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Alleviating the energy & safety contradiction to construct new low sensitivity and highly energetic materials through crystal engineering

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Low sensitivity and highly energetic materials (LSHEMs), with both high energy and sufficient safety, are highly desired in practical applications. With respect to energy and safety, as the two most important and hottest concerns in the field of energetic materials (EMs), it is extensively deemed that there is an inevitable and inherent contradiction between them: a higher energy goes with a lower safety. This is the so-called energy and safety (E&S) contradiction. This article highlights this contradiction and finds that this contradiction is structure-level dependent. That is, it appears most necessarily and remarkably as an inherent one only at the molecular level, while at the crystal level and other higher ones, it can be largely alleviated. Moreover, we think that the energy and safety originate from the thermodynamics and kinetics of the decomposition reactions of EMs, respectively, and accordingly the contradiction becomes a thermodynamic–kinetic one. We thereby propose a strategy for developing LSHEMs, *i.e.*, increasing the energy by increasing the chemical energy stored in molecules and by enhancing the molecular packing compactness, while, enhancing safety by making external stimuli more and more insufficient to ignite the EMs, through crystal engineering and mixing technologies. As an intrinsic structure of EMs, the crystal packing with face-to-face π–π stacking supported by strong interlayered intermolecular interactions favors the formation of LSHEMs or it is proposed to enhance intermolecular interactions and the anisotropy of these interactions to build low impact sensitivity energetic crystals.

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1. Introduction

Energy and safety (E&S) are the two most important and hottest topics in the field of energetic materials (EMs). The energy refers to reaction heat (heat of detonation or combustion), detonation properties (velocity, pressure and heat of detonation), power or working ability. And the safety is usually evaluated by sensitivity. Sensitivity is the degree of response of an EM to external stimulation: a higher sensitivity represents a lower safety. According to the type of stimulation, the sensitivity may refer to thermal sensitivity, impact sensitivity, shock sensitivity, friction sensitivity, electrostatic spark sensitivity or light sensitivity.[1,2] Thereby, we should clarify which type of sensitivity is present before we start to discuss the topic of sensitivity. In EMs, energy determines the effectiveness of application and safety guarantees the application. That is, people are required to take the safety seriously when they are in pursuit of higher and higher energy of EMs in practice, otherwise the highly energetic molecules will eventually be put on the shelf once they don't possess sufficient stability or safety to be processed for applications.

From the viewpoint of the effectiveness and safety guarantee of applications of EMs, a higher energy together with sufficient safety should be more expected. Nevertheless, it is extensively deemed that the energy and safety are in conflict with each other, *i.e.*, the so-called E&S contradiction exists in practice: a high energy goes with a low safety.[3,4] Still, low

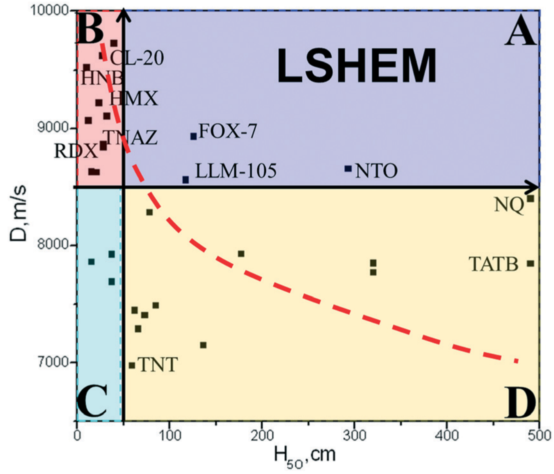

Fig. 1 Classification of EMs according to their energy and safety, denoted by detonation velocity (D) and drop hammer height (H_{50}), respectively.

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sensitivity and highly energetic materials (LSHEMs) are highly desired to increase safety and decrease self-destruction incidents. With respect to LSHEMs, there is still no clear definition for them. In this article, we might as well adopt two parameters, D = 8500 m s^{-1} and H_{50} = 50 cm, as criteria to define a LSHEM, *i.e.*, when an EM exhibits $D \geq$ 8500 m s^{-1} and $H_{50} \geq$ 50 cm, it is a LSHEM. D and H_{50} respectively denote the detonation velocity and drop hammer height, from where a given weight falling upon the compound gives a 50% probability of initiating explosion. These criteria are not random, and they refer to the properties and performances of two energetic benchmarks, representing the two generations of EMs, TNT and RDX. That is, the criterion D = 8500 m s^{-1} is referred to as the energy value of RDX, D = 8800 m s^{-1}, and the criterion H_{50} = 50 cm is referred to as the impact sensitivity value of TNT, H_{50} = 59 cm.[1] As illustrated in Fig. 1, only three EMs including LLM-105, FOX-7 and NTO are found to meet the criteria for LSHEMs in area **A**, exhibiting the rareness of LSHEMs. For the EMs in the remaining areas, both their energy and safety can hardly satisfy the criteria simultaneously.

The E&S contradiction can be represented by a red dashed line in Fig. 1, as a general change tendency of the energy–safety dependence: a higher energy is accompanied by a lower safety. Nevertheless, regarding the above mentioned rare LLM-105, FOX-7 and NTO with high levels of both energy and safety as LSHEMs, they couldn't simply be regarded as the balance products of energy and safety or the compromises of the E&S contradiction. In fact, they are positioned well above the red dashed line. Although the existence of the three LSHEMs doesn't break through the E&S contradiction as a general tendency, at least, it shows that the contradiction can be largely alleviated. Because LSHEMs are highly desired for practical applications, it is necessary to address the issues of the nature of contradiction and the way to alleviate the contradiction.

Therefore, in this article, we analyze the E&S contradiction and conclude that (1) the energy is more thermodynamic, while the safety is more kinetic; (2) the contradiction is fundamental only at the molecular level; and (3) the contradiction can be largely alleviated at structural levels above the molecular level, like energetic crystals and mixtures. That is to say, on the basis of energetic molecules, we can significantly improve the energy–safety relationship to achieve highly energetic and highly safe EMs. Also, it should be noted that we don't pay much attention to the crystal structures above molecular packing (*e.g.*, defects, shapes, sizes, size distributions, *etc.*) and the energetic mixtures in the present article, because they aren't intrinsic structures and can significantly be variable in practice. That is, we will highlight the alleviation of the contradiction through molecular packing or crystal engineering.

