The Summary of Synthesis and Theoretical Research into Cocrystal Explosives

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Abstract: With the complexity of the using environment, traditional energetic materials can no longer meet the requirements, and it is urgent to synthesize new energetic materials. As a new type of explosive modification technology, cocrystallization is utilized widely in the field of energetic materials. The researchers mainly employ solvent method to synthesize different kinds of cocrystal explosives and utilise molecular dynamics simulation method to study the properties of different cocrystal explosives. In this paper, the theoretical research and experimental preparation of cocrystal explosives are summarized, and the application of cocrystal technology in energetic materials is analyzed. Both theoretically and experimentally, the results show that cocrystallization can improve the properties of explosives and provide a new and effective way for the modification of explosives.

1. Introduction
High energy density materials (HEDMs) are defined as a class of compounds with a large amount of chemical energy stored in the molecular structure, and it plays an important role in the field of military, aerospace, industry, environmental protection and national economy. The common explosives include 1,1-diamino-2,2-dinitroethylene (FOX-7), hexanitrohexaazaisowurtzitane (CL-20), 2,4,6-trinitrotoluene (TNT), cyclotrimethylene trinitroamine (RDX), cyclotetramethylenetetranitramine (HMX) and so on. However, high energy is always accompanied by poor sensitivity, which will be a knotty problem to be solved when transporting, storing and utilizing the HEDMs. With the development of modern military technology and the increasingly complex using environment of military weapons, traditional energetic materials have been unable to meet the needs. Therefore, the research on new type of insensitive high explosive (IHE) has not only become the research focus of energetic materials, but also the urgent need of national defense construction. For the sake of improving energy density and decreasing the sensitivity of energetic materials, lots of means have been performed, such as coating, adding insensitive agent, controlling of crystal morphology, and so on. The appearance of supramolecular cocrystal compounds is very bright, which provides some new ideas for solving the difficulties in the preparation of new high-energy insensitive explosives. Compared with the above several traditional methods, cocrystallization is considered a novel and effective approach [1,2]. Cocrystal refers to the combination of two or more different molecules through non covalent bond to form a new type of crystal, which can effectively improve its physical and chemical properties and properties.
2. Research progress of cocrystal explosives

2.1. Experimental research progress of cocrystal explosive
Cocrystals are a type of supramoleculars, exhibiting interactions arising from hydrogen bonds, π-stacking, van der Waals forces, electrostatic interactions and so on. Recently, the cocrystal explosives have attracted much attention in the synthesis and application [3].

In 1978, Levinthal et al. [4] formally reported that they used the solvent evaporation method to synthesize cyclotetramethylenetetranitramine/ammonium perchlorate (HMX/AP) cocrystal explosives, which improved the hygroscopicity of AP and maintained the excellent detonation parameters of HMX. Ma et al. [5] synthesized 2,4,6-trinitrotoluene/2,4,6-trinitrochlorobenzene (TNT/TNCB) cocrystal explosive with a molar ratio of 1:1 by solvent evaporation method, whose test result showed that the impact sensitivity of cocrystal explosive has been significantly improved compared with TNCB. Guo et al. [6] prepared 2,4,6-trinitrotoluene/2,4,6-trinitrobenzene (TNT/TNB) cocrystal explosives successfully by using alcohol as solvent and volatilizing at room temperature. The TNT/TNB cocrystal explosives were characterized by DSC, X-ray diffraction and impact sensitivity test, which the result proved that the explosive properties and melting point of the cocrystal explosive were different from the original single crystal explosive.

Lin et al. [7-10] successfully prepared several kinds of cocrystal energetic materials of cyclotetramethylenetetranitramine, including cyclotetramethylenetetranitramine/1,3-dimethyl-2-imidazolinone (HMX/DMI), cyclotetramethylenetetranitramine/3-nitro-1,2,4-triazol-5-one (HMX/NTO), cyclotetramethylenetetranitramine/2,6-diamo-no-3,5-dinitropyrazine-1-oxide (HMX/LLM-105). And, it was found that the formation of cocrystal explosive was restrained by increasing the external pressure, while the cocrystal explosive could be formed by increasing the temperature. Song et al. [11] prepared hexanitrohexaazaisowurtzite/dinitrotoluene (CL-20/DNT) cocrystal explosive by evaporative crystallization, studied the structure and morphology of the product, tested the impact sensitivities of cocrystal explosive and calculated its theoretical explosion speed. Zhang et al. [12] synthesized the cocrystal energetic materials of benzotrioxide/trinitrobenzene (BTF/TNB) by using the solvent volatilization method, which improved the safety performance of BTF and the detonation parameters of the cocrystal explosives have not weakened obviously. Guo et al. [13] synthesized cocrystal explosives of hexanitrohexaazaisowurtzite/caprolactam (CL-20/CPL) by solvent evaporation method. According to the results of characteristic drop weight test, the impact sensitivity was significantly improved.

Through the work of the above researchers, it is known that the application of cocrystal technology in the field of energetic materials can effectively improve the relevant properties of explosives, improve the safety and maintain the characteristics of high energy. In addition, it is obvious that the researchers mainly employ solvent method to synthesize different kinds of cocrystal explosives.

2.2. Theoretical research progress of cocrystal explosive
Due to the particularity of high energy, there are many restrictions for HEDMs, such as experimental environment, research cost, and operation risks. With the advancement of modern science and technology, especially the rapid development of computers, the use of high-performance computer platforms combined with theoretical methods of computational chemistry has provided a new way of thinking and means for the study of cocrystal energetic materials. Not only can it effectively ensure the safety of the experiment, but