

Molecular dynamics study on the correlation between structure and sensitivity for defective RDX crystals and their PBXs

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Abstract Molecular dynamics simulation was applied to investigate the sensitivities of perfect and defective RDX (cyclotrimethylene trinitramine) crystals, as well as their PBXs (polymer-bonded explosives) with the polymeric binder F₂₃₁₁, in the NPT (constant number of particles, constant pressure, constant temperature) ensemble using the COMPASS force field. Five kinds of defects—two dislocations, one vacancy, and two types of doping—were considered separately. The bond length distribution and the maximum (L_{\max}) and average (L_{ave}) bond lengths of the N–NO₂ trigger bonds in RDX were obtained and their relationships to the sensitivities of RDX and PBXs are discussed. L_{\max} was found to be an important structural parameter for judging the relative sensitivity, and defects were observed to have little effect on the sensitivities of PBXs, due to the strong desensitizing effect of the polymer F₂₃₁₁.

Keywords Defective crystals · Molecular structure · Molecular dynamics (MD) simulation · RDX (cyclotrimethylene trinitramine) · PBXs (polymer-bonded explosives) · Sensitivity

Introduction

RDX (cyclotrimethylene trinitramine) is a high-performance energetic compound that is widely used in a number of polymer-bonded explosives (PBXs) and propellant formulations. Its crystalline grain size, purity, and perfection significantly affect its properties, such as its sensitivity, thermostability, etc. Due to various disadvantageous conditions during crystalline growth, it is impossible to produce a perfect crystal—all crystals have some defects, including vacancies, dopants, and dislocations. Besides, crystals that do not have strictly periodic characteristics are also called defective crystals. The presence of defects in crystals make them more energetic and thus more active.

If we consider an explosive, the presence of defects lowers its thermostability and increases its sensitivity. Furthermore, according to the famous principle of “hotspot-induced explosions,” decomposition usually begins in defective areas [1]. Therefore, it is important to study the effects of defects on various properties of explosives, especially their sensitivities. In the work described in the present paper, the sensitivities of crystalline explosive RDX and its corresponding polymer-bonded explosives (PBXs) were investigated theoretically using molecular dynamics (MD) simulation. It is worth noting that the crystal structure and physical and chemical properties of RDX have already been extensively investigated in [2–13] ([2–5] describe experimental work, while [6–13] present theoretical results).

In recent years, molecular dynamics (MD) simulation has played an increasingly important role in the investigation of the thermophysical, mechanical, cohesion and sensitivity

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properties of energetic compounds and their composite materials. Classical molecular dynamics can be applied to simulate large and complicated systems such as PBXs, and it yields approximate statistical results. Results from MD simulations of RDX and its PBXs are reported in [10–13]. Also, the COMPASS force field [14]—which is particularly applicable to condensed phases and composites of various types of components—is frequently used in our research work.

The sensitivity of an energetic material (e.g., an explosive) is the degree to which it can be prompted to explode by external stimuli. The energetic material has separate sensitivities to each stimulus: impact, heat, friction, and electrical sparks. A less sensitive energetic material is safer—it is less likely to explode if accidentally mishandled. The sensitivity of an energetic material is therefore used as a measure of its safety, and is a property that significantly influences the process used to produce the material, as well as applications of the material. The sensitivity is mainly determined experimentally. A statistical theory for modeling the impact-based initiation of explosions of reactive materials (explosives and propellants) containing brittle constituents was presented in [15]. In [16], it was suggested that explosive sensitivity is closely related to the intragranular—not extragranular—voids in the material. However, it was proposed in [17] that the observation that ultrafine PETN (pentaerythritol tetranitrate) and RDX samples are less susceptible to drop-weight impact can be explained by the smaller interstices between grains in ultrafine powders. Also, a recent work [18] explored the association between internal voids (actually vacancy defects) in RDX crystals and sensitivity.