2. Nature of the E&S contradiction of EMs

We collected available characteristic values of 26 EMs (most of them are applied as explosives)[1] as listed in Table 1, with molecular structures shown in Fig. 2, to discuss the origin of the E&S contradiction. These values include the molecular formula (MF), oxygen balance (OB), H_{50}, peak of thermal decomposition (T_p), D, packing density (d), nitro group charge (Q_{Nitro})[5–7] and bond dissociation energy (BDE).[8] Among these values, H_{50} and T_p are experimentally measured to evaluate impact safety and thermal stability, respectively, *i.e.*, a higher H_{50} or T_p suggests a higher safety and stability; Q_{Nitro} and BDE are derived from theoretical calculations to represent molecular stability (a more negative Q_{Nitro} and a larger BDE represent higher molecular stability), having a positive correlation with the safety; D denotes energy and d has a positive correlation with D. In a word, H_{50}, T_p, Q_{Nitro} and BDE are indicators of safety, while D and d are indicators of energy. Thereby, we can discuss the nature of the contradiction by means of these values. Nevertheless, it should be noted that, as pointed out above, there are various types of sensitivity, and they thereby should be specified. For example, for the EMs in Table 1, their H_{50} and T_p can hardly be ordered in the same way. Thus, in general, we can hardly say that EM **A** is always safer than EM **B**, for example, EM **A** is more impact-insensitive than EM **B**, while maybe, EM **A** is less thermally insensitive than EM **B**.

In addition, we revised our previous publication to exhibit the multiscale and hierarchical structures of EMs, exemplified by the micro- to macrostructures of a plastic bonded explosive (PBX) in Fig. 3. As illustrated in the figure, besides the above molecules, crystals and mixtures are also involved in practical EMs. Moreover, main concerns about the energy and safety are demonstrated in the figure too. Based on the characteristic values in Table 1 and multiscale structures in Fig. 3, it is convenient to discuss the E&S contradiction.

Fig. 1 exhibits the so-called E&S contradiction of EMs, a tendency for all EMs, *i.e.*, D increases with decreasing H_{50}. However, it is just a tendency, instead of a strict dependence. Here, we will provide some counterexamples (CEs) to show this. That is to say, it is not a necessary case that EM **A** with a higher D than EM **B** should be more sensitive (or less safe) than EM **B**. Such a case is general for some given EMs. It also implies that there is a possibility that we can achieve a new EM with both energy and safety being superior to those of an existing one.

The first CE is a group of EMs, four trinitrobenzenes, with similar molecular structures, including TNB, TNA, DATB and TATB. This case shows that both energy and safety can exist simultaneously and suggests that there is no E&S contradiction for such a group of EMs. As listed in Table 1, from TNB to TNA, DATB and TATB, D increases from 7432, 7626, 7770 and 7845 m s^{-1}, and H_{50} increases too from 100, 177, 320 and 490 cm, suggesting that both energy and safety are simultaneously promoted. From the viewpoint of molecular decay, the reaction heat (Q) decreases in the order TNB to TNA, DATB and TATB, due to the worsening of the oxygen balance (OB). Nevertheless, the promotion of both energy and safety is governed by the improvement of crystal packing and molecular stability. That is, on the one hand, from TNB to TNA,

Table 1 Characteristics of interesting EMs. BDE and Q_{Nitro} were respectively calculated at the levels of GGA/PBE/DNP and LDA/PWC/DNP using the Dmol^3 module

Compounds	MF	OB, %	H_{50}, cm	T_p, °C	D, m s^{-1}	d, g cm^{-3}	Q_{Nitro}, e	BDE, kcal mol^{-1}
HNB	$C_6N_6O_{12}$	0	10	—	9521	2.01	−0.134	54.9
2#	$C_6H_8N_{10}O_{16}$	0	12	197.2	9066	1.87	−0.051	35.3
PETN	$C_5H_8N_4O_{12}$	−14	15	202	8627	1.778	0.058	41.6
BTF	$C_6N_6O_6$	−50	21	285	8622	1.901	—	21.5
CL-20	$C_6H_6N_{12}O_{12}$	−20	27	244.8	9619	2.035	−0.081	42.0
RDX	$C_3H_6N_6O_6$	−33	28	219.5	8835	1.816	−0.105	44.0
TNAZ	$C_3H_4N_4O_6$	−25	28	265.25	8868	1.84	−0.114	47.1
HMX	$C_4H_8N_8O_8$	−33	32	275	9105	1.905	−0.112	46.3
Tetryl	$C_7H_5N_5O_8$	−52	37	209.2	7691	1.73	−0.106	32.8
HNAB	$C_{12}H_4N_8O_{12}$	−54	37	—	7925	1.799	−0.211	56.1
7201	$C_6H_4N_{12}O_{14}$	0	40	196	9724	2.07	0.006	38.2
TNT	$C_7H_5N_3O_6$	−64	59	294.8	6978	1.654	−0.249	63.5
PYX	$C_{17}H_7N_{11}O_{16}$	−57	62	375.4	7448	1.77	−0.239	56.3
HNS	$C_{14}H_6N_6O_{12}$	−61	66	332.6	7289	1.74	−0.233	64.2
PA	$C_6H_3N_3O_7$	−48	73	280	7406	1.76	−0.254	64.1
DINGU	$C_4H_4N_6O_6$	−40	78	240	8285	1.95	−0.088	43.9
DIPAM	$C_{12}H_6N_8O_{12}$	−56	85	315	7488	1.79	−0.267	70.7
TNB	$C_6H_3N_3O_6$	−56	100	—	7432	1.69	−0.228	68.1
LLM-105	$C_4H_4N_6O_5$	−50	117	347	8560	1.913	−0.292	66.6
FOX-7	$C_2H_4N_4O_4$	−33	126	238	8930	1.878	−0.365	68.9
TNA	$C_6H_4N_4O_6$	−57	177	220	7626	1.773	−0.289	72.0
NTO	$C_2H_2N_4O_3$	−40	293	267.8	8654	1.93	−0.264	68.9
DATB	$C_6H_5N_5O_6$	−59	320	300	7770	1.837	−0.330	74.2
PATO	$C_8H_5N_7O_6$	−68	320	—	7850	1.88	−0.254	59.2
NQ	$CH_4N_4O_2$	−50	490	246	8401	1.77	−0.294	54.0
TATB	$C_6H_6N_6O_6$	−60	490	370.6	7845	1.938	−0.416	74.9

DATB and TATB, the packing coefficient (PC) increases from 0.72 to 0.74, 0.78 and 0.79,[10] and the d value increases from 1.690 to 1.773, 1.837 and 1.937 g cm^{-3}.[11–14] This increase of packing density favors the increase of D, making up for the Q reduction, as d more remarkably influences D than Q, which can be deduced from the K–J equation.[15] Meanwhile, crystal packing modes can play an important role in the safety mechanism of EMs. Previous studies[16–24] showed that the ability to disperse external impact into sliding movement decreases in the order face-to-face, wavelike, crossing and mixed π–π stacking. With respect to the above four trinitrobenzenes, as demonstrated in Fig. 4, TATB, DATB and TNA, and TNB feature face-to-face, crossing, and mixed π–π stacking, respectively, exhibiting the decreasing ability to disperse impact or the increasing impact sensitivity; moreover, the decrease of their molecular stability also contributes to their sensitivity enhancement.[22] On the other hand, from TNB to TNA, DATB and TATB, the molecular stability increases with increasing NH_2 group, which offers more conjugated π-electrons (from TNB to TNA, DATB and TATB, the amounts of π-electrons are 18, 20, 22 and 24, respectively) and intermolecular and intramolecular hydrogen bonds (HBs).[22] This leads to the increase of their BDE in Table 1. Thus, from this group of trinitrobenzenes, both the energy and safety are expected to be simultaneously enhanced.

