sub>2</sub> bond makes it easy to rotate and disperse the external energy caused by shock; On the contrary, high rotational energy barrier of N–NO<sub>2</sub> bond will result in its breakage under shock because the relaxed structure is hard to restore to the state of minimum energy. So it is easy to understand that shock sensitivity of N–NO<sub>2</sub> compounds (nitroamine) is higher than C–NO<sub>2</sub> compounds (including gem-dinitro compounds). With the introduction of a carbonyl (–C=O), or an imine group (–C=NH), or an amine group (–NH<sub>2</sub>) to the azaheterocycle nitro derivatives, the distribution of charges of nitro groups changes apparently, especially the introduction of a carbonyl (–C=O) and an imine group (–C=NH) causes a great decrease (absolute value) of charges of nitro groups and a increase of ring strain energy. These new compound will show high shock sensitivity or low shock-initiated pressure. The experimental results of small scale gap test of TNAZ, RDX and k6 are in agreement with this point of view.

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