To date, theoretical simulations of sensitivity have mainly focused on energetic molecules and crystals. Similar works on energetic composites, to the best of our knowledge, are much rarer. In [19, 20], the impact and heat sensitivities of the two-component HMX/AP(NH_4ClO_4) system were related to the maximum bond length of the N–NO₂ trigger bonds in the sensitive component HMX (cyclotetramethylene tetranitramine). The notion of a trigger bond [21–24]—the chemical bond that is the first to break during decomposition triggered by external stimuli—is used extensively in studies of sensitivity. In [19], it was observed that the maximum bond length

of the N–NO₂ trigger bond first increases and then decreases as the mass ratio of HMX/AP is increased, leading to a parabolic curve for the maximum bond length versus mass ratio, with the peak length occurring at a mass ratio of 1:1. This curve shape agrees well with experimental results for the sensitivity, and the composite is indeed found to be most sensitive at a mass ratio of 1:1 [19]. In [20], it was reported that the maximum bond length of the N–NO₂ trigger bond in HMX/AP increased with temperature, and this correlated well with the experimental observation that increasing the temperature enhanced the sensitivity of the composite.

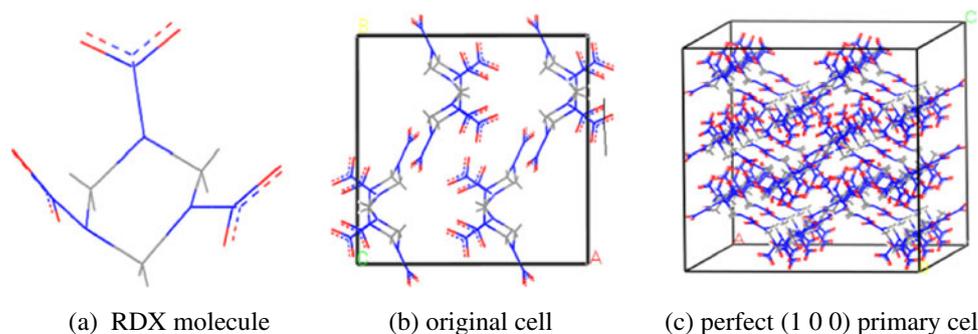
In the present work, the relationship between structure and sensitivity was investigated for perfect and defective RDX crystals as well as their PBXs, using MD simulation. Five kinds of defects—two dislocations, one vacancy, and two dopants—were separately introduced into a perfect RDX crystal. Below, we analyze and discuss the effects of these defects on the structure and the sensitivity in order to identify the key factor that can be used to judge the sensitivities of energetic crystals with defects and composites that include them.

MD modeling and simulation

In this work, the COMPASS force field [14] was employed in the MD simulation. This force field was successfully used in [13, 25], where models of composites of a nitramine compound and a similar fluorine polymer were simulated using MD. This shows that the COMPASS force field can be effectively applied to this type of composite. The MD modeling and computations performed in this work were all carried out using the software program MS (Materials Studio) from Accelrys Inc. (San Diego, CA, USA).

To build the primary cell of RDX for simulation purposes, the original RDX periodic cell [2] was cut along the (100) crystalline surface with the Cartesian *z*-axis parallel to lattice vector *c* and at the same time perpendicular to the (100) crystalline surface. The vacuum layer height was set to zero. The area of the (100) crystalline surface was $(23.15 \times 32.13) \text{ \AA}^2$. A periodic simulation cell of a perfect RDX crystal, containing 72 RDX molecules (1,512 atoms), was built and denoted “(100) RDX.” Figure 1 shows the

Fig. 1 Structures of a perfect RDX molecule (a), an original cell (b), and a perfect (100) RDX primary cell (c)



structures of an RDX molecule, an original crystal cell, and a perfect (100) RDX primary cell.

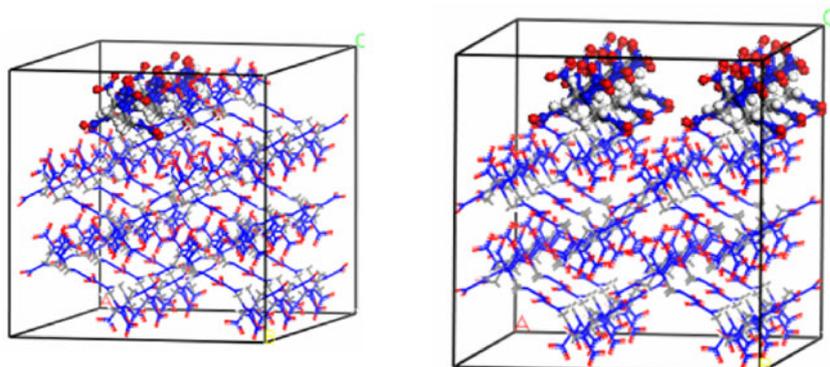
Five kinds of defects were induced on the (100) RDX crystalline surface: two dislocations, one vacancy, and two dopants (note: only one type of defect was present in each simulation). In “dislocation 1,” one line of RDX molecules on the top surface was translated 5.787 Å by changing their centroid coordinates. In “dislocation 2,” two lines of RDX molecules on the top surface underwent the same translation, as indicated in Fig. 2 (comparison of Fig. 2 with Fig. 1c shows that line(s) of molecules has/have clearly been moved in the RDX with dislocations).