The second CE shows that exceptions for the dependence of impact sensitivity on the molecular stability of EMs represented by BDE and Q_{Nitro} usually exist, implying that there are exceptions to the so-called E&S contradiction. Molecular stability is one of the important factors for determining the safety of EMs. Thus, some indicators representing the molecular stability of EMs are used to correlate it with safety. The BDE–H_{50} and Q_{Nitro}–H_{50} dependences in Fig. 5(a) show that, generally, a lower molecular stability (less BDE or more positive Q_{Nitro}) represents low safety (smaller H_{50}). Nevertheless, they are not strict, as many points depart more or less from the two fitting lines (two dashed lines), *i.e.*, exceptions exist. Furthermore, the two indicators BDE and Q_{Nitro} aren't strictly dependent on each other too, as illustrated in Fig. 5(b). Interestingly, if we neglect the points on the right of the figure, those for TNA, NTO, PATO, DATB, NQ and TATB, and fit the remaining ones, two linear fitting lines ***a*** and ***b*** are obtained with much improved correlation coefficients. It suggests their great particularity.

As a matter of fact, TNA, NTO, PATO, DATB, NQ and TATB are all π-bonded with large BDEs and highly negative Q_{Nitro}, showing high molecular stability. Meanwhile, with respect to the BDEs of NQ and PATO, it seems that they aren't high enough to contribute to the high H_{50}, and a similar case appears for NTO, NQ and PATO, in terms of Q_{Nitro}. The effect of crystal packing is the reason behind this. In Fig. 4(a) to (c), the face-to-face and crossing π–π stacking interactions of TATB, DATB and TNA facilitate their shear sliding and contribute to their high H_{50}. For the remaining molecules, NTO, NQ and PATO, they possess similar packing structures resulting in high H_{50}, even though they don't exhibit enough molecular stability.

Besides, our recent work[22] showed that DAAF (Fig. 6(a)) and DAAzF (Fig. 6(b)) are very closely face-to-face π–π stacked, as TATB. We have stressed that the face-to-face π–π stacking

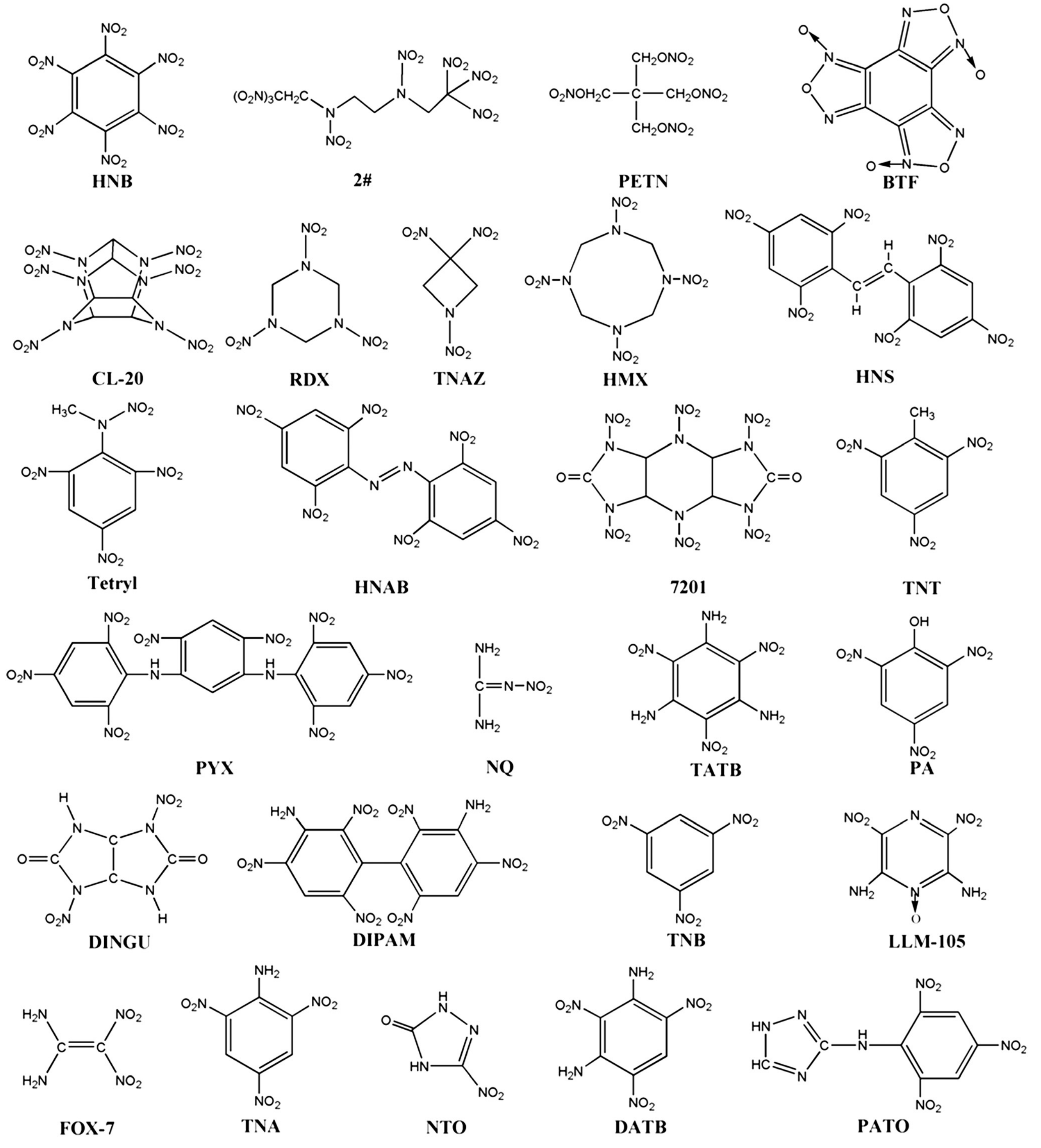


Fig. 2 Molecular structures of interesting EMs.

facilitates the interlayered sliding and buffers readily against external mechanical stimuli to favor low mechanical sensitivity. NQ exhibits crossing π–π stacking (Fig. 6(c)) with a larger difficulty in sliding relative to DAAF and DAAzF, leading to the possible increase of sensitivity. However, the dense intermolecular HBs in NQ (Fig. 7) makes up for this. It shows that the complete face-to-face π–π stacking with strong interlayered intermolecular HBs favors low mechanical sensitivity, as well as compact packing to increase packing densities and detonation properties.

