

## Categorizing and Understanding Energetic Crystals

Rupeng Bu, Fangbao Jiao, Guangrui Liu, Jingyu Zhao, and Chaoyang Zhang\*

Cite This: <https://dx.doi.org/10.1021/acs.cgd.0c01300>

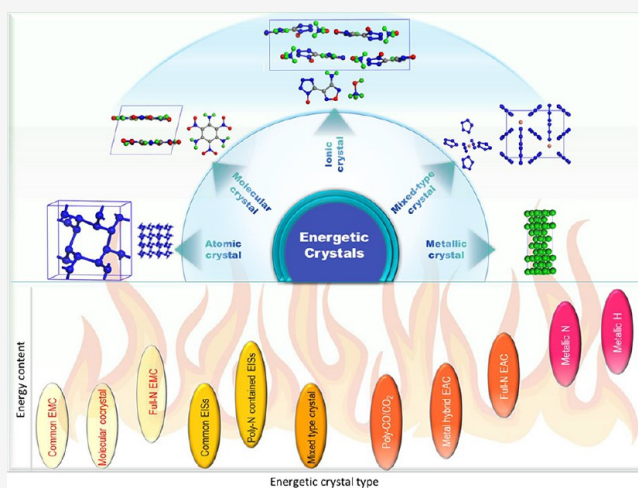
Read Online

ACCESS |

Metrics &amp; More

Article Recommendations

**ABSTRACT:** The subject of energetic crystals has been significantly enriched in the past several decades, with the number rising rapidly. Meanwhile, some new types of crystals have appeared, such as energetic extended solids, energetic ionic salts, energetic metal organic frames, energetic cocrystals, metallic hydrogen, and energetic perovskites. They may dazzle us but give rise to a difficulty in understanding these compounds and work to achieve general knowledge from them and design new ones; thus, it becomes interesting and crucial to categorize energetic crystals. In this work, on the basis of the types of primary constituent parts and their interactions in crystal, we classify experimentally observed and theoretically predicted energetic crystals into five types, including molecular crystal, ionic crystal, atomic crystal, metallic crystal, and mixed-type crystal; i.e., energetic crystals cover all the five crystal types and exhibit a high diversity. By categorization, it will become much easier to understand and predict various formation and energy release mechanisms of energetic crystals. Furthermore, a dependence of energy level on crystal type is summarized, as the energy content increase follows an order of molecular crystal, ionic crystal and mixed type crystal, atomic crystal, and metallic crystal. In general, a highly energetic crystal should exist under high pressure, while a crystal with a moderate or low energy content can exist under common conditions. Thus, this work presents an overall perspective on the crystal structures of energetic materials and makes the increasing energetic crystals roughly and readily understandable, despite the increasing diversity and complexity of these structures.



## 1. INTRODUCTION

Energetic materials (EMs) are a special class of substances. They are in principle thermodynamically metastable while kinetically stable and can release large quantities of gas and heat in a short time by self-decomposition once stimulated sufficiently.<sup>1–5</sup> In general, EMs can be classified into three categories including explosives, propellants, and pyrotechnics, depending on their functions and applications. These applications in both military and civilian fields stem from the rapid release of gas and heat. Largely, EMs have promoted human technological advances and are still highly desired in many situations. Thus, promoting the development of EMs is still of great interest to promote some social progress. For example, nowadays, highly heat-resistant EMs are urgently required that are capable of operating in deep Earth and deep space and satisfying related safety requirements.

Three elementary points can be summarized for an EM: self-redox decomposition reaction, fast release of gas and heat, and a certain kinetic stability.<sup>1–11</sup> It should be noted that the heat release is not always necessary for an EM, as there is no heat release in the decomposition of an entropic explosive like TATP.<sup>12</sup> The decomposition reaction occurs after a sufficient

external stimulation loaded while without participation of any external substance. An EM can either be a compound or a mixture, traditionally containing CHNO, but other elements like Al and B can be added to energetic formulations for a special purpose sometimes. In general, a conventional CHNO energetic molecule can be readily partitioned into oxidizing and reducing moieties, while for new-concept EMs such as metallic hydrogen<sup>13,14</sup> and polymer nitrogen,<sup>15</sup> it is difficult to distinguish them. Thermodynamically, an EM is a metastable substance; in other words, it is located at a local minimum on a potential energy surface, and it should be controllable to ignite an EM for application. Compared with final stable products, the EM is thermodynamically unstable. Electronically, the energy release of EMs results from the interatomic rearrangement of valence electrons or from the release of chemical

Received: September 21, 2020

Revised: November 13, 2020

energy stored in a reactant. Thereby, the energy release is limited to a level of several kJ/g, even though these have not been strictly deduced yet. Kinetically, the decomposition of EMs proceeds fast,  $\sim 0.01$  s. In principle, the energy barrier of decay governs the kinetic stability of EMs. Regarding the detonation reaction of a common EM, it can be finished as fast as  $10^{-6}$  s ( $\mu\text{s}$ ). Therein, the stored chemical energy is transferred to mechanical energy quickly as shock with a propagation velocity above the sound velocity. This is the root for the shock.<sup>6–9</sup> When one combines thermodynamics and kinetics together, it becomes clear that the EMs are a group of high-power energy release materials, instead of high energy density materials, as EMs usually outperform traditional fuels such as coal and oil in the energy release rate, instead of energy density (unit mass or unit volume). These characteristics are the bases for defining, understanding, and designing EMs.

The performances of EMs are originally determined by the structural evolution under external stimuli. With respect to an applied EM, for example, a typical applied polymer-bonded explosive (PBX), has hierarchical structure, covering micro-, meso- and macro-scales; i.e., the multiscale structures involve molecule, crystal, and composite particle.<sup>16</sup> Among these structures, crystal is the core, as it mediates between a molecule and an applied composite form. The basic characteristic indexes that are employed to describe an energetic crystal usually refer to composition, purity, density, packing structure, shape, particle size and distribution, and defect.<sup>1–11</sup> Regarding an energetic crystal, it generally contains some issues such as polymorph prediction, morphology prediction, crystal design, crystallization kinetics, structure–property relationship, and origin of macroscopic properties.<sup>17–19</sup> On the basis of the structure and composition of an energetic crystal, we can deduce its macroscopic properties, such as energy content, detonation property, stability, safety, mechanical property, and so forth. In fact, numerous insights into the origins of properties and performance of EMs are derived from the crystals.<sup>20,21</sup>

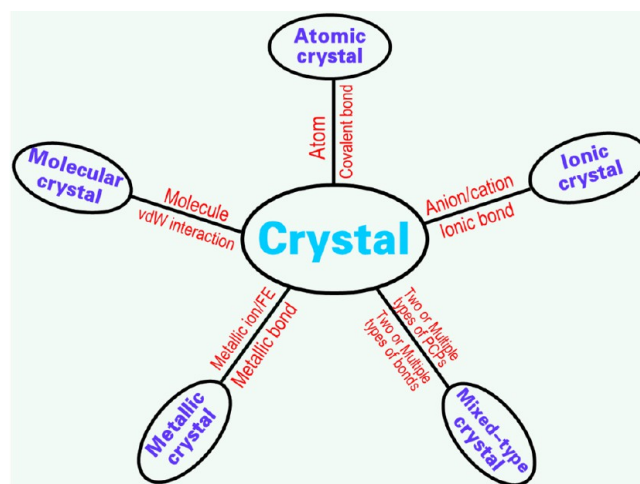
Molecule and crystal are the two intrinsic structures of an energetic molecular material, as they keep invariable in a rather large scope of conditions of temperature and pressure variations. For example, in various  $\beta$ -HMX-based PBXs, the HMX molecules and crystals are invariable. Compared with a molecule, a crystal is much closer to practical material; thus, studying an energetic crystal is more practically meaningful. Certainly, the issues in a crystal are more complex than those of an isolated molecule, as a consequence caused by intermolecular interactions.

Nowadays, many new kinds of EMs, such as energetic extended solids,<sup>15</sup> energetic ionic salts,<sup>22</sup> energetic metal organic frames,<sup>23</sup> energetic cocrystals,<sup>24</sup> and energetic perovskites,<sup>25</sup> have been created in combination with various theory and simulation aided design technologies. Even though most of these novel EMs have not been applied yet, more selections and ideas for potential applications have been presented. More importantly, it makes EMs more scientific and rational, with an increasingly lessened empirical sense. While being cheerful for the increasing types of new EMs, we should clarify their structures, in particular, on the crystal level. Thus, it encourages us to systematically categorize all the types of energetic crystals in this Perspective, which were reported as experimental observations or theoretically predictions. On the basis of the categorization, it will allow the reader to distinguish, understand, and clarify all kinds of energetic

crystals. Furthermore, some crucial characteristics such as energetics and stability (or sensitivity) can also be assessed by the elementary interactions in these crystals.

## 2. CRITERION FOR CLASSIFYING ENERGETIC CRYSTALS

Recently, we redefined the term cocrystal and broadened its intention into five types.<sup>26</sup> In classifying crystals, it is key to clarify which are the closest substructures to crystals. These closest substructures can be molecule, atom, ion, or free electron, and can be specified as the primary constituent part (PCP). Figure 1 shows various PCPs involved in all five kinds



**Figure 1.** Crystal categorization based on a primary constituent part (PCP) and the nature of PCP interactions. FE represents free electron. Reprinted with permission from ref 26. Copyright 2019 American Chemical Society.

of crystals, i.e., the PCPs of atomic crystal, molecular crystal, ionic crystal, and metallic crystal are atom, molecule, ion (cation/anion), and metallic ion/free electron, respectively. Furthermore, if two or multiple types of PCPs coexist in the same crystal, the crystal is named a mixed-type crystal.

The aforementioned PCP type is not identical to the component type, and it only refers to atom, molecule, ion, or metallic ion and free electron. For example, in the cocrystal of CL-20/TNT,<sup>27</sup> there are two components (CL-20 and TNT) of the same PCP type, i.e., molecule; therefore, it belongs to a molecular crystal. The interactions among the PCPs in a crystal reflect the physical nature of the crystal. Thus, the PCP type and the PCP interaction type are the criteria for the crystal classifications. Atomic crystals are called covalent crystals because the atoms are held in the lattice by covalent bonds; molecular crystals are composed of discrete molecules and held by weak intermolecular interactions; ionic crystals consist of ions bound together by their electrostatic attraction, as well as intermolecular interaction; metallic crystals are composed of metallic ions and free electrons, and the metallic bonds are present in all metals, in which the outer electrons are shared by the crystals as a gas of valence electrons which are free to move throughout the metal lattice; and finally, mixed-type crystals are crystals held by at least two types of interactions among the PCPs.<sup>26</sup> On the basis of these criteria, all the reported energetic crystals can be categorized, as discussed in the next section.