In other simulation, a vacancy was created by removing two RDX molecules from one corner on the top surface, as shown in Fig. 3 (comparison with the perfect (100) RDX primary cell in Fig. 1c highlights the removal of the two RDX molecules).

In the simulations focusing on the doped RDX, one RDX molecule on the top surface was replaced with one HMX molecule (fractional coordinates of the center of mass: 0.8289, 0.8792, 0.8464), or two H₂O molecules were inserted into the top surface of the perfect (100) RDX primary cell. These two kinds of doping are shown in Fig. 4, and were denoted “doping 1” and “doping 2,” respectively. The fractional coordinates of the oxygen atom and the two hydrogen atoms in one water molecule were (0.6741, 0.7222, 0.8974), (0.7127, 0.7373, 0.9163) and (0.6378, 0.7448, 0.8965), respectively, and those for the other water molecule were (0.6833, 0.6266, 0.8643), (0.7219, 0.6417, 0.8832) and (0.6470, 0.6491, 0.8635), respectively.

In order to study the effect of F₂₃₁₁ on structure and sensitivity, one F₂₃₁₁ molecular chain was added onto the surface layer of the perfect RDX and the surface layers of the five defective RDX cells. F₂₃₁₁ is a random copolymer that is polymerized from vinylidene difluoride and chlorotrifluoroethylene in a 1:1 molar ratio, and the F₂₃₁₁ molecular chain includes ten repeating units. A periodic cell containing the F₂₃₁₁ molecular chain was built in which

Fig. 2 Structures of defective (100) RDX with two types of dislocation: **a** dislocation 1; **b** dislocation 2. The *ball and stick models* represent the RDX molecules that have been moved from their original positions in the perfect crystal



(a) Dislocation 1

(b) Dislocation 2

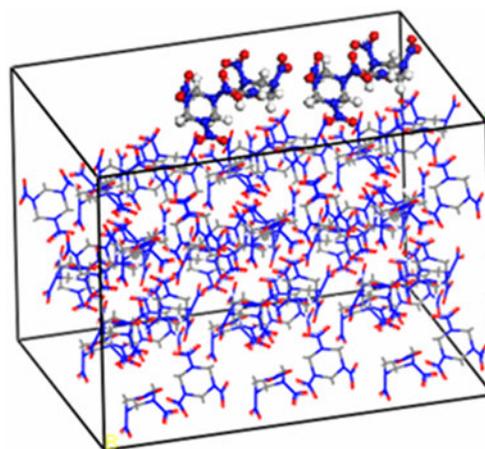
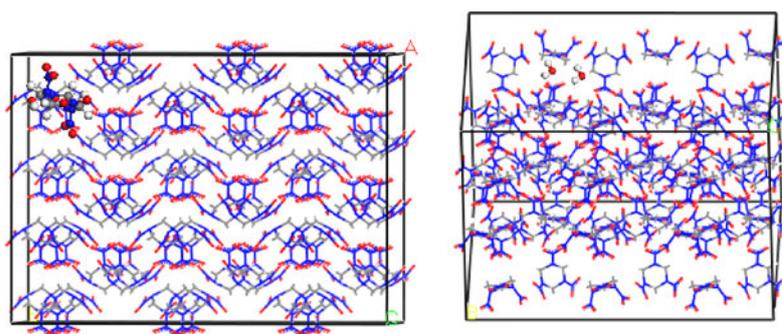


Fig. 3 Structure of the defective (100) RDX with the vacancy. The two RDX molecules beside the *ball and stick models* were removed

the bottom plane had the same shape and size as the (100) surface of (100) RDX and the *c* axis was perpendicular to the bottom plane. The *c* value was set such that the periodic cell density was about half of the density of the polymer F₂₃₁₁. The *c* value was then reduced in a series of steps, and the F₂₃₁₁ chain was optimized after each step until its total energy was minimized. This process was performed until the cell density was about the same as that of the polymer F₂₃₁₁. The resulting periodic cell was saved, and the corresponding *c* value was denoted \bar{c} . Another (100) RDX periodic simulation cell was then set up, but in this case with the vacuum layer height set to \bar{c} . Next, the saved F₂₃₁₁ cell was merged with the (100) RDX crystalline surface, thus creating a periodic simulation cell of PBX, which is denoted “(100) RDX/F₂₃₁₁” below. As an example, Fig. 5 shows one perfect (100) RDX/F₂₃₁₁ periodic primary cell.