The above two cases show the exceptional dependences of impact sensitivity on the molecular stability of EMs, suggesting that the sensitivity mechanism is complicated and related to many factors and the molecular stability cannot be responsible for the sensitivity alone. Also, these exceptional dependences imply the exceptions to the so-called E&S

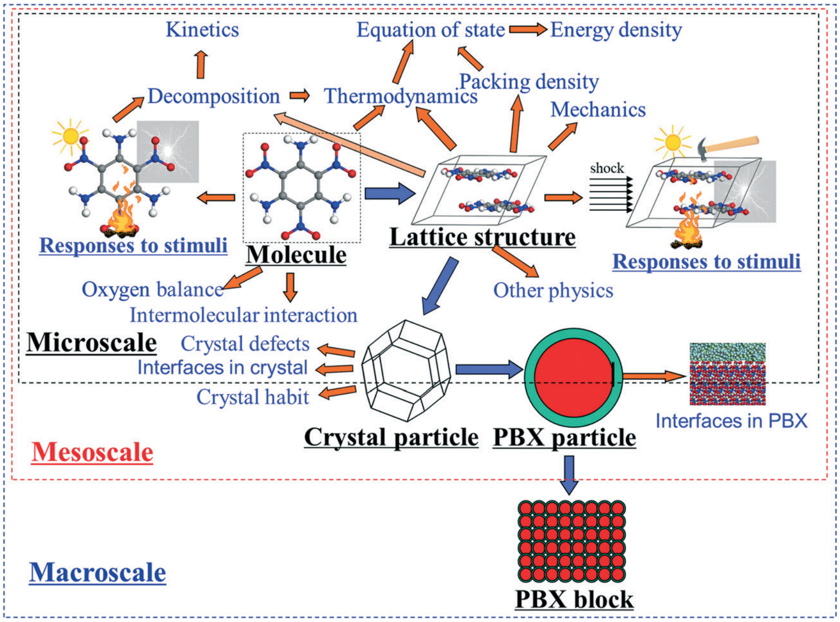


Fig. 3 Micro- to macrostructures of a plastic bonded explosive (PBX) and main concerns about the energy and safety, cited from ref. 9 with some revisions.

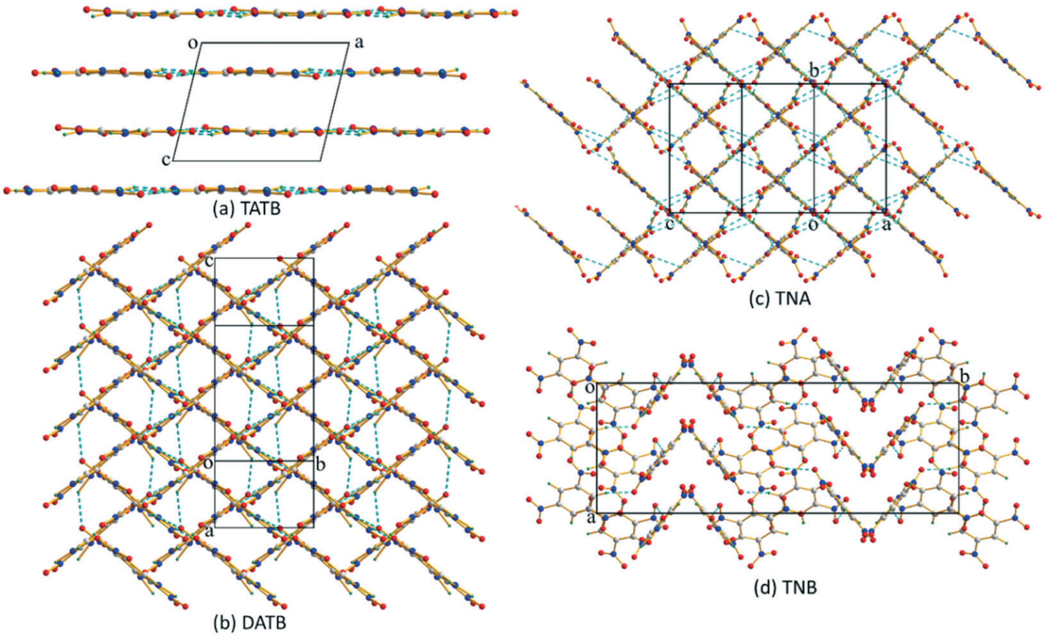


Fig. 4 Molecular stacking structures of four trinitrobenzenes of TATB (a), DATB (b), TNA (c) and TNB (d). Green dashed represents intermolecular hydrogen bonds. And C, H, N and O atoms are represented in grey, green, blue and red, respectively. These representations are also considered in following figures.

contradiction, because both the energy and safety of EMs can be reflected to a certain extent from the molecular characteristics. Thereby, with this CE, we reaffirm that the E&S contradiction is only a tendency, and not a strict dependence.

The third CE shows that a sensitivity discrepancy for two given EMs usually exists, leading to a difficulty in evaluating the E&S contradiction. As mentioned above, various types of sensitivity exist in practice for an EM; however, these types of sensitivity of different EMs cannot be strictly ordered in the same way. We used H_{50} and T_p in Table 1 and plotted them in Fig. 8, which shows that there is no obvious correlation between them. This suggests a universal discrepancy between H_{50} and T_p. Thus, this discrepancy in the sensitivity order of the two EMs tells us that there may be no simple and obvious E&S contradiction for some given EMs.

The above three CEs are EMs with different components. Here, cases of the same components are provided. The fourth CE shows that, for polymorphs of CL-20, the form with the

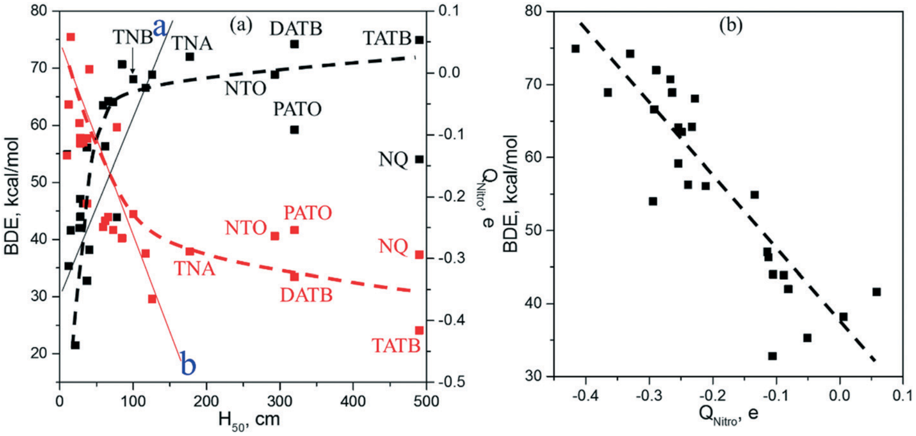
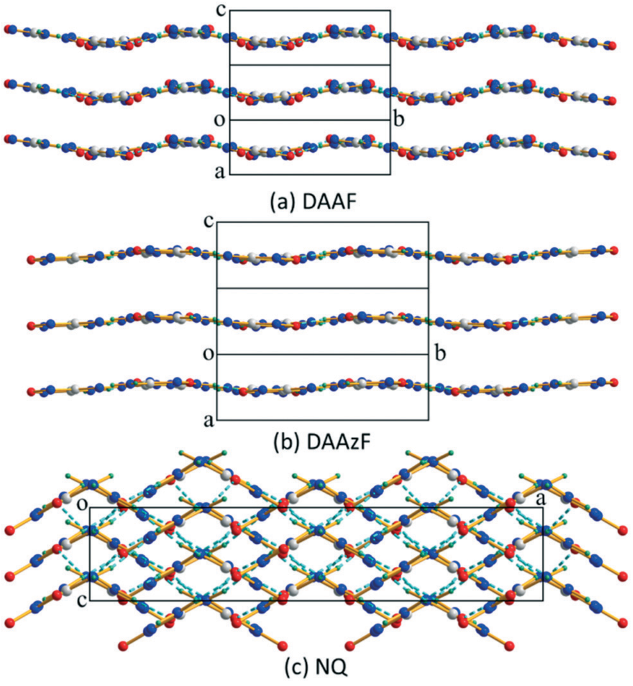