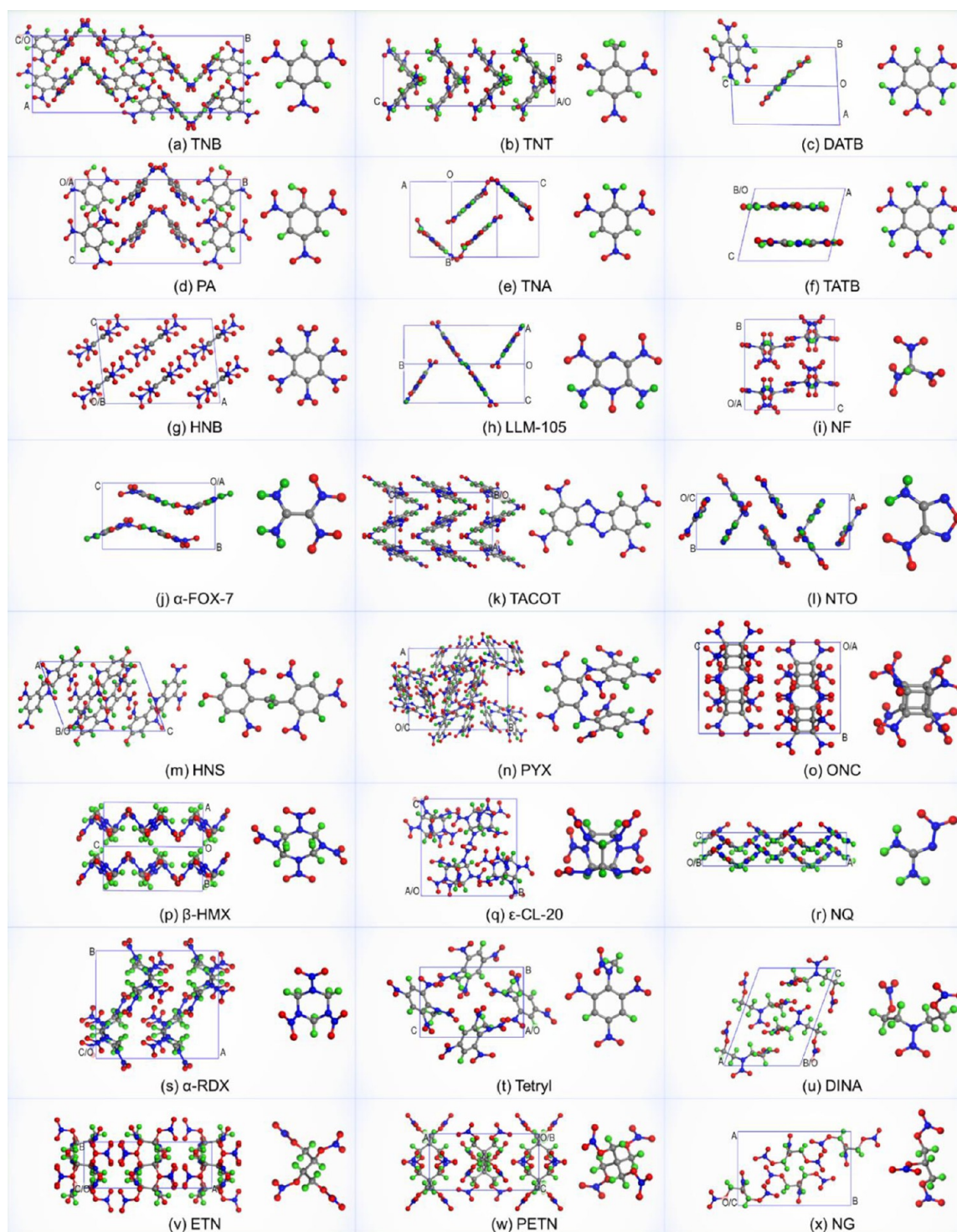


Figure 2. (a–x) Crystal packing of some typical  $\text{NO}_2$ -containing compounds.

### 3. CATEGORIZATION OF ENERGETIC CRYSTALS

The energetic crystals discussed in this work cover the experimentally observed and theoretically predicted. Checking all the related reports to our best ability, we found examples of all five types of energetic crystals. Thus, the categorization of these crystals is performed based on the aforementioned criteria; in particular, more attention is paid to new crystal structures.

**3.1. Energetic Molecular Crystals.** The single-component energetic molecular crystals, or energetic molecular

compounds, are the type with the longest history, the largest quantity, and the most popular research and applications. This kind of compound is just regarded as the common or traditional EMs. According to the aforementioned criteria, the PCP of a single-component energetic molecular crystal is just the component, i.e., molecule. The molecules of this kind are generally composed of C, H, O, and N atoms. Because of the low molecular polarity, intermolecular interactions in these crystals are generally weak.<sup>18</sup> Nitro compounds possess the largest population among traditional EMs, in particular, the

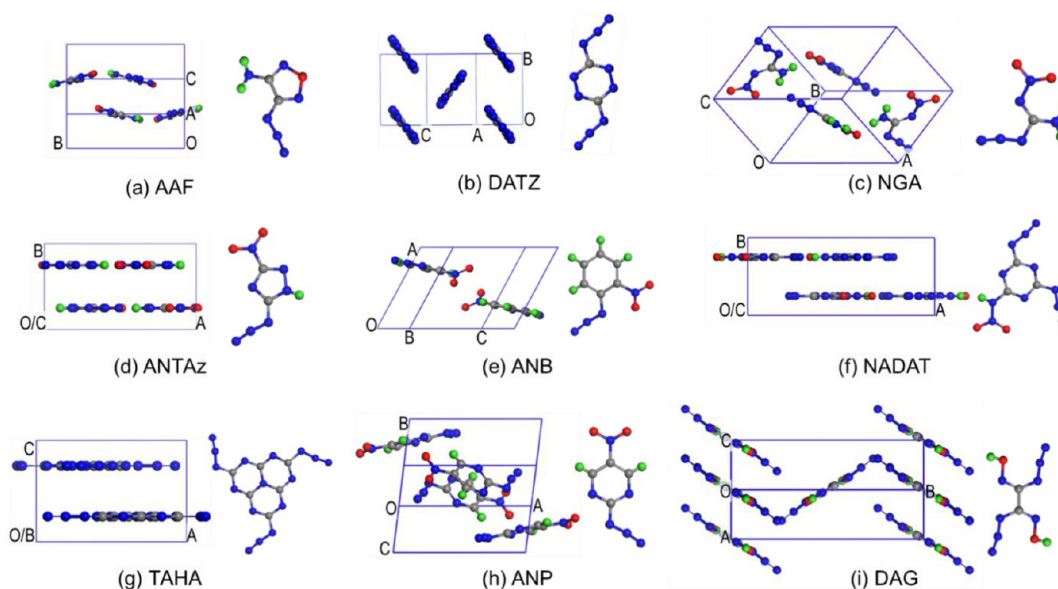


Figure 3. (a–i) Crystal packing of some organic azides.

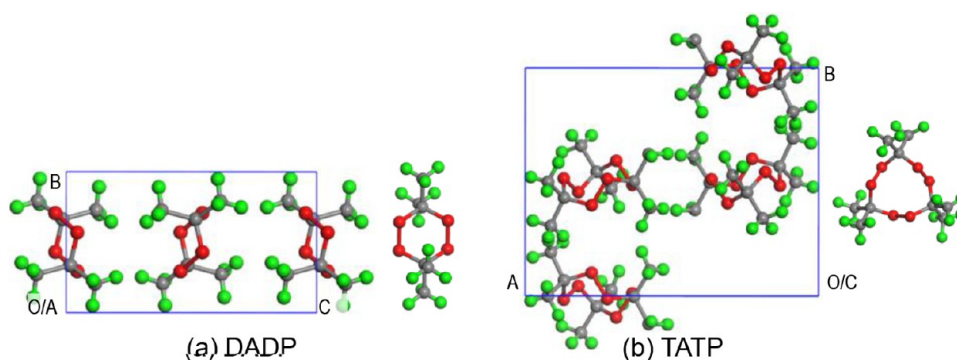


Figure 4. (a, b) Crystal packing of two typical peroxides.

applied EMs. As demonstrated in Figure 2,  $\text{NO}_2$  can be linked with C, N, and O atoms, and the related compounds can accordingly exhibit different molecular stabilities, as the bond strength decreases in the order of C- $\text{NO}_2$ , N- $\text{NO}_2$ , and O- $\text{NO}_2$ .<sup>28–51</sup> For example, low sensitive or highly heat-resistant EMs, such as TNB, DATB, TATB, TNT, and TNA,<sup>28–32</sup> are often molecularly stable bonding  $\text{NO}_2$  with conjugated structures, while the molecular stability of geminal-dinitro and nitroform compounds such as  $\text{NF}^{36}$  is weakened due to the lessened electrons shared by the increased  $\text{NO}_2$ . Of course, energetic molecules with N- $\text{NO}_2$  and O- $\text{NO}_2$  moieties are usually less stable than aromatic nitro compounds, the same as geminal-dinitro and nitroform compounds.<sup>37–42</sup>

Most EMs applied already are shown in Figure 2, including TNT, DATB, PA, TATB, LLM-105, FOX-7, NTO, HNX, PYX, HMX, CL-20, NQ, RDX, Tetryl, PETN, and NG. These EMs are used as primary or secondary explosives, depending on performances and properties. Meanwhile, some EMs such as HNB and ONC shown in the figure are highly energetic, but have not been applied because of poor environmental adaptability. In fact, a huge quantity of EMs had been forgotten immediately after being synthesized, due to the aforementioned strict and comprehensive requirements of application. Thus, EMs are wholly evolved slowly.

The energy-safety contradiction is elementary to prevent the fast evolution of EMs. It is believed that it is feasible to alleviate the contradiction by improving molecular stacking style, as the face-to-face  $\pi$ -stacking is prone to low impact sensitivity.<sup>21</sup> Some energetic crystals such as TATB possess not only high molecular stability but also the face-to-face  $\pi$ -stacking preferred to ready shear sliding and low impact sensitivity. Compared with impact sensitive energetic crystals, it requires more energy to break stronger intermolecular hydrogen bonding (HB) in less sensitive ones when stimulated. Because the covalent bonds in energetic molecules are significantly stronger than the noncovalent intermolecular interactions, it is deemed that the decay of an entire crystal starts from the breaking of intermolecular interactions once an external stimuli is loaded, and the strong intermolecular interactions contribute to low sensitivity. Combining all of these, three points are found behind the low impact sensitivity: high molecular stability, strong intermolecular interactions, and face-to-face  $\pi$ -stacking (layered stacking). Thus, much attention should be paid to the relationship between molecular composition and structure, and intermolecular interaction and molecular stacking style. It is the basis for designing new low sensitive energetic molecular crystals to alleviate the energy–safety contradiction.

Besides  $\text{NO}_2$ , energetic molecules can also contain azide<sup>52–60</sup> and peroxide groups,<sup>12,61</sup> as illustrated in Figures

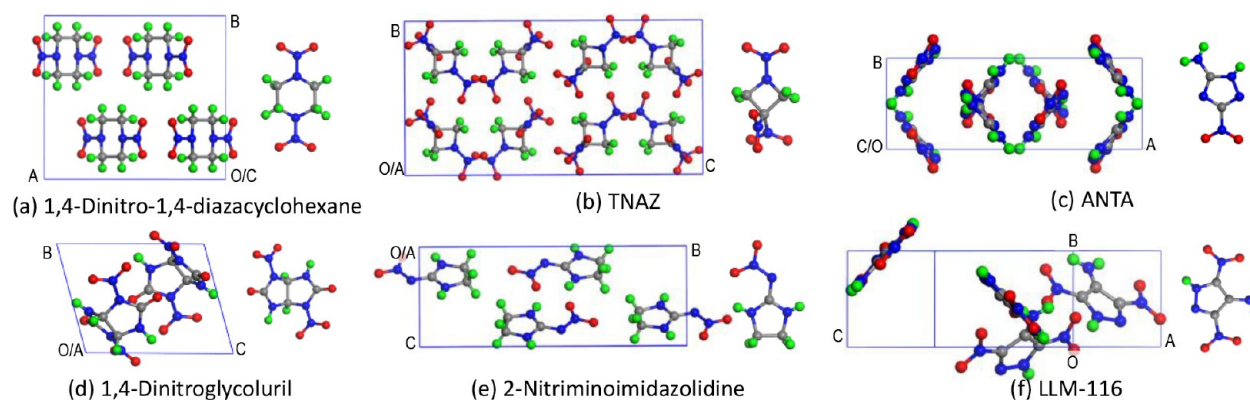


Figure 5. (a–f) Crystal packing of some N-heterocyclic compounds.