After the molecules had been optimized to minimize their energies, all of these (100) RDX and (100) RDX/F₂₃₁₁ periodic cells were allowed to evolve dynamically in isothermal–isobaric (NPT) ensembles with the Andersen

Fig. 4 Structures of defective (100) RDX with two kinds of doping: **a** doping 1 with one HMX molecule; **b** doping 2 with two H₂O molecules. The HMX molecule and H₂O molecules are represented by *ball and stick models*



Doping 1 with one HMX molecule

Doping 2 with two H₂O molecules

thermostat [26] locked at 295 K and under Parrinello–Rahman pressure control [27] at atmospheric pressure. During the condensed-phase simulations, van der Waals interactions were truncated at 9.5 Å, electrostatic interactions were calculated via standard Ewald summation [28], and the equations of motion were integrated using steps of 1 fs. Equilibration runs lasting for 1 ns were performed, followed by production runs of 1 ns; during these production runs, data were collected for subsequent analysis (the sampling interval was 10 fs).

Results and discussion

There is a criterion [29, 30] that can be used to judge the relative impact sensitivities of energetic compounds based on a comparison of the bond orders of trigger bonds, which would appear to be a logical and convenient approach. This “principle of the smallest bond order” (PSBO) says that, for a series of energetic compounds with similar molecular structures, the smaller the bond order of the trigger bond in a molecule, the more sensitive the compound. In general, for the chemical bond in a molecule, as the bond order

increases, the bond length shortens, and vice versa. Classical MD simulation does not provide electronic structures, and cannot produce bond order data. However, it is able to give the statistical distribution of a bond length. Because the chemical bond strength is usually characterized by the bond order and bond length in molecules, it is possible to evaluate sensitivity based on molecular structure parameters—bond lengths—obtained through MD simulation.

It is well known that the N–NO₂ bond in nitramine explosives is a trigger bond [21–24]. In this section, we discuss the N–NO₂ trigger bond in perfect and defective RDX crystals and their PBXs.

N–NO₂ trigger bond length distribution

Figure 6 shows the statistical distribution of the N–NO₂ trigger bond length in perfect (100) RDX as a representative example. This distribution can mainly be attributed to atomic vibrations in RDX molecules. From Fig. 6, we can see that 98 % of the N–N bonds have lengths of 1.33–1.46 Å, so only a small proportion of the molecules have smaller or larger N–N bond lengths than these. Also, the L_{\max} of the