Fig. 5 BDE–H_{50} and Q_{Nitro}–H_{50} (a) and BDE–Q_{Nitro} dependences (b) of the EMs in Table 1.

highest energy exhibits the highest safety. This case shows mutual benefits between energy and safety and no E&S contradiction. CL-20 possesses three polymorphs under common conditions, β-, γ- and ε-forms.[25] For various polymorphs with the same component, their energy increases with increasing packing density. That is to say, the energy of the CL-20 polymorphs increases in the order γ-, β-, and ε-forms, as their packing densities increase from 1.916, 1.985 and 2.044, g cm^{-3} under common conditions. According to experimental measurements of H_{50} with a 2 kg hammer, we can know that the most compact form or the form with the highest energy, ε-CL-20, is the most impact insensitive, with a H_{50} of 53.1 cm *vs.* 36.9 and 13.5 cm for γ- and β-CL-20, respectively.[25] The observation that the highly compact packing favors high safety is thought to be related to the fact that the less free volume results in more difficult molecular decay and thus higher safety.[26] Interestingly, for the CL-20 polymorphs, it seems that there is no E&S contradiction, as one form can favor both the highest energy and the highest safety.

Besides the same component, we provide the fifth CE, a case of the same material. It shows the anisotropic shock sensitivity of PETN. It suggests that, for a given energetic crystal, its sensitivity can vary in terms of shock orientation. Now that sensitivity-anisotropy exists, the E&S contradiction will be largely alleviated in the future. It was reported in 2000 that the shock ignition threshold of PETN along the (100) face is at least four times that along the (110) face, showing the less shock sensitivity of the (100) face.[27] This anisotropy of shock sensitivity was confirmed afterwards by molecular dynamics (MD) simulations, as the (110) face exhibits a stronger response to shock, with faster increases of temperature, internal stress and NO_2 formation.[28] In this case, for a crystal with various sensitivity values, it may be difficult to observe the so-called E&S contradiction, as the sensitivity can be varied within a large range. Meanwhile, regarding the sensitivity anisotropy, by means of advanced preparation and charge technologies, the safety of some EMs will be largely improved in the future. That is, the E&S contradiction can be largely alleviated.

The final CE shows that, for crystals with a given polymorph, their energy varies a little, while their sensitivity can significantly be varied, depending on their qualities. Such crystal qualities refer to the shape, perfection, purity, and so forth.[29] Recently, we found that, for all three explosives, RDX, HMX and CL-20, their shock sensitivities are lowered by increasing their crystal apparent densities or decreasing their particle sizes and are almost not affected by particle morphologies; crystal twins are readily formed for HMX which are the most distinct factor influencing its shock sensitivity, and the crystal apparent density affects most obviously the shock sensitivities of RDX and CL-20.[30] From these findings, we can learn that the sensitivity of energetic crystals can significantly vary while maintaining their energy level. Thus, obtaining spherical shapes, high perfection and high purity is regarded as a strategy for decreasing sensitivity or increasing safety.[29] Because sensitivity can significantly be varied, it becomes difficult to discuss the E&S contradiction.

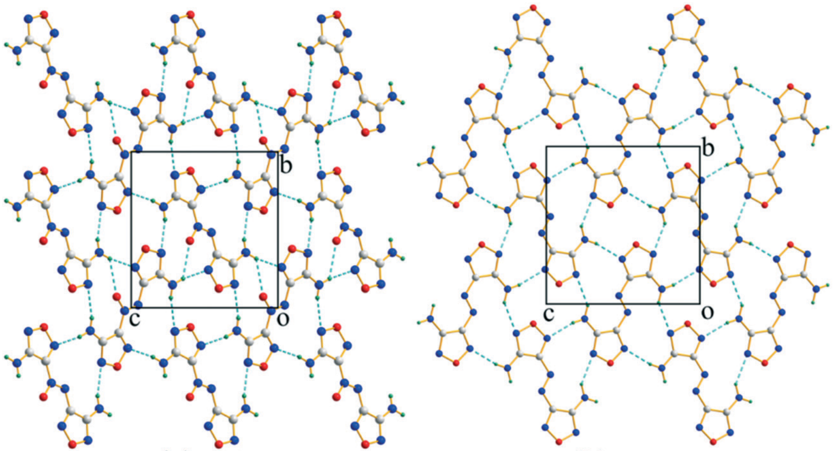


(a) DAAF

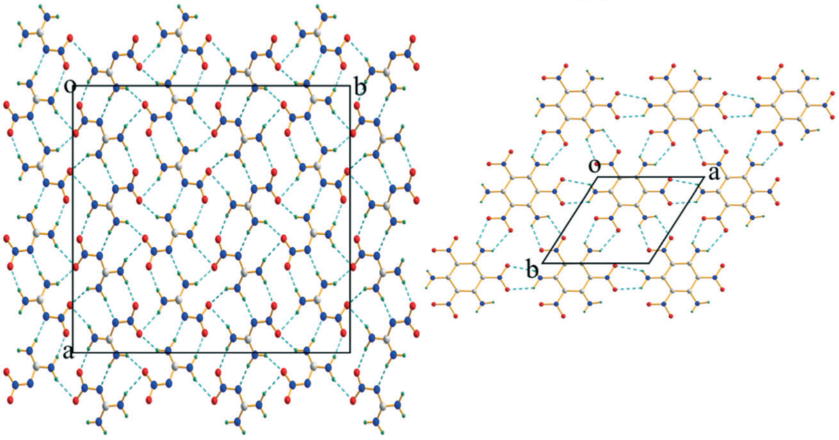
(b) DAAzF

(c) NQ

Fig. 6 Crystal packing of DAAF (a), DAAzF (b) and NQ (c).



(a) DAAF (b) DAAzF



(c) NQ (d) TATB

Fig. 7 Intralayered intermolecular HBs of DAAF (a), DAAzF (b), NQ (c) and TATB (d).