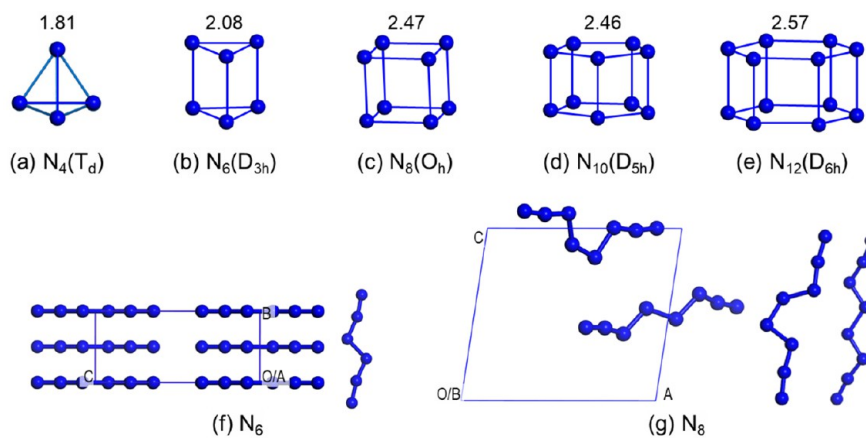


Figure 6. (a–g) Predicted molecular structures and crystal packing of some full-nitrogen compounds.

3 and 4, respectively. Compared with  $\text{NO}_2$ -containing compounds, azides and peroxides are usually more unstable, owing to the readier dissociation of azide and peroxide groups. Thus, azides are generally used as primary explosives, and peroxides are seldom applied due to low safety, as well as low power. Because azide is weakly polar, the intermolecular interactions in azide compounds are accordingly weak, leading to low packing coefficients. Figure 3 shows the planar molecular structures and the face-to-face  $\pi$ -stacking of the layers of some azides with a single atomic thickness, such as ANTAz, NADAT, and TAHA.<sup>52–54</sup> This kind of stacking mode contributes to low impact sensitivity, remedying the low molecular stability. It also verifies that the energy–sensitivity contradiction can be alleviated by improving the molecular stacking mode. The peroxides DADP and TATP shown in Figure 4 feature an entropic explosive, with gas released while without heat release when ignited, and are more accessible and less powerful than the common  $\text{NO}_2$ -containing energetic materials such as TNT and RDX.<sup>12,61</sup>

Energetic N-heterocyclic compounds also possess a high population among energetic molecules, due to a high structural diversity of N-heterocycle.<sup>62–67</sup> Some N-heterocyclic compounds, such as the known CL-20, HMX, RDX, and TNAZ, possess nonplanar N-heterocyclic structures. More N-heterocycles are planar each with a conjugated planar molecular skeleton, which thereby increases the molecular stability, such as various azoles, azines, furazans, and their fused or bridged cycles. ANTA, 2-nitriminoimidazolidine, and LLM-116<sup>62–64</sup>

possess planar molecular structures, setting a base for  $\pi$ -stacking (Figure 5) and rather low impact sensitivity.

In summary, the aforementioned conventional single-component energetic molecular crystals are still the main source of applicable EMs. However, there is a limited space to elevate energy based on energetic molecular crystals, due to the limits of molecular composition of C, H, O, and N, as well as F sometimes, weak intermolecular interactions, and chemical energy stored in a molecule. To a certain extent, this limit stems from the intrinsic energy–safety contradiction of energetic molecules. It is a predicament in developing new traditional EMs.

Because the N–N and N=N bonds possess much less than one-third and two-thirds of the bond energy of a  $\text{N}\equiv\text{N}$  bond, respectively, a very large amount of energy will get released when the conversion of N–N or N=N into  $\text{N}\equiv\text{N}$  bonds occurs. Thereby, N-rich compounds, in particular, full-N molecular crystals have not been synthesized yet, with theoretical results reported only. Recently, Liu et al. predicted the packing densities of  $\text{N}_4$ ,  $\text{N}_6$ ,  $\text{N}_8$ ,  $\text{N}_{10}$ , and  $\text{N}_{12}$  with Lennard–Jones potentials to be 1.81, 2.08, 2.47, 2.46, and 2.57  $\text{g}/\text{cm}^3$ , respectively, in the absence of a packing structure.<sup>68</sup> Also, Greschner et al. and Hirshberg et al. reported the predicted packing structures of chained  $\text{N}_6$  and  $\text{N}_8$ , with densities of 1.95 and 1.561  $\text{g}/\text{cm}^3$ , respectively.<sup>69,70</sup> In these energetic crystals, the intermolecular interactions are weak van

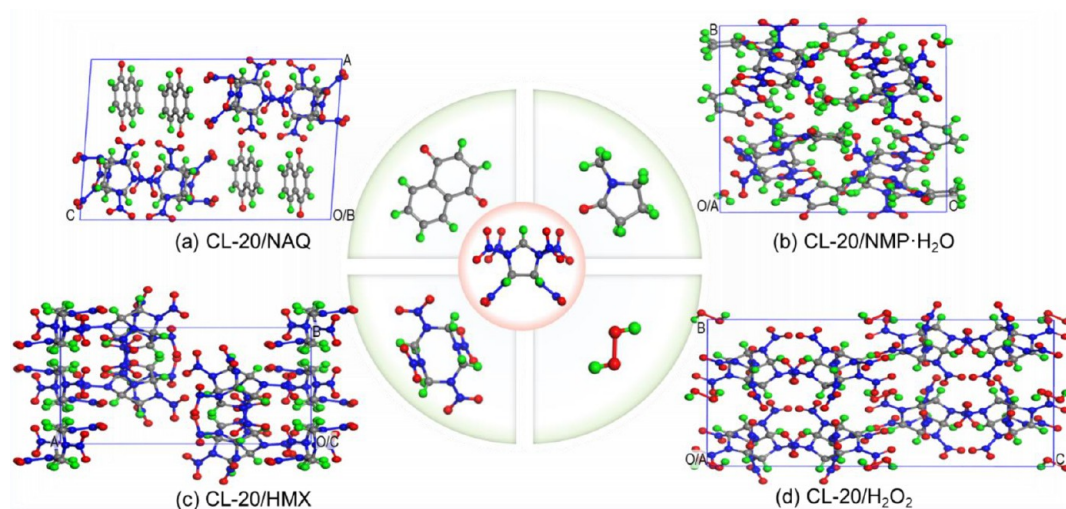


Figure 7. (a–d) Packing structures of some CL-20-based molecular cocrystals.

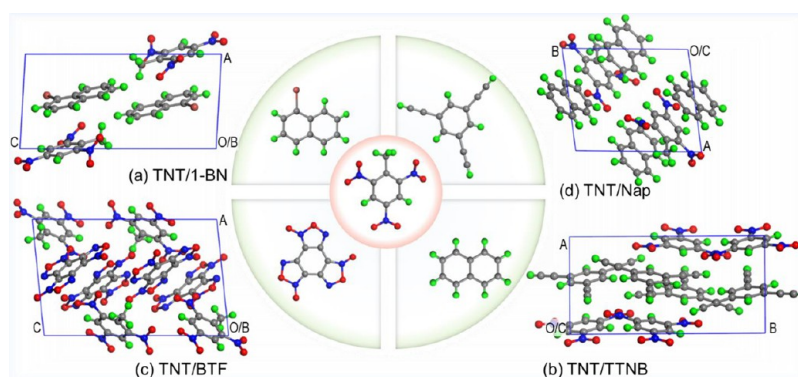


Figure 8. (a–d) Packing structures of some TNT-based molecular cocrystals.

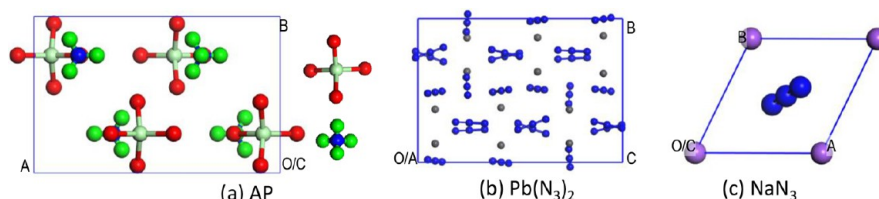


Figure 9. (a–c) Packing structures of some energetic inorganic ionic crystals.

der Waals interactions and electrostatic interactions, belonging to the same type as the aforementioned traditional EMs.

Energetic cocrystals are not new because the energetic solvates reported early are in fact energetic cocrystals.<sup>26</sup> Nevertheless, energetic cocrystals are nowadays thriving, with a rapid increase in quantity, such as the CL-20<sup>71–74</sup> and TNT-based<sup>75–78</sup> molecular cocrystals shown in Figures 7 and 8, respectively. Compared with the single-component molecular crystals, more components belonging to same types of PCPs and PCP intermolecular interactions coexist in cocrystals. This can be referenced from a very recent review by Liu et al, with the details of the intermolecular interactions of energetic molecular cocrystals presented.<sup>79</sup>

**3.2. Energetic Ionic Crystals.** The energetic ionic crystals consist of ions, which can be metallic, organic, or inorganic, and all or partially energetic. Figure 9 exhibits some traditional energetic inorganic ionic crystals, such as AP,  $\text{Pb}(\text{N}_3)_2$ , and  $\text{NaN}_3$ .<sup>80–82</sup> For AP, the heat release comes from the reactions

among anions and cations, while for  $\text{Pb}(\text{N}_3)_2$  and  $\text{NaN}_3$ , it is mainly resulting from the decomposition and rearrangement of  $\text{N}_3^-$ . Compared with the common energetic molecular crystals, the interactions among ions and counterions of traditional energetic inorganic ionic crystals are enhanced because they belong to strong electrostatic interactions.

Energetic ionic compounds are also called energetic ionic salts (EISs). Compared with the common energetic molecular compounds, EISs possess some advantages. The combination of differently signed ions in pairs will yield a series of EISs once a new ion is successfully synthesized. Such a combination reduces the preparation cost and contributes to scientific findings of new rules and regularities in a systematic and comprehensive way. Furthermore, ionization favors the enhancement of molecular stability, in particular, for N-rich compounds. In fact, the EISs have been thriving in the past decade, as numerous EISs have been prepared. In contrast to the common energetic salts shown in Figure 9, the organic ions

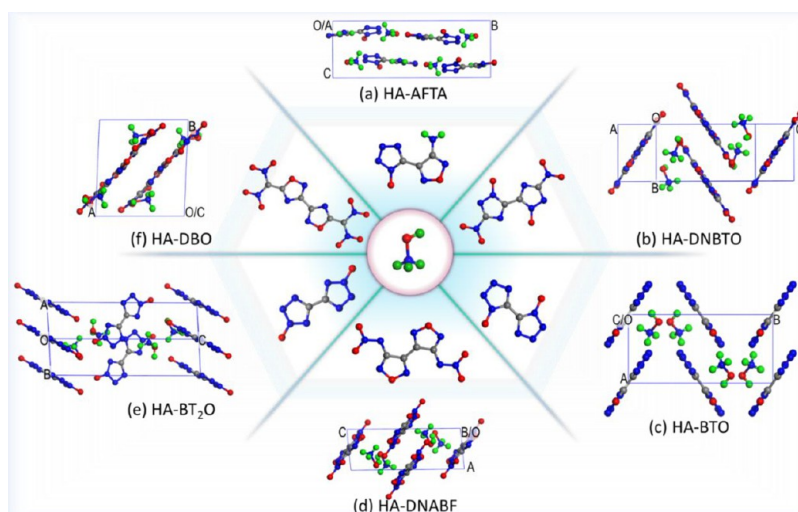


Figure 10. (a–f) Packing structures of some  $\text{HA}^+$ -containing energetic ionic crystals.

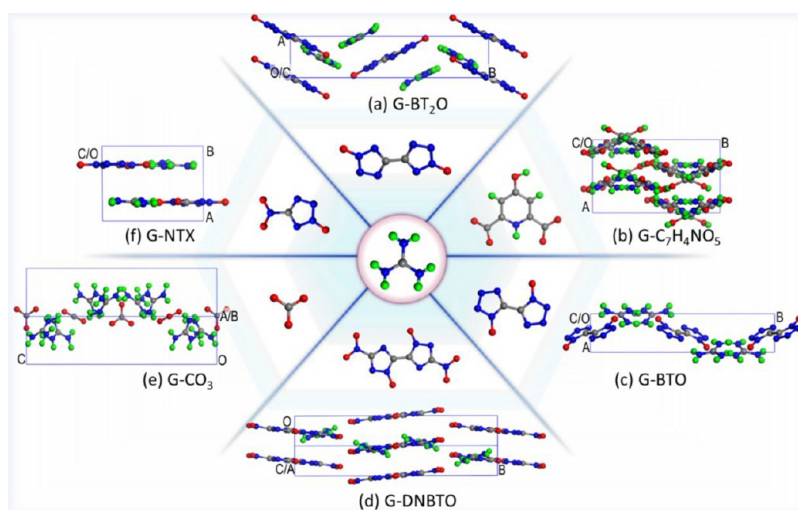


Figure 11. (a–f) Crystal packing of some  $\text{G}^+$ -containing energetic organic crystals.

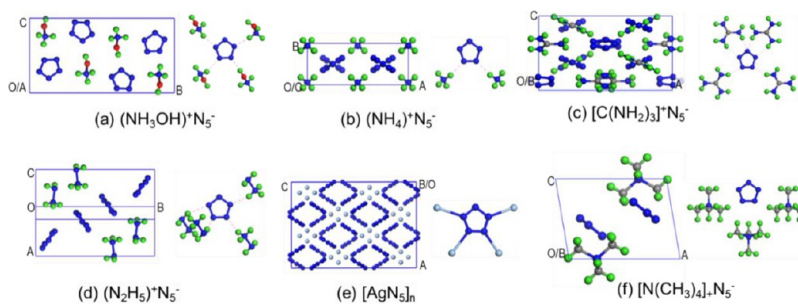


Figure 12. (a–f) Crystal packing of some  $\text{N}_5^-$ -containing energetic inorganic crystals.

that can be negatively or positively signed are introduced into the new types of EISs. For example, among the  $\text{NH}_3\text{OH}^+$ -based EISs exhibited in Figure 10,<sup>83–88</sup> all of the anions are organic. Similarly, both anions and cations of the EISs shown in Figure 11<sup>83,88–92</sup> are organic. The introduction of organic ions into EISs significantly increases their quantity. Besides, more and more  $\text{N}_5^-$ -based EISs (Figure 12)<sup>93</sup> came into being after the successful synthesis of  $\text{N}_5^-$ . The considerable stability of these EISs results from the anionization of  $\text{cyclo-N}_5^-$ , which

enhances the stability of both the  $\text{cyclo-N}_5^-$  itself and the entire crystal by ionic bonds.<sup>94</sup>

**3.3. Energetic Atomic Crystals.** Most experimentally observed and theoretically predicted energetic atomic crystals are poly-nitrogen (Figure 13), poly-CO, and poly- $\text{CO}_2$  compounds. This group of energetic crystals are produced at high pressure. For example, the cubic gauche structure of poly-nitrogen (cg-N) was synthesized directly from  $\text{N}_2$  at temperatures above 2000 K and pressures above 110 GPa using a laser-heated diamond cell.<sup>95</sup> In the cg-N, the neighboring N

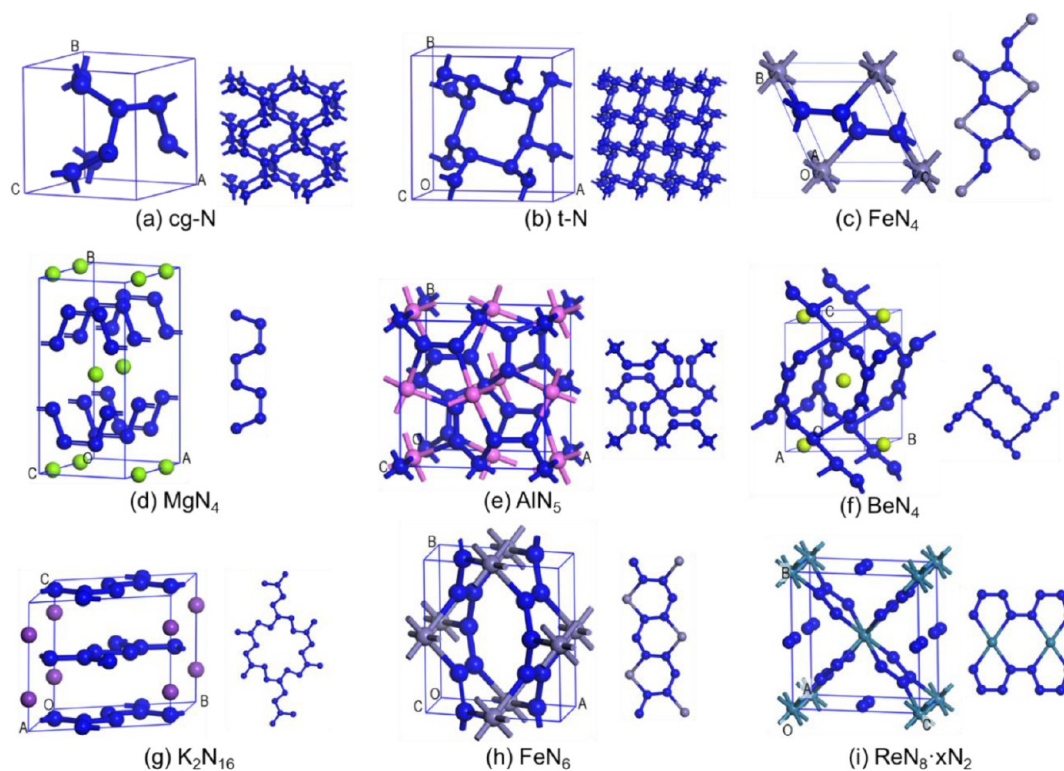


Figure 13. (a–i) Crystal packing of some observed and predicted poly-nitrogen compounds.

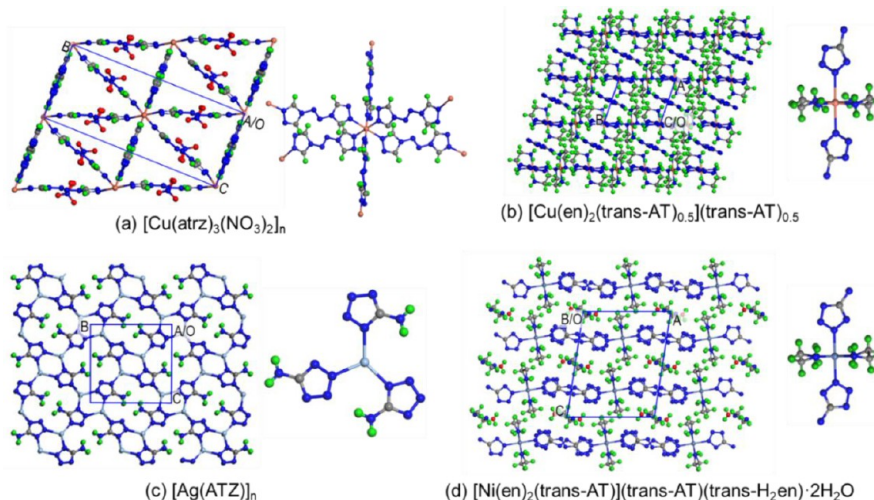


Figure 14. (a–d) Packing structures of some mixed-type cocrystals with metallic organic frames.

atoms are linked by single bonds only, representing a crystal type of atomic crystal. This polymeric N structure can also appear in other compounds<sup>96–103</sup> shown in Figure 13. Nevertheless, some compounds such as  $\text{MgN}_4$ ,  $\text{BeN}_4$  and  $\text{K}_2\text{N}_{16}$ , and  $\text{ReN}_8 \cdot x\text{N}_2$  belong to ionic crystals and composites, respectively, instead of atomic crystals, even though they all contain polymeric N structures.

**3.4. Energetic Metallic Crystals.** In 2017, *Science* reported a transition from solid molecular hydrogen to metallic hydrogen at an extraordinarily high pressure of 495 GPa, verified by the measured reflectivity as high as 0.91, the plasma frequency of  $32.5 \pm 2.1$  eV at a temperature of 5.5 K (Drude free-electron model) or an electron carrier density of  $7.7 \pm 1.1 \times 10^{23}$  particles per cubic centimeter,<sup>13</sup> in agreement with

earlier theoretical prediction.<sup>104</sup> Moreover, a transformation from insulating (molecular) to conducting dense fluid nitrogen was observed by dynamic laser heating compressed  $\text{N}_2$  and fast optical spectroscopy; i.e., the metallization and fluid polymerization occurs  $>125$  GPa at 2500 K.<sup>105</sup> Because a huge quantity of heat will be released when these energetic metallic crystals decompress, they are thought to possess ultrahigh energy contents. Obviously, the crystal type will change to molecular crystal when decompressed, accompanied by the energy release.

**3.5. Energetic Mixed-type Crystals.** The mixed-type crystal is also a mixed-type cocrystal, as it contains two or more PCPs.<sup>26</sup> The mixed-type crystals are now thriving, due to the rapid extension of the new structures, which are originally



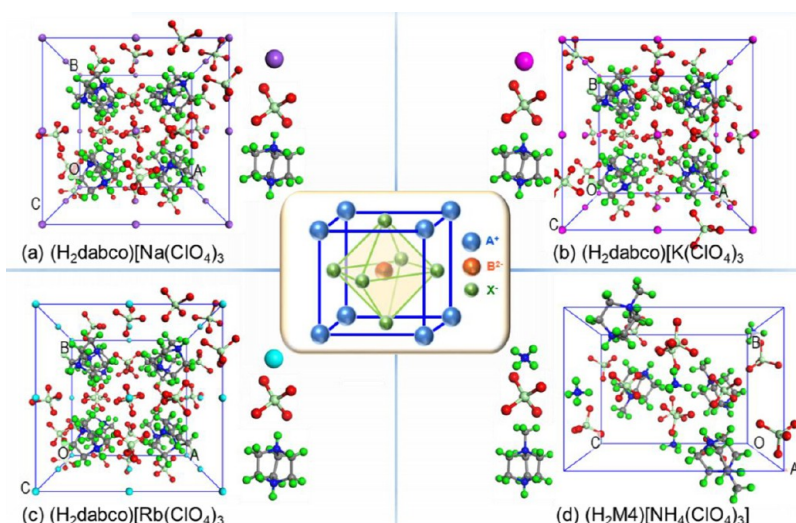


Figure 15. (a–d) Packing structures of some energetic perovskites.

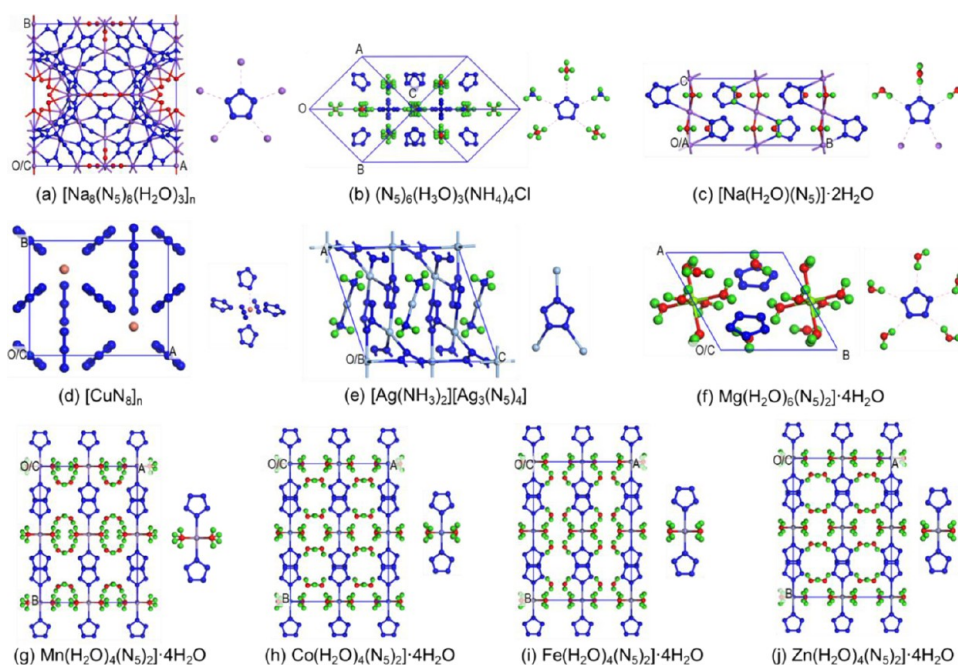


Figure 16. (a–j) Packing structures of some  $N_5^-$ -contained mixed-type cocrystals.

nonenergetic. For example, the energetic metallic organic frame (EMOF) structures<sup>23,106,107</sup> shown in Figure 14 have appeared in the research excitement for MOF. In EMOF structures, the negatively signed moieties on the frames are generally energetic and are strongly coordinated with central metallic ions. Similarly, energetic perovskites<sup>25,108</sup> meet a criterion of perovskite, as shown in Figure 15. The origin of the heat release of EMOFs and energetic perovskites should be the same as EISs, the reaction between anions and cations.

The cyclo- $N_5^-$  also gives rise to the rapid increase of energetic mixed-type crystals.<sup>109–114</sup> As illustrated in Figure 16, more than one type of ion and/or molecule around the central cyclo- $N_5^-$  is advantageous to stabilize it and consolidate the entire crystal by forming HB, coordination bonding, and  $\pi$ - $\pi$  stacking.<sup>94</sup>

#### 4. UNDERSTANDING ENERGETIC CRYSTALS

As stressed above, the type of any energetic crystal can be ascertained by the types of PCPs and interactions among the PCPs. For the energetic molecular crystals, the PCP should be molecule and can be homogeneous (single-component crystal) or heterogeneous (cocrystal), and the interactions among the PCPs are van de Waals and electrostatic interactions. In general, the intermolecular interactions in a common energetic molecular crystal are rather weak, due to the absence of strong polarity, and HB acceptor or donor. Because the more energy stored in an energetic molecule implies more weakened bonds, the heat release of a common energetic crystal is limited on the level of several kJ/g. This is also the limitation of the intrinsic contradiction between energy and molecular stability. The full-nitrogen molecular crystals were predicted to possess a high energy content, while it has not been verified yet as they have not been successfully synthesized.

Compared with energetic molecular crystals, interionic interactions are significantly strengthened with more negative lattice energy. It is also the origin of the consolidation effect in EISs. In EISs, the HBs are generally ionic, and the reversible hydrogen transfer can take place when heating, a reasoning for their low impact sensitivity. However, the ready hydrogen transfer can also facilitate the low thermal stability and the bad compatibility of EISs, constraining the use of EISs. Another kind of EIS, like  $K_2N_{12}$  shown in Figure 13, may possess a high energy content, while it is far from use due to the severe existing condition of high pressure, the same as some atomic energetic crystals.

Energetic atomic crystals mostly exist as poly-nitrogen or metallic hybrid compounds at high pressure. These kinds of energetic atomic crystals can release a larger quantity of energy than the common energetic molecular crystals or EISs. However, the severe existing condition of extremely high pressure makes them far from a practical application. Regarding another kind of atomic energetic crystal, poly-CO and poly-CO<sub>2</sub> can exist at common conditions, while, unfortunately, they possess limited energy contents, even inferior to a common energetic molecular crystal.

As for energetic metallic crystals, such as metallic hydrogen and metallic nitrogen (as fluid), they can exist at extraordinarily high pressure, as high as 495 GPa. This extreme condition can hardly make them applicable under common conditions too. Presumably, their use as EM could proceed a transition from metallic crystal to molecular crystal and gas finally, with a huge heat release.

Finally, for energetic mixed-type crystals, two or more types of PCPs and PCP interactions coexist. Interestingly, many novel structures such as MOFs and perovskites belong to this type. Because metallic ions often exist in them, they are expected to produce less gaseous products, and lower detonation velocity and pressure, compared with common energetic molecular crystals.

From the above discussion, we can get a rough comparison in energy content of various energetic crystals. As demonstrated in Figure 17, there is a rough increasing order of energy content for differently types of energetic crystals, as molecular crystal, ionic crystal, mixed type crystal < atomic crystal < metallic crystal. In general, the highly energetic crystal can exist

at high pressure, and vice versa. Thus, we should have a long way to go before we can use these highly energetic materials.

## 5. CONCLUSIONS

In summary, we categorize and understand the increasingly thriving energetic crystals based on the types of primary constituents and their interactions. It is found that the experimentally determined and theoretically predicted energetic crystals cover all the five crystal types, including molecular crystal, atomic crystal, ionic crystal, metallic crystal, and mixed-type crystal. Furthermore, there exists a rough increasing order of energy content for differently typed energetic crystals, as molecular crystal, ionic crystal, mixed type crystal < atomic crystal < metallic crystal. In general, the highly energetic crystal can exist at high pressure, and vice versa. By the categorization, the formation and energy-release mechanisms can be readily and roughly understood, when we examine the increasingly dazzling energetic compounds.

## AUTHOR INFORMATION

### Corresponding Author

**Chaoyang Zhang** – Institute of Chemical Materials, China Academy of Engineering Physics (CAEP), Mianyang, Sichuan 621999, China; Beijing Computational Science Research Center, Beijing 100048, China; [orcid.org/0000-0003-3634-7324](https://orcid.org/0000-0003-3634-7324); Phone: 86-816-2493506; Email: [chaoyangzhang@caep.cn](mailto:chaoyangzhang@caep.cn)

### Authors

**Rupeng Bu** – Institute of Chemical Materials, China Academy of Engineering Physics (CAEP), Mianyang, Sichuan 621999, China

**Fangbao Jiao** – Institute of Chemical Materials, China Academy of Engineering Physics (CAEP), Mianyang, Sichuan 621999, China

**Guangrui Liu** – Institute of Chemical Materials, China Academy of Engineering Physics (CAEP), Mianyang, Sichuan 621999, China; Beijing Computational Science Research Center, Beijing 100048, China

**Jingyu Zhao** – Institute of Chemical Materials, China Academy of Engineering Physics (CAEP), Mianyang, Sichuan 621999, China

Complete contact information is available at:

<https://pubs.acs.org/10.1021/acs.cgd.0c01300>

### Notes

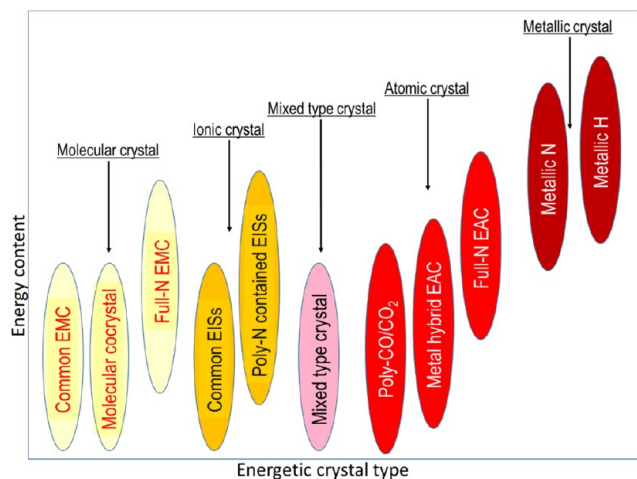
The authors declare no competing financial interest.

## ACKNOWLEDGMENTS

The authors are very grateful for the financial support of the Science Challenge Project (TZ-2018004) and the National Natural Science Foundation of China (21875227 and 21673210).

## ABBREVIATIONS

AP, ammonium perchlorate;  $[Ag(ATZ)]_n$ ,  $[Ag(5\text{-aminotetrazole})]_n$ ; 1-BN, 1-bromonaphthalene; AAF, 3-azido-4-aminofurazan; ANB, 1-azido-2-nitrobenzene; ANP, 2-azido-5-nitropyrimidine; ANTA, 3-amino-5-nitro-1,2,4-triazole; ANTaz, 5-azido-3-nitro-1H-1,2,4-triazole; Atrz, 4,4'-azo-1,2,4-triazole; BTF, benzotrifuroxan; CL-20, 2,4,6,8,10,12-hexanitro-2,4,6,8,10,12-hexaazaisowurtzitane; Dabco, 1,4-diazabicyclo-



**Figure 17.** Rough comparison in energy content of various energetic crystals.

[2.2.2]octane; DADP, diacetone diperoxide; DAG, diazido-glyoxime; DATB, 1,3-diamino-2,4,6-trinitrobenzene; DATZ, 3,6-diazido-1,2,4,5-tetrazine; DINA, 2,2'-dinitroxydiethylnitramine; ETN, butane-1,2,3,4-tetraol tetranitrate; FOX-7, 1,1-diamino-2,2-dinitroethylene; G+, guanidinium; G-BT2O, bis(guanidinium) 5,5'-bi(tetrazole-2-oxide); G-BTO, bis(guanidinium) 1H,1'-H-5,5'-bitetrazole-1,1'-diolate; G-C7H4NOS, guanidinium 4-hydroxypyridinium-2,6-dicarboxylate; G-CO3, guanidinium carbonate; G-DNBTO, 3,3'-dinitro-5,5'-bis-1,2,4-triazole-1,1'-diolate; G-NTX, guanidinium 5-nitro-2H-tetrazol-2-olate; H2M4, 1-methyl-1,4-diazabicyclo-[2.2.2]octane-1,4-dium; HA-AFTA, hydroxyammonium 5-(4-amino-1,2,5-oxadiazol-3-yl)-1H-tetrazol-1-olate; HA-BT2O, bis(hydroxylammonium) 5,5'-bi(tetrazole-2-oxide); HA-BTO, bis(hydroxylammonium) 1H,1'-H-5,5'-bitetrazole-1,1'-diolate; HA-DBO, bis(hydroxylammonium) 5,5'-bis(dinitromethylene)-3,3'-bi-1,2,4-oxadiazol-4-ide; HA-DNABF, bis(hydroxylammonium) 3,3'-bi-1,2,5-oxadiazole-4,4'-diylbis(nitroazanide); HA-DNBTO, bis(hydroxylammonium) 5,5'-bi(tetrazole-2-oxide); HMX, 1,3,5,7-tetranitro-1,3,5,7-tetrazocane; HNB, hexanitrobenzene; HNS, 3,5-dinitro-4-(2-(2,4,6-trinitrophenyl)vinyl)phenol; LLM-105, 2,6-diamino-3,5-dinitro-1,4-pyrazine 1-oxide; LLM-116, 4-amino-3,5-dinitro-1H-pyrazole; NADAT, 6-nitroamino-2,4-diazido [1,3,5]-triazine anion; Nap, naphthalene; NAQ, 1,4-aphthoquinone; NF, trinitromethane; NG, 1,2,3-propanetriol trinitrate; NGA, nitroguanil azide; NH<sub>3</sub>OH<sup>+</sup>, hydroxylammonium; NMP, N-methyl-2-pyrrolidone; NQ, 2-nitroguanidine; NTO, 3-amino-4-nitrofurazane; ONC, octanitrocubane; PA, trinitrophenol; PETN, pentaerythritol tetranitrate; PYX, 3,5-dinitro-N,N'-bis(2,4,6-trinitrophenyl)pyridine-2,6-diamine; RDX, 1,3,5-trinitro-1,3,5-triazinane; TACOT, 2,4,8,10-tetranitrobenzotriazole(2,1-a)benzotriazole; TAHA, 2,5,8-triazido-s-Heptazine; TATB, 1,3,5-triamino-2,4,6-trinitrobenzene; TATP, 3,3,6,6,9,9-hexamethyl-1,2,4,5,7,8-hexa-oxacyclononane; tetryl, N-methyl-N-2,4,6-tetranitroaniline; TNA, 2,4,6-trinitroaniline; TNAZ, 1,3,3-trinitroazetidine; TNB, 1,3,5-trinitrobenzene; TNT, 2,4,6-trinitrotoluene; TTNB, 1,3,5-triethynylbenzene

## REFERENCES

- (1) Dong, H.; Zhou, F. *Properties of High Energetic Explosives and Relatives*; Science Press: Beijing, 1994.
- (2) Teipel, U. *Energetic Materials: Particle Processing and Characterization*; Wiley-VCH Verlag GmbH & Co.: Weinheim, 2005.
- (3) Fried, L. E.; Manaa, M. R.; Pagoria, P. F.; Simpson, R. L. Design and Synthesis of Energetic Materials. *Annu. Rev. Mater. Res.* **2001**, *31*, 291–321.
- (4) Politzer, P.; Alper, H. E. In *Computational Chemistry: Reviews of Current Trends*; Leszczynski, J., Ed.; World Scientific: River Edge, NJ, 1999; pp 271–286.
- (5) Zeman, S. In *Energetic Materials, Part 2. Detonation, Combustion*; Politzer, P., Murray, J. S., Eds.; Elsevier: Amsterdam, 2003; pp 25–52.
- (6) Meyer, R.; Köhler, J.; Homburg, A. *Explosives*, 7th, completely revised ed.; Wiley-VCH: Weinheim, 2003.
- (7) Kubota, N. *Propellants and Explosives*; Wiley-VCH: Weinheim, 2015.
- (8) Agrawal, J. P.; Hodgson, R. D. *Organic Chemistry of Explosives*; John Wiley & Sons Ltd: Chichester, 2007.
- (9) Agrawal, P. *High Energy Materials*; WILEY-VCH: Weinheim, 2010.
- (10) Millar, D. I. A. *Energetic Materials at Extreme Conditions*; Springer-Verlag: Berlin Heidelberg, 2012.
- (11) Shukla, M. k.; Boddu, V. M.; Jeffery, A.; Steevens, J. A.; Reddy Damavarapu, R.; Leszczynski, J. *Energetic Materials: Challenges and*

*Advances in Computational Chemistry and Physics*; Springer International Publishing AG: Switzerland, 2017.

- (12) Groth, P.; Baxter, R. M.; Sletten, J.; Nielsen, P. H.; Lindberg, A. A.; Jansen, G.; Lamm, B.; Samuelsson, B. Crystal Structure of 3,3,6,6,9,9-Hexamethyl-1,2,4,5,7,8-hexa-oxacyclononane (“Trimeric Acetone Peroxide”). *Acta Chem. Scand.* **1969**, *23*, 1311–1329.
- (13) Dias, R. P.; Silvera, I. F. Observation of the Wigner-Huntington Transition to Metallic Hydrogen. *Science* **2017**, *355*, 715–718.
- (14) Ji, C.; Li, B.; Liu, W.; Smith, J. S.; Majumdar, A.; Luo, W.; Ahuja, R.; Shu, J.; Wang, J.; Sinogeikin, S.; Meng, Y.; Prakapenka, V. B.; Greenberg, E.; Xu, R.; Huang, X.; Yang, W.; Shen, G.; Mao, W. L.; Mao, H. Ultrahigh-pressure Isostructural Electronic Transitions in Hydrogen. *Nature* **2019**, *573*, 558–562.
- (15) Eremets, M. I.; Gavriluk, A. G.; Trojan, I. A.; Dzivenko, D. A.; Boehler, R. Single-bonded Cubic Form of Nitrogen. *Nat. Mater.* **2004**, *3*, 558–563.
- (16) Li, G.; Zhang, C. Review of the Molecular and Crystal Correlations on Sensitivities of Energetic Materials. *J. Hazard. Mater.* **2020**, *398*, 122910.
- (17) Bu, R.; Xiong, Y.; Wei, X.; Li, H.; Zhang, C. Hydrogen Bonding in CHON Contained Energetic Crystals: A Review. *Cryst. Growth Des.* **2019**, *19*, 5981–5997.
- (18) Bu, R.; Xiong, Y.; Zhang, C.  $\Pi$ - $\Pi$  Stacking Contributing to the Low or Reduced Impact Sensitivity of Energetic Materials. *Cryst. Growth Des.* **2020**, *20*, 2824–2841.
- (19) Bu, R.; Li, H.; Zhang, C. Polymorphic Transition in Traditional Energetic Materials: Influencing Factors and Effects on Structure, Property and Performance. *Cryst. Growth Des.* **2020**, *20*, 3561–3576.
- (20) Jiao, F.; Xiong, Y.; Li, H.; Zhang, C. Alleviating the Energy & Safety Contradiction to Construct New Low Sensitivity and Highly Energetic Materials through Crystal Engineering. *CrystEngComm* **2018**, *20*, 1757–1768.
- (21) Zhang, C.; Jiao, F.; Li, H. Crystal Engineering for Creating Low Sensitivity and Highly Energetic Materials. *Cryst. Growth Des.* **2018**, *18*, 5713–5726.
- (22) Gao, H.; Shreeve, J. M. Azole-based Energetic Salts. *Chem. Rev.* **2011**, *111*, 7377–7436.
- (23) Li, S.; Wang, Y.; Qi, C.; Zhao, X.; Zhang, J.; Zhang, S.; Pang, S. 3D Energetic Metal-Organic Frameworks: Synthesis and Properties of High Energy Materials. *Angew. Chem., Int. Ed.* **2013**, *52*, 14031–14035.
- (24) Landenberger, K. B.; Bolton, O.; Matzger, A. J. Energetic-energetic Cocrystals of Diacetone Diperoxide (DADP): Dramatic and Divergent Sensitivity Modifications via Cocrystallization. *J. Am. Chem. Soc.* **2015**, *137*, 5074–5079.
- (25) Chen, S.; Yang, Z.; Wang, B.; Shang, Y.; Sun, L.; He, C.; Zhou, H.; Zhang, W.; Chen, X. Molecular Perovskite High-energetic Materials. *Sci. China Mater.* **2018**, *61*, 1123–1128.
- (26) Zhang, C.; Xiong, Y.; Jiao, F.; Wang, M.; Li, H. Redefining the Term of Cocrystal and Broadening Its Intension. *Cryst. Growth Des.* **2019**, *19*, 1471–1478.
- (27) Bolton, O.; Matzger, A. J. Improved Stability and Smart-material Functionality Realized in an Energetic Cocrystal. *Angew. Chem., Int. Ed.* **2011**, *50*, 8960–8963.
- (28) Choi, C. S.; Abel, J. E. The Crystal Structure of 1,3,5-Trinitrobenzene by Neutron Diffraction. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1972**, *B28*, 193–201.
- (29) Cady, H. H.; Larson, A. C. The Crystal Structure of 1,3,5-Triamino-2,4,6-trinitrobenzene. *Acta Crystallogr.* **1965**, *18*, 485–496.
- (30) Carper, W. R.; Davis, L. P.; Extine, M. W. Molecular Structure of 2,4,6-Trinitrotoluene. *J. Phys. Chem.* **1982**, *86*, 459–462.
- (31) Holden, J. R. The Structure of 1,3-Diamino-2,4,6-trinitrobenzene, Form I. *Acta Crystallogr.* **1967**, *22*, 545–550.
- (32) Holden, J. R.; Dickinson, C.; Bock, C. M. Crystal Structure of 2,4,6-Trinitroaniline. *J. Phys. Chem.* **1972**, *76*, 3597–3602.
- (33) Gilardi, R. D.; Butcher, R. J. 2,6-Diamino-3,5-dinitro-1,4-pyrazine 1-oxide. *Acta Crystallogr., Sect. E: Struct. Rep. Online* **2001**, *E57*, o657–o658.

- (34) Altmann, K. L.; Chafin, A. P.; Merwin, L. H.; Wilson, W. S.; Gilardi, R. Chemistry of Tetraazapentalenes. *J. Org. Chem.* **1998**, *63*, 3352–3356.
- (35) Evers, J.; Klapötke, T. M.; Mayer, P.; Oehlinger, G.; Welch, J.  $\alpha$ - and  $\beta$ -FOX-7, Polymorphs of a High Energy Density Material, Studied by X-ray Single Crystal and Powder Investigations in the Temperature Range from 200 to 423 K. *Inorg. Chem.* **2006**, *45*, 4996–5007.
- (36) Schödel, H.; Dienelt, R.; Bock, H. Trinitromethane. *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **1994**, *C50*, 1790–1792.
- (37) Nielsen, A. T.; Chafin, A. P.; Christian, S. L.; Moore, D. W.; Nadler, M. P.; Nissan, R. A.; Vanderah, D. J.; Gilardi, R. D.; George, C. F.; Flippen-Anderson, J. L. Synthesis of polyazapolycyclic caged polynitramines. *Tetrahedron* **1998**, *54*, 11793–11812.
- (38) Choi, C. S.; Prince, E. The Crystal Structure of Cyclo-trimethylenetrinitramine. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1972**, *B28*, 2857–2862.
- (39) Batsanov, A. S.; Struchkov, Y. T. Crystal Structure of 3,4-Diaminofurazan and 3-Amino-4-nitrofurazan. *J. Struct. Chem.* **1985**, *26*, 52–56.
- (40) Espenbetov, A. A.; Antipin, Y. M.; Struchkov, Y. T.; Philippov, V. A.; Tsirel'son, V. G.; Ozerov, R. P.; Svetlov, B. S. Structure of 1,2,3-Propanetriol Trinitrate ( $\beta$  Modification),  $C_3H_5N_3O_9$ . *Acta Crystallogr.* **1984**, *C40*, 2096–2098.
- (41) Cady, H. H.; Larson, A. C. Pentaerythritol Tetranitrate II: Its Crystal Structure and Transformation to PETN I; an Algorithm for Refinement of Crystal Structures with Poor Data. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1975**, *B31*, 1864–1869.
- (42) Halfpenny, J.; Small, R. W. H. The Structure of 2,2'-Dinitroxydiethylnitramine (DINA). *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1978**, *B34*, 3452–3454.
- (43) Duesler, E. N.; Engelmann, J. H.; Curtin, D. Y.; Paul, I. C. Picric Acid:  $C_6H_3N_3O_7$ . *Cryst. Struct. Commun.* **1978**, *7*, 449.
- (44) Akopyan, Z. A.; Struchkov, Yu. T.; Dashevii, V. G. Crystal and Molecular Structure of Hexanitrobenzene. *J. Struct. Chem.* **1966**, *7*, 408–416.
- (45) Choi, C. S.; Boutin, H. P. A Study of the Crystal structure of  $\beta$ -Cyclotetramethylene Tetranitramine by Neutron Diffraction. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1970**, *B26*, 1235–1240.
- (46) Choi, C. S. Refinement of 2-Nitroguanidine by Neutron Powder Diffraction. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1981**, *B37*, 1955–1957.
- (47) Cady, H. H. The Crystal Structure of N-Methyl-N-2,4,6-tetranitroaniline (Tetryl). *Acta Crystallogr.* **1967**, *23*, 601–609.
- (48) Manner, V. W.; Tappan, B. C.; Scott, B. L.; Preston, D. N.; Brown, G. W. Crystal Structure, Packing Analysis, and Structural-Sensitivity Correlations of Erythritol Tetranitrate. *Cryst. Growth Des.* **2014**, *14*, 6154–6160.
- (49) Bellamy, A. J.; Mahon, M. F.; Drake, R.; Mansell, J.; Golding, P. *Cent. Eur. J. Energy Mater.* **2005**, *2*, 3.
- (50) Klapötke, T. M.; Stierstorfer, J.; Weyrauther, M.; Witkowski, T. G. Synthesis and Investigation of 2,6-Bis(picrylamino)-3,5-dinitropyridine (PYX) and Its Salts. *Chem. - Eur. J.* **2016**, *22*, 8619–8626.
- (51) Zhang, M.; Eaton, P. E.; Gilardi, R. Hepta- and Octanitrocubanes. *Angew. Chem., Int. Ed.* **2000**, *39*, 401–403.
- (52) Izsák, D.; Klapötke, T. M. Preparation and Crystal Structure of 5-Azido-3-nitro-1H-1, 2, 4-triazole, Its Methyl Derivative and Potassium Salt. *Crystals* **2012**, *2*, 294–305.
- (53) Miller, D. R.; Swenson, D. C.; Gillan, E. G. Synthesis and Structure of 2, 5, 8-Triazido-s-heptazine: An Energetic and Luminescent Precursor to Nitrogen-rich Carbon Nitrides. *J. Am. Chem. Soc.* **2004**, *126*, 5372–5373.
- (54) Huang, Y.; Zhang, Y.; Shreeve, J. M. Nitrogen-Rich Salts Based on Energetic Nitroaminodiazido [1,3,5] triazine and Guanazine. *Chem. - Eur. J.* **2011**, *17*, 1538–1546.
- (55) Li, H.; Huang, M.; Li, J.; Cheng, B.; Zhou, X. Synthesis and Crystal Structure of 3-azido-4-aminofurazan. *Chin. J. Synthetic Chem.* **2007**.
- (56) Huynh, M. H. V.; Hiskey, M. A.; Archuleta, J. G.; Roemer, E. L.; Gilardi, R. 3,6-Di(azido)-1,2,4,5-Tetrazine: A Precursor for the Preparation of Carbon Nanospheres and Nitrogen-Rich Carbon Nitrides. *Angew. Chem., Int. Ed.* **2004**, *43*, 5658–5661.
- (57) Vasiliev, A. D.; Astachov, A. M.; Nefedov, A. A.; Kruglyakova, L. A.; Stepanov, R. S. Nitroguanyl Azide. *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **2001**, *57*, 625–626.
- (58) Takayama, T.; Kawano, M.; Uekusa, H.; Ohashi, Y.; Sugawara, T. Crystalline-State Photoreaction of 1-Azido-2-nitrobenzene—Direct Observation of Heterocycle Formation by X-Ray Crystallography. *Helv. Chim. Acta* **2003**, *86*, 1352–1358.
- (59) Gorbunov, E. B.; Novikova, R. K.; Plekhanov, P. V.; Slepukhin, P. A.; Rusinov, G. L.; Rusinov, V. L.; Charushin, V. N.; Chupakhin, O. N. 2-Azido-5-nitropyrimidine: Synthesis, Molecular Structure, and Reactions with n-, o-, and s-Nucleophiles. *Chem. Heterocycl. Compd.* **2013**, *49*, 768–775.
- (60) Fischer, D.; Klapötke, T. M.; Stierstorfer, J. Synthesis and Characterization of Guanidinium Difluoroiodate,  $[C-(NH_2)_3]^+[IF_2O_2]^-$  and Its Evaluation as An Ingredient in Agent Defeat Weapons. *Z. Anorg. Allg. Chem.* **2011**, *637*, 660–665.
- (61) Gelalcha, F. G.; Schulze, B.; Lönnecke, P. 3,3,6,6-Tetramethyl-1,2,4,5-tetroxane: a Twinned Crystal Structure. *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **2004**, *C60*, o180–o182.
- (62) Garcia, E.; Lee, K. Y. Structure of 3-Amino-5-nitro-1,2,4-triazole. *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **1992**, *C48*, 1682–1683.
- (63) Nordenson, S. Structure of 2-Nitriminoimidazolidine. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1981**, *B37*, 1774–1776.
- (64) Schmidt, R. D.; Lee, G. S.; Pagoria, P. F.; Mitchell, A. R.; Gilardi, R. Synthesis of 4-Amino-3,5-dinitro-1H-pyrazole Using Vicarious Nucleophilic Substitution of Hydrogen. *J. Heterocycl. Chem.* **2001**, *38*, 1227–1230.
- (65) Gilardi, R. Private Communication, 1999; CCDC: 136083. DOI: 10.5517/cc4kls1.
- (66) Gilardi, R. D.; George, C. F. The Use of X-ray Diffraction Analyses of Molecular Mechanics to Predict Structures of Hypothetical Organic Molecules. *Acta Crystallogr., Sect. A: Found. Crystallogr.* **1984**, *A40*, C432.
- (67) Boileau, J.; Wimmer, E.; Gilardi, R.; Stinecipher, M. M.; Gallo, R.; Pierrot, M. Structure of 1,4-Dinitroglucuril. *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **1988**, *C44*, 696–699.
- (68) Li, Y.; Lai, W.; Wei, T.; Ge, Z.; Xu, T.; Luo, Y.; Yin, S. Theoretical Investigations on Fundamental Properties of All-Nitrogen Materials: I. Prediction of Crystal Densities. *Chin. J. Energy Mater.* **2017**, *25*, 100–105.
- (69) Greschner, M. J.; Zhang, M.; Majumdar, A.; Liu, H.; Peng, F.; Tse, J. S.; Yao, Y. A New Allotrope of Nitrogen as High-energy Density Material. *J. Phys. Chem. A* **2016**, *120*, 2920–2925.
- (70) Hirshberg, B.; Gerber, R. B.; Krylov, A. I. Calculations Predict a Stable Molecular Crystal of  $N_8$ . *Nat. Chem.* **2014**, *6*, 52–56.
- (71) Zhang, C.; Yang, Z.; Zhou, X.; Zhang, C.; Ma, Y.; Xu, J.; Zhang, Q.; Nie, F.; Li, H. Evident Hydrogen Bonded Chains Building CL-20-Based Cocrystals. *Cryst. Growth Des.* **2014**, *14*, 3923–3928.
- (72) Bennion, J. C.; Chowdhury, N.; Kampf, J. W.; Matzger, A. J. Hydrogen Peroxide Solvates of 2,4,6,8,10,12-Hexanitro-2,4,6,8,10,12-hexaazaisowurtzitane. *Angew. Chem., Int. Ed.* **2016**, *55*, 13118–13121.
- (73) Yang, Z.; Zeng, Q.; Zhou, X.; Zhang, Q.; Nie, F.; Huang, H.; Li, H. Cocrystal Explosive Hydrate of a Powerful Explosive, HNIW, with Enhanced Safety. *RSC Adv.* **2014**, *4*, 65121–65126.
- (74) Bolton, O.; Simke, L. R.; Pagoria, P. F.; Matzger, A. J. High Power Explosive with Good Sensitivity: a 2:1 Cocrystal of CL-20:HMx. *Cryst. Growth Des.* **2012**, *12*, 4311–4314.
- (75) Landenberger, K. B.; Matzger, A. J. Cocrystal Engineering of a Prototype Energetic Material: Supramolecular Chemistry of 2,4,6-Trinitrotoluene. *Cryst. Growth Des.* **2010**, *10*, 5341–5347.
- (76) Robinson, J. M. A.; Philp, D.; Harris, K. D. M.; Kariuki, B. M. Weak interactions in Crystal Engineering-understanding the Recog-

- nition Properties of the Nitro Group. *New J. Chem.* **2000**, *24*, 799–806.
- (77) Zhang, H.; Guo, C.; Wang, X.; Xu, J.; He, X.; Liu, Y.; Liu, X.; Huang, H.; Sun, J. Five Energetic Cocrystals of BTF by Intermolecular Hydrogen Bond and  $\pi$ -Stacking Interactions. *Cryst. Growth Des.* **2013**, *13*, 679–687.
- (78) Landenberger, K. B.; Matzger, A. J. Cocrystal Engineering of a Prototype Energetic Material: Supramolecular Chemistry of 2,4,6-Trinitrotoluene. *Cryst. Growth Des.* **2010**, *10*, 5341–5347.
- (79) Liu, G.; Wei, S.; Zhang, C. Review of the Intermolecular Interactions in Energetic Molecular Cocrystals. *Cryst. Growth Des.* **2020**, *20*, 7065–7079.
- (80) Kumar, D.; Kapoor, I. P. S.; Singh, G.; Frohlich, R. X-Ray Crystallography and Thermolysis of Ammonium Perchlorate and Protonated Hexamethylenetetramine Perchlorate Prepared by Newer Methods. Part 69. *Int. J. Energ. Mater. Chem. Propul.* **2010**, *9*, 549–560.
- (81) Hendricks, S. B.; Pauling, L. The Crystal Structures of Sodium and Potassium Trinitrates and Potassium Cyanate and the Nature of the Trinitrate Group. *J. Am. Chem. Soc.* **1925**, *47*, 2904–2920.
- (82) Saha, P. The Crystal Structure of alpha-Lead Azide, alpha-Pb(N<sub>3</sub>)<sub>2</sub>. *Indian J. Phys. Proc. Indian Assoc. Cultiv. Sci.* **1965**, *39*, 494–497.
- (83) Fischer, N.; Gao, L.; Klapötke, T. M.; Stierstorfer, J. Energetic Salts of 5,5'-Bis(tetrazole-2-oxide) in a Comparison to 5,5'-Bis(tetrazole-1-oxide) Derivatives. *Polyhedron* **2013**, *51*, 201–210.
- (84) Klapötke, T. M.; Mayr, N.; Stierstorfer, J.; Weyrauther, M. Maximum Compaction of Ionic Organic Explosives: Bis-(Hydroxylammonium) 5,5'-Dinitromethyl-3,3'-bis(1,2,4-oxadiazolate) and its Derivatives. *Chem. - Eur. J.* **2014**, *20*, 1410–1417.
- (85) Fischer, N.; Klapötke, T. M.; Reymann, M.; Stierstorfer, J. *Chem. - Eur. J.* **2014**, *20*, 6401–6411.
- (86) Zhang, J.; Mitchell, L. A.; Parrish, D. A.; Shreeve, J. M. Enforced Layer-by-Layer Stacking of Energetic Salts towards High-Performance Insensitive Energetic Materials. *J. Am. Chem. Soc.* **2015**, *137*, 10532–10535.
- (87) Fischer, N.; Fischer, D.; Klapötke, T. M.; Piercey, D. G.; Stierstorfer, J. Pushing the Limits of Energetic Materials – the synthesis and Characterization of Dihydroxylammonium 5,5'-Bistetrazole-1,1'-diolate. *J. Mater. Chem.* **2012**, *22*, 20418–20422.
- (88) Dippold, A.; Klapötke, T. M. A Study of Dinitro-bis-1,2,4-triazole-1,1'-diol and Derivatives: Design of High-Performance Insensitive Energetic Materials by the Introduction of N-Oxides. *J. Am. Chem. Soc.* **2013**, *135*, 9931–9938.
- (89) Göbel, M.; Karaghiosoff, K.; Klapötke, T. M.; Piercey, D. G.; Stierstorfer, J. Nitrotetrazolate-2N-oxides and the Strategy of N-Oxide Introduction. *J. Am. Chem. Soc.* **2010**, *132*, 17216–17226.
- (90) Moghimi, A.; Aghabozorg, H.; Soleimannejad, J.; Ramezani-pour, F. Guanidinium 4-Hydroxypyridinium-2,6-dicarboxylate. *Acta Crystallogr., Sect. E: Struct. Rep. Online* **2005**, *E61*, o442–o444.
- (91) Fischer, N.; Klapötke, T. M.; Reymann, M.; Stierstorfer, J. Nitrogen-Rich Salts of 1H,1'H-5,5'-Bitetrazole-1,1'-diol: Energetic Materials with High Thermal Stability. *Eur. J. Inorg. Chem.* **2013**, *2013*, 2167–2180.
- (92) Adams, J. M.; Small, R. W. H. The Crystal Structure of Guanidinium Carbonate. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1974**, *B30*, 2191–2193.
- (93) Yang, C.; Zhang, C.; Zheng, Z.; Jiang, C.; Luo, J.; Du, Y.; Hu, B.; Sun, C.; Christe, K. O. Synthesis and Characterization of Cyclopentazolate Salts of NH<sub>4</sub><sup>+</sup>, NH<sub>3</sub>OH<sup>+</sup>, N<sub>2</sub>H<sub>5</sub><sup>+</sup>, C(NH<sub>2</sub>)<sub>3</sub><sup>+</sup>, and N(CH<sub>3</sub>)<sub>4</sub><sup>+</sup>. *J. Am. Chem. Soc.* **2018**, *140*, 16488–16494.
- (94) Jiao, F.; Zhang, C. Origin of the Considerably High Thermal Stability of Cyclo-N<sub>5</sub><sup>-</sup> Contained Salts at Ambient Conditions. *CrystEngComm* **2019**, *21*, 3592–3604.
- (95) Eremets, M. I.; Gavriluk, A. G.; Trojan, I. A.; Dzivenko, D. A.; Boehler, R. Single-bonded Cubic Form of Nitrogen. *Nat. Mater.* **2004**, *3*, 558–563.
- (96) Li, Y.; Feng, X.; Liu, H.; Hao, J.; Redfern, S. A.; Lei, W.; Liu, D.; Ma, Y. Route to High-energy Density Polymeric Nitrogen t-N via He-N Compounds. *Nat. Commun.* **2018**, *9*, 1–7.
- (97) Liu, Z.; Li, D.; Liu, Y.; Cui, T.; Tian, F.; Duan, D. Metallic and Anti-metallic Properties of Strongly Covalently Bonded Energetic AlN<sub>5</sub> Nitrides. *Phys. Chem. Chem. Phys.* **2019**, *21*, 12029–12035.
- (98) Wei, S.; Li, D.; Liu, Z.; Wang, W.; Tian, F.; Bao, K.; Duan, D.; Liu, B.; Cui, T. A Novel Polymerization of Nitrogen in Beryllium Tetranitride at High Pressure. *J. Phys. Chem. C* **2017**, *121*, 9766–9772.
- (99) Steele, B. A.; Oleynik, I. I. Novel Potassium Polynitrides at High Pressures. *J. Phys. Chem. A* **2017**, *121*, 8955–8961.
- (100) Wei, S.; Li, D.; Liu, Z.; Li, X.; Tian, F.; Duan, D.; Liu, B.; Cui, T. Alkaline-earth Metal (Mg) Polynitrides at High Pressure as Possible High-energy Materials. *Phys. Chem. Chem. Phys.* **2017**, *19*, 9246–9252.
- (101) Bykov, M.; Bykova, E.; Koemets, E.; Fedotenko, T.; Aprilis, G.; Glazyrin, K.; Liermann, H.-P.; Ponomareva, A. V.; Tidholm, J.; Tasnadi, F.; Abrikosov, I. A.; Dubrovinskaia, N.; Dubrovinsky, L. High-pressure Synthesis of a Nitrogen-rich Inclusion Compound Ren<sub>8</sub>xN<sub>2</sub> with Conjugated Polymeric Nitrogen Chains. *Angew. Chem., Int. Ed.* **2018**, *57*, 9048–9053.
- (102) Bykov, M.; Bykova, E.; Aprilis, G.; Glazyrin, K.; Koemets, E.; Chuvashova, I.; Kupenko, I.; McCammon, C.; Mezouar, M.; Prakapenka, V.; Liermann, H. P.; Tasnadi, F.; Ponomareva, A. V.; Abrikosov, I. A.; Dubrovinskaia, N.; Dubrovinsky, L. Fe-N System at High Pressure Reveals a Compound Featuring Polymeric Nitrogen Chains. *Nat. Commun.* **2018**, *9*, 2756–2764.
- (103) Wu, L.; Tian, R.; Wan, B.; Liu, H.; Gong, N.; Chen, P.; Shen, T.; Yao, Y.; Gou, H.; Gao, F. Prediction of Stable Iron Nitrides at Ambient and High Pressures with Progressive Formation of New Polynitrogen Species. *Chem. Mater.* **2018**, *30*, 8476–8485.
- (104) McMahon, J. M.; Ceperley, D. M. Ground-State Structures of Atomic Metallic Hydrogen. *Phys. Rev. Lett.* **2011**, *106*, 165302.
- (105) Jiang, S.; Holtgrewe, N.; Lobanov, S. S.; Su, F.; Mahmood, M. F.; McWilliams, R. S.; Goncharov, A. F. Metallization and Molecular Dissociation of Dense Fluid Nitrogen. *Nat. Commun.* **2018**, *9*, 2624.
- (106) Lin, J.; Qiu, Y.; Chen, W.; Yang, M.; Zhou, A.; Dong, W.; Tian, C. Unusual  $\pi$ - $\pi$  Stacking Interactions between 5,50-Azotetrazolate(AT) Anions in Six AT Based 3D Metal Photochromic Complexes. *CrystEngComm* **2012**, *14*, 2779–2786.
- (107) Zhang, Q.; Chen, D.; He, X.; Huang, S.; Huang, J.; Zhou, X.; Yang, Z.; Li, J.; Li, H.; Nie, F. Structures, Photoluminescence and Photocatalytic Properties of Two Novel Metal–Organic Frameworks Based on Tetrazole Derivatives. *CrystEngComm* **2014**, *16*, 10485–10491.
- (108) Shang, Y.; Huang, R.; Chen, S.; He, C.; Yu, Z.; Ye, Z.; Zhang, W.; Chen, X. Metal-Free Molecular Perovskite High-Energetic Materials. *Cryst. Growth Des.* **2020**, *20*, 1891–189.
- (109) Zhang, C.; Sun, C.; Hu, B.; Yu, C.; Lu, M. Synthesis and Characterization of the Pentazolate Anion Cyclo-N<sub>5</sub> in (N<sub>5</sub>)<sub>6</sub>(H<sub>3</sub>O)<sub>3</sub>(NH<sub>4</sub>)<sub>4</sub>Cl. *Science* **2017**, *355*, 374–376.
- (110) Xu, Y.; Wang, Q.; Shen, C.; Lin, Q.; Wang, P.; Lu, M. A Series of Energetic Metal Pentazolate Hydrates. *Nature* **2017**, *549*, 78–81.
- (111) Xu, Y.; Wang, P.; Lin, Q.; Lu, M. A Carbon-free Inorganic–metal Complex Consisting of an All-nitrogen Pentazole Anion, a Zn(II) Cation and H<sub>2</sub>O. *Dalton Trans.* **2017**, *46*, 14088–14093.
- (112) Xu, Y.; Wang, P.; Lin, Q.; Mei, X.; Lu, M. Self-assembled Energetic 3D Metal–organic Framework [Na<sub>8</sub>(N<sub>5</sub>)<sub>8</sub>(H<sub>2</sub>O)<sub>3</sub>]<sub>n</sub> Based on Cyclo-N<sub>5</sub><sup>-</sup>. *Dalton Trans.* **2018**, *47*, 1398–1401.
- (113) Xu, Y.; Lin, Q.; Wang, P.; Lu, M. Syntheses, Crystal Structures and Properties of a Series of 3D Metal–Inorganic Frameworks Containing Pentazolate Anion. *Chem. - Asian J.* **2018**, *13*, 1669–1673.
- (114) Sun, C.; Zhang, C.; Jiang, C.; Yang, C.; Du, Y.; Zhao, Y.; Hu, B.; Zheng, Z.; Christe, K. O. Synthesis of AgN<sub>5</sub> and Its Extended 3D Energetic Framework. *Nat. Commun.* **2018**, *9*, 1269.