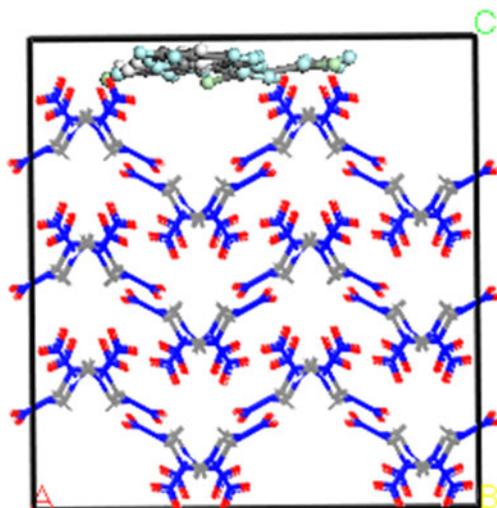


Fig. 5 The perfect (100) RDX/F2311 simulation cell

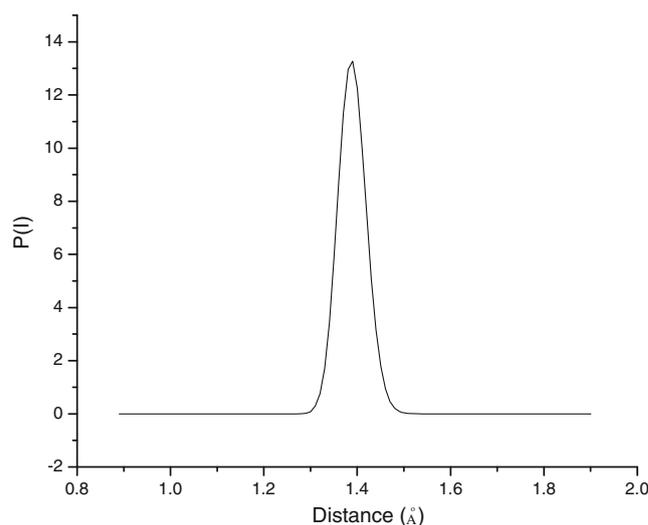


Fig. 6 N–NO₂ trigger bond length distributions in: **a** RDX molecule; **b** original cell; **c** perfect (100) primary cell

Table 1 L_{\max} and L_{ave} (Å) for the N–NO₂ trigger bonds in perfect and defective (100) RDX

	Perfect (100)RDX	Dislocation 1	Dislocation 2	Vacancy	Doping 1	Doping 2
L_{\max}	1.540	1.555	1.563	1.568	1.547	1.559
L_{ave}	1.405	1.385	1.393	1.388	1.387	1.389

N–N bond based on the trajectory of perfect (100) RDX is 1.540 Å; the bond is this long during $2.3 \times 10^{-5}\%$ of the whole trajectory.

We should emphasize that only one value for the length of a bond can be obtained from an experiment or quantum chemistry calculation. For example, the N–N bond length in RDX in the crystalline state is 1.413 Å according to experiment [2], and 1.424 Å in the gaseous state, as calculated by B3LYP/6-31* [7]. In this work, the statistical average for a perfect (100) RDX crystal was found to be 1.405 Å using MD simulation. Upon comparing this value to the experimental data, the absolute deviation is 0.008 Å, and the relative deviation is 0.6 %, which indicates that the value from the MD simulation is very close to the experimental one.

When the bond length is longer, the bond is more easily broken, which makes the molecules more active and more likely to decompose. The molecule with the maximum bond length is exceptionally active and resembles an activated molecule. It tends to decompose very easily. Thus, it is wise to pay attention to the maximum bond length (L_{\max}) in the N–NO₂ trigger bond distribution.

Perfect and defective RDX crystals

As discussed previously, molecules with bonds of length L_{\max} are active, easily undergoing decomposition and explosion, and are therefore of particular concern. In general, the L_{\max} value of a defective crystal is larger than that of a perfect crystal, which means that the presence of defects will increase the sensitivity of the system to some extent, and is not advantageous to the stability of an energetic material. Furthermore, different defects have different effects on L_{\max} . Table 1 gives the L_{\max} values of N–NO₂ trigger bonds in perfect and defective RDX crystals. As seen in Table 1, L_{\max} for RDX with dislocation 2 is higher than that for RDX with dislocation 1, which is the same type of defect but with a lower defect percentage. This tells us that increasing the defect percentage makes the energetic material more sensitive.

Among the two kinds of doping investigated here, doping with H₂O molecules yielded a larger L_{\max} value than doping with HMX did, meaning that the presence of water in the

system will increase the sensitivity of RDX. This is because HMX, which has a similar molecular structure to RDX, is less sensitive than RDX, and doping it into RDX desensitizes the system.

In Table 1, the L_{\max} value for RDX with a vacancy is 1.568 Å, which is the largest of all values for the defective RDX crystals, meaning that RDX with a vacancy is the most sensitive of the defective RDX crystals. This is because the vacancy disrupts the local structure of the crystal, making it much easier for a hotspot [1] to form in this area.

Overall, based on the hotspot principle [1] and the notion of a trigger bond [21–24], which were proposed based on a variety of experimental results, as well as the maximum trigger bond length criterion [19, 20] suggested by us for energetic composites, the results in Table 1 indicate that the maximum bond length (L_{\max}) of the N–NO₂ trigger bond is indeed correlated with impact and heat sensitivity, and can be used as a criterion for the relative sensitivity. The sensitivities of the perfect and defective RDX crystals investigated in this work can be ordered as follows: vacancy > dislocation 2 > doping 2 > dislocation 1 > doping 1 > perfect, since their L_{\max} values are: 1.568 > 1.563 > 1.559 > 1.555 > 1.547 > 1.540 Å.

On the other hand, the values of L_{ave} in Table 1 vary in a rather more complicated manner than L_{\max} , making it much more difficult to pinpoint a relationship between the type of defect and the sensitivity.

RDX-based PBXs

Table 2 gives the maximum (L_{\max}) and the average (L_{ave}) bond lengths of the N–NO₂ trigger bonds in various perfect and defective PBXs. Mixing RDX with F₂₃₁₁ should lead to a safer (i.e., less sensitive) explosive than pure RDX, which is indeed found experimentally [31]. If we compare the values for the (100) RDX/F₂₃₁₁ PBXs given in Table 2 to those in Table 1, we can see that the relationship between L_{\max} and the type of defect for the PBXs is much more complicated than that seen for the RDX crystals. If we compared the L_{\max} values of perfect RDX and RDX with dislocation 1 in Table 1 with the corresponding values for the perfect PBX and PBX with dislocation 1 in Table 2, we

Table 2 L_{\max} and L_{ave} (Å) values for N–NO₂ trigger bonds in perfect and defective (100) RDX/F₂₃₁₁

	Perfect (100) RDX/F ₂₃₁₁	Dislocation 1	Dislocation 2	Vacancy	Doping 1	Doping 2
L_{\max}	1.561	1.558	1.550	1.541	1.548	1.547
L_{ave}	1.391	1.388	1.390	1.391	1.388	1.387

can see that the PBX values are larger. In this situation, the structure factor L_{\max} cannot be used to gauge the sensitivity any more. However, the L_{\max} values for PBX with dislocation 2, a vacancy, and doping 2 are smaller than the corresponding values for RDX, meaning that they do correlate with the sensitivity. Then again, the value for RDX with doping 1 is almost the same as that observed after adding F_{2311} .

As shown in Table 2, the L_{\max} values of all five defective (100) RDX/ F_{2311} PBXs are smaller than that (1.561 Å) of the perfect (100) RDX/ F_{2311} . This indicates that the structure parameter L_{\max} of the base explosive RDX does not correlate with the sensitivity for these PBXs. For the PBXs of perfect and defective RDX crystals, the presence of F_{2311} weakens the correlation between L_{\max} and the sensitivity. Note that F_{2311} shows significant elasticity and a large thermal capacity. The buffering effect and thermal insulation due to F_{2311} have a strong desensitizing effect on the PBXs, meaning that desensitization leads to the enhanced safety of the PBXs; the structure factor L_{\max} is not relevant for these composites.

Conclusions

This work investigated the correlation between sensitivity and N–NO₂ trigger bond length for perfect and defective RDX crystals and their corresponding PBXs with F_{2311} , using MD atomistic simulation. Five kinds of defects were considered: two dislocations, one vacancy, and two types of doping. Several conclusions can be drawn based on the results obtained:

- MD simulation can provide the statistical distribution of a bond length in a molecule. The average bond length obtained from the distribution is very similar to that obtained experimentally, and for the N–N bond studied in this work, the calculated average bond length was very close to the experimental value. On the other hand, the most active molecule has the maximum bond length. It is therefore important to pay attention to the maximum bond length of the trigger bond in an energetic material.
 - Defects affect the N–NO₂ trigger bond length and thus the impact and heat sensitivity of an energetic material. Among the five kinds of defect added to RDX crystals in this work, adding a vacancy to the crystal had the greatest effect on the maximum N–NO₂ trigger bond length L_{\max} , meaning that the crystal with a vacancy showed the highest sensitivity among all the crystals.
 - Upon analyzing the L_{\max} values for perfect RDX and the five defective RDX crystals, the maximum N–NO₂ trigger bond length L_{\max} was found to correlate well with the sensitivity. Thus, the maximum trigger bond length L_{\max} is suitable for use as a theoretical criterion to judge the impact and heat sensitivity.
- Adding F_{2311} to RDX was thought to reduce the maximum trigger bond length and thus the sensitivity. However, due to the strong desensitizing effect of F_{2311} , which is stronger than the effect of the structure factor L_{\max} , the L_{\max} value of RDX is observed to have a much more complicated relationship with sensitivity for (100) RDX/ F_{2311} composites (PBXs). In other words, for PBXs, the defect present in the base explosive crystal is not the main influence on the sensitivity (and therefore safety) of the composite.

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