From the above CEs, we can conclude that the E&S contradiction does not always exist. To clarify the nature of the contradiction, we should first pay attention to the origins of both the energy and safety of EMs. As pointed out above, the energy of EMs refers to energy content, energy release, detonation properties, or working ability. The practical utility of an EM is often determined by its energy content, in particular, its available energy content. The available energy content is strongly related to the anticipated release mechanism. Straightforwardly, we can regard the energy release mechanism through thermodynamic cycles. That is, detonation can be thought of as a cycle that transforms an unreacted explosive into stable products in the Chapman–Jouget (C–J) state, in which the slowest steady-shock exists with the conservation of mass, momentum and energy.[31–33] Because the detonation occurs on a microsecond timescale, any reaction above this timescale is not relevant when considering detonation. It means that only a part of the energy is useful for detonation. Therefore, understanding the energy release with the thermodynamic cycle theory ignores the important question of the timescale of reaction. Nevertheless, the detonation can produce high pressure (several tens of GP) and high temperature (several millions of K) conditions, and these conditions can almost make the reaction fully completed. This implies the feasibility of the thermodynamic cycle theory in these cases. Even though relatively little is known about the material equations of state (EOS) under these conditions, shock experimentation on a wide range of materials has generated

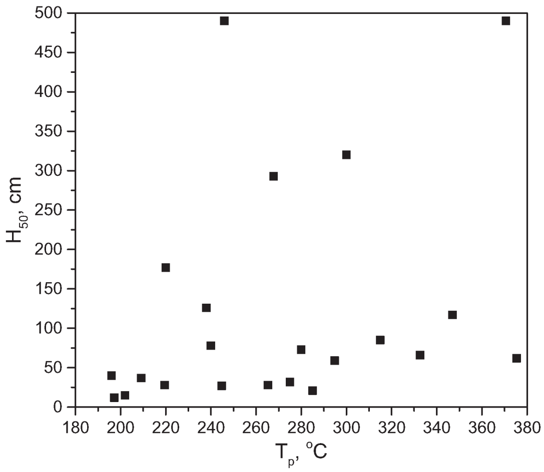


Fig. 8 Plot showing the discrepancy between T_p and H_{50}.

sufficient information to allow reasonably reliable thermodynamic modeling to proceed.[4] That is, the energy can reliably be described by thermodynamic modeling, in which, as in the K–J equation, only composition, density and heat of formation are required. In practice, thermodynamics is allowed to describe the energy performance, with a premise that the allowed thermodynamic states behind a shock are intersections of the Rayleigh line (denoting mass and momentum conservations) and the shock Hugoniot (denoting energy conservation). The C–J theory states that a stable detonation takes place when the Rayleigh line is tangent to the shock Hugoniot. This point of tangency can be determined with the given EOS of the products. Because the chemical composition of the products varies with the thermodynamic state, thermochemical codes should be capable of simultaneously solving for state variables and chemical concentrations. By means of EOS and rate laws, the energy of EMs can be assessed.

On the other hand, rationally, the energy of EMs has a strong relationship to the chemical energy release of detonation. Simply, regarding this chemical energy release, it can be seen as the heat of reaction, which is a state function, is only determined by the primary and final states and has nothing on the detailed intermediate steps. In this case, the energy is in fact the variation of bond energy, *i.e.*, the result of the bond energy of reactants minus that of products. For the energy of EMs, their densities should also be stressed. Thus, it is extensively believed that the component and density together determine the energy of EMs. For example, as demonstrated in Fig. 9, d largely influences D (both d and D were taken from Table 1). That is to say, for various EMs with the same component and the same density, their energy is almost the same as one another. Thereby, the energy is more thermodynamic. This is also the reason why we have already been able to exactly predict the energy of EMs composed of C, H, N and O atoms, and even of other atoms. Moreover, these prediction methods possess a small quantity (such as the K–J equation, BKW and BLW EOS, and their derivatives) and feature good generality and simplicity. Meanwhile, because the safety is strongly related to the detailed paths from the initial to final states of an EM in response to external stimulation, it is more kinetic. Thus, we can understand why there exist so many empirical equations for predicting sensitivity and any of them is not general, as we have checked out more than 10 such empirical equations each for a special group of EMs.[34,35] Thereby, the energy and safety can be described by eqn (1) and (2), respectively.

$$E = f(c, d, q) \tag{1}$$

$$S = g(c, d, q, f1, f2, f3, \ldots) \tag{2}$$

In the above two equations, c, d and q represent the component, packing density, and energy release, and $f1$, $f2$, $f3$, *etc.* represent the efficiencies of energy transfer, energy absorption and accumulation, lattice vibration, *etc.* to ignite EMs, respectively.

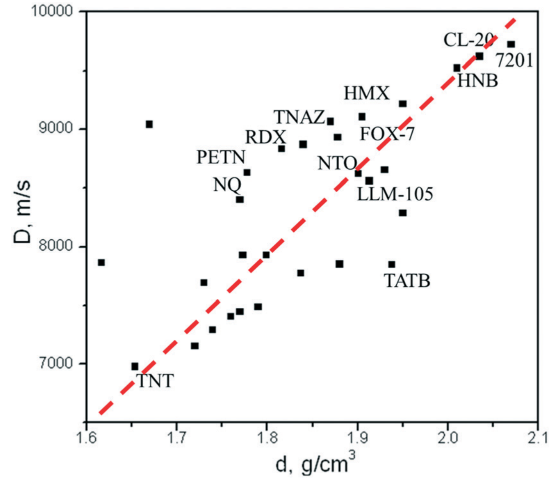


Fig. 9 Plot showing the d–D dependence.

Reasonably, the E&S contradiction is a type of thermodynamic–kinetic contradiction. This can be simply illustrated in Fig. 10. EMs are a class of kinetically stable while thermodynamically unstable substances. Their chemical energy releases (ΔE_1) are the heats of detonation reactions, which are the difference in potentials between an energetic reactant and final products, which are usually stable small molecules: a larger difference suggests a higher ΔE_1 (or a higher energy (E)). On the other hand, the energy barrier (ΔE_2) for decaying an EM should be higher if it is required to be more stable. Obviously, ΔE_2 is strongly responsible for the safety (S). Therefore, the so-called E&S contradiction can simply be regarded as the ΔE_1 & ΔE_2 contradiction.

Is the ΔE_1 & ΔE_2 contradiction necessary? This issue might as well be addressed at different levels. First, at the molecular level, we can discuss the ΔE_1 & ΔE_2 contradiction from the heat of molecular decomposition and molecular stability, which are represented by ΔE_1 and ΔE_2, respectively. In principle, ΔE_1 is determined by the difference in bond energy summation between the reactant and products. For the given products, a higher ΔE_1 requires a smaller bond energy summation of the reactant. A smaller bond energy summation of

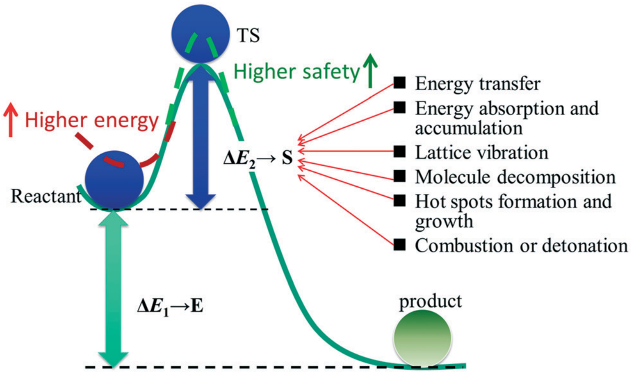


Fig. 10 Plot showing the origins of the energy and safety of EMs and factors influencing ΔE_2. The figure is partly cited from ref. 3.

the reactant may imply a less stable reactant. On the other hand, a higher ΔE_2, indicative of a higher molecular stability, requires a more stable reactant. Thus, the ΔE_1 & ΔE_2 contradiction indeed exists at the molecular level: for one thing, a higher ΔE_1 requires a smaller bond energy of the reactant; for another thing, contrarily, a higher ΔE_2 requires a larger bond energy. For instance, the C–NO_2, N–NO_2 and O–NO_2 bonds are the weakest in TNT, HMX and PENT, respectively, and their breakages trigger molecular decomposition and contribute greatly to the chemical release. Obviously, strengthening these bonds facilitates ΔE_2 to stabilize the molecules, while the low dissociation energies of these bonds are the origin of high ΔE_1, *i.e.*, the lower the dissociation energy, the higher the ΔE_1.

Additionally, we stress the low bond energy summation, instead of the energy of any bond alone, contributing to the high chemical energy release. In general, the molecular stability is assessed by the strength of the weakest bond. Despite this, universally, a higher energy release suggests the lower molecular stability of the applied EMs.

3. Alleviation of the E&S contradiction

In general, the applied EMs have multiscale and hierarchical structures, as illustrated in Fig. 3. Besides multiscale structures, the main concerns about the energy and safety are demonstrated in the figure too, including the thermodynamics and kinetics for an energetic molecule in response to external stimuli, the packing, the habit, and the thermodynamics and kinetics in response to external stimuli for an energetic crystal, and the interfacial interactions in a PBX. Therefore, some suggestions are proposed to alleviate the E&S contradiction and to increase energy with accepted safety in terms of the structural levels as follows. Moreover, as a consequence of alleviating the contradiction, LSHEMs can be achieved. That is, the proposal to alleviate the E&S contradiction is just a core for constructing LSHEMs.

At the molecular level, as pointed out above, the E&S contradiction appears inherently and most remarkably, *i.e.*, the high energy results from the low bond energy of energetic molecules, while the low bond energy suggests necessarily the low molecular stability. Nevertheless, it should be noted that the bond energy is the energy of all bonds of an energetic molecule, while the stability of the energetic molecule is most strongly related to the strength of the weakest bond once its breakage triggers the decomposition of the entire molecule. Thus, strengthening the weakest bond could be an approach to increase molecular stability. Averaging the bond dissociation energy of all bonds in the molecule, for example by conjugation, should be the most efficient way to increase energy while keeping safety.

At the crystal level, it has already been verified that the molecular packing mode can influence mechanical sensitivity through shear sliding.[16–24] In a recent study,[22] as demonstrated in Fig. 11, we divided the molecular packing of π-bonded EMs into four modes. The face-to-face π–π stacking was found to be preferred to most efficiently buffer against external mechanical stimuli, contributing to low mechanical sensitivity. As pointed out above, conjugating a molecule facilitates its stability. Also, conjugating a molecule sets a base for π–π stacking, possibly, the face-to-face π–π stacking and compact stacking. That is to say, a conjugated energetic molecule could be a premise for constructing LSHEMs. Indeed, recent analyses of 11 LSHEMs, including TATB, NQ, DAAzF, DAAF, DATB, DNDP, NTO, TNA, FOX-7, LLM-105 and TNB, whose both detonation velocity and impact energy are superior to those of TNT, show that all the molecules of the low impact sensitivity EMs are conjugated with all non-hydrogen atoms of each molecule.[22] Maybe, someone argues for non-conjugated molecules can also serve as stable molecules. However, these stable non-conjugated molecules should not be sufficient to possess high energy.

In addition, as another important factor responsible for the low sensitivity, intermolecular HBs can hardly be overlooked. Reasonably, these HBs can enhance intermolecular interactions to support the π–π stacking. Unexceptionally, this support appears in all the above mentioned LSHEMs, FOX-7, LLM-105 and NTO, composed of neutral single component molecules in Fig. 12. It is just the HB-aided π–π stacking that leads to the low sensitivity. Moreover, strengthening the intralayered intermolecular interactions by energetic co-crystallization is also thought to favor low mechanical sensitivity.[36–40] Interestingly, Fig. 13 exhibits the single atomic thickened layers (SATLs) of 5,5′-bistetrazole-1,1′-diolate·H_2O (BTO·H_2O), a solvate, or a co-crystal. Due to such SATLs, BTO·H_2O is expected to be impact insensitive with ready sliding characteristics. A recent H_{50} measurement of BTO·H_2O of above 126 cm (hammer weight, 2 kg; sample, 30 mg) shows the impact insensitivity as expected.[41] The crystal packing of BTO·H_2O enriches our knowledge of constructing LSHEMs with different components. Even though the enhanced intermolecular interactions, or the elevated lattice energy, can decrease ΔE_1 a little, the impact sensitivity can remarkably be improved. This is a part of the crystal engineering of EMs. Similarly, energetic ionization is also a kind of crystal engineering of EMs, by which both the molecular stability and the intermolecular interactions are enhanced to increase energy performances while keeping safety.[42–44]

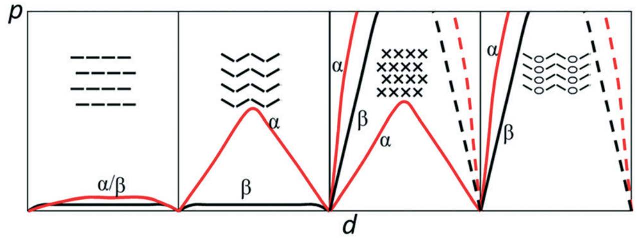


Fig. 11 Inter/intramolecular potential (*p*)–sliding distance (*d*) dependences of four kinds of stacking. α and β denote the sliding along right/left and front/back, respectively. The figure is cited from ref. 22.

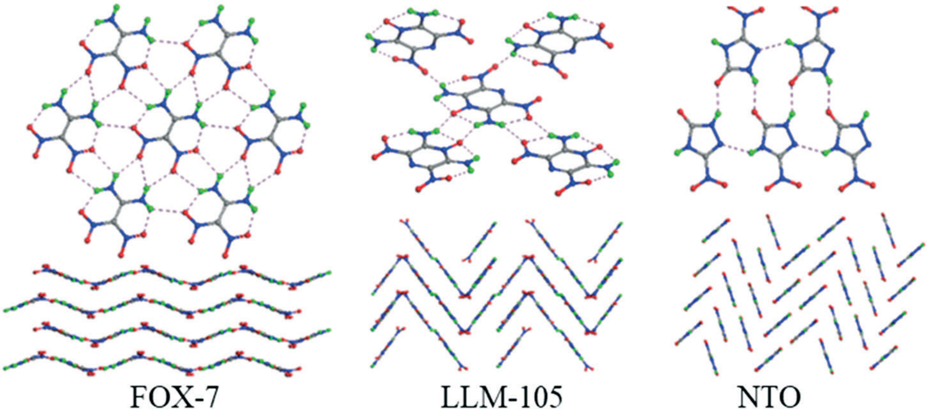


Fig. 12 Intralayered HBs (top) and π–π stacking (bottom) of typical LSHEMs composed of neutral single component molecules.

We checked the intermolecular HBs and π–π stacking of some typical EMs in Fig. 14 and developed a strategy for constructing LSHEMs using strong HBs and π-stacking.[45] For the group of CL-20, HMX, RDX and TNT, which possess very weak intermolecular HBs and no π-stacking, the impact sensitivity (IS)–*D* dependence exhibits a big slope showing a sharp *D* reduction when IS increases. As for the group of FOX-7, LLM-105, NTO and TATB, by comparison, the intermolecular HBs are enhanced with remarkable π-stacking. The slope of the IS–*D* dependence becomes much flatter, indicating that impact sensitivity can be largely improved while *D* is reduced a little in this case. As a matter of fact, all the four EMs of this group have been seen as LSHEMs. When the intermolecular HBs are rather strong while the π-stacking is maintained, the IS–*D* dependence can be largely improved in energetic ionic salts, with high energy and high safety.

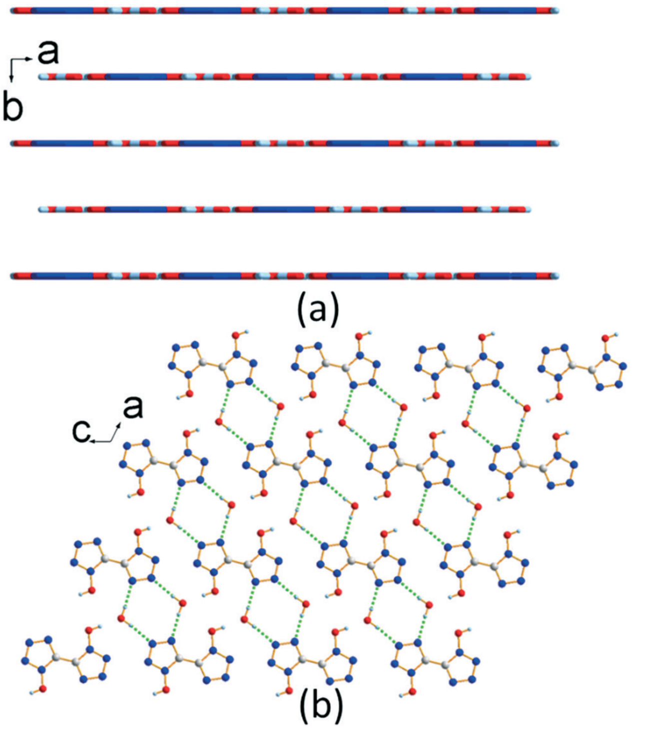


Fig. 13 Crystal packing (a) and intralayered HBs (b) of 5,5′-bistetrazole-1,1′-diolate·H_2O (BTO·H_2O).

Defects, shapes, sizes, size distributions, *etc.* are the structures above a single crystal and not intrinsic ones. That is, they are governed by preparation techniques, instead of the emergent molecular packing in crystals. Thus, we pay no attention to them. We do so also for energetic mixtures. Mixtures are the final forms of EMs. Numerous efforts have been implemented to add up various additives to improve the sensitivity of EMs, as well as other properties and performances, which are just the usual formula techniques in practice. Even though these formula techniques are various, they are forced to prevent the hot spot formation by reducing the efficiency of external simulation energy initiating molecular decomposition.

4. Conclusions

In summary, we discuss the E&S contradiction of EMs in the present work, which is a necessary topic in the related field,

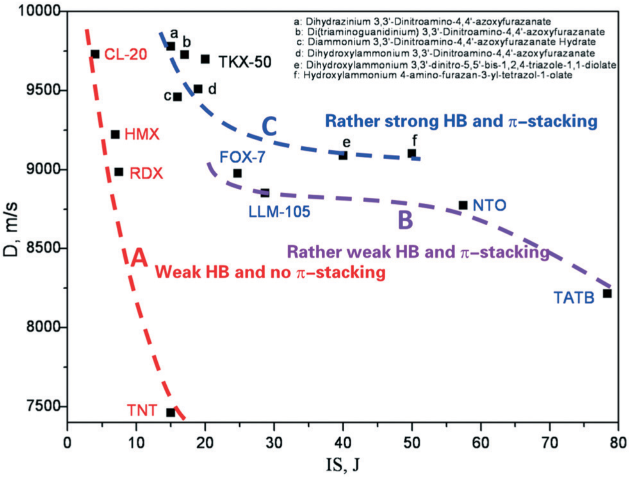


Fig. 14 Impact sensitivity (IS) and energy (shown by detonation velocity *D*) of some typical EMs. The figure is cited from ref. 3.

as both energy and safety are two of the most crucial concerns in EMs: energy determines effectiveness and safety guarantees application. The E&S contradiction appears in a rough tendency, instead of a strict dependence for all EMs. In principle, the energy is more thermodynamic and determined by the original and final states, while the safety is more kinetic and strongly related to the detailed path of an EM against external stimuli. At the molecular level, the E&S contradiction appears more remarkably and inherently, while above the molecular level, it can be largely alleviated. Owing to the applied EMs at structural levels above the molecular level, we should cherish a beautiful hope to alleviate the contradiction from the viewpoint of kinetics by crystal engineering and composite technologies. Thereby, more and more LSHEMs are expected to be achieved.

Definition of abbreviations

BTF	Benzotrifuroxan
DAAF	*trans*-(*d*,*d*)-3,3′-Diamino-4,4′-azofurazan
DAAzF	*trans*-(*p*,*p*)-3,3′-Diamino-4,4′-azofurazan
DATB	1,3-Diamino-2,4,6-trinitrobrnzene
FOX-7	1,1-Diamino-2,2-dinitroethylene
LLM-105	2,6-Diamino-3,5-dinitro-1,4-pyrazine-1-oxide
NQ	2-Nitroguanidine
NTO	5-Nitro-2,4-dihydro-3 h-1,2,4-triazol-3-one
PETN	pentaerythritol tetranitrate
RDX	1,3,5-Trinitro-1,3-5-triazacyclohexane
TATB	1,3,5-Triamino-2,4,6-trinitrobenzene
TNA	2,3,4,6-Tetranitroaniline
TNB	1,3,5-Trinitrobenzene
TNT	2,4,6-Trinitrotoluene
HMX	β-1,3,5,7-Tetranitro-1,3,5,7-azacyclo-octane
CL-20	2,4,6,8-Hexanitro-2,4,6,8,10,12-hexa-azatetracyclododecane

Conflicts of interest

The authors declare no competing financial interest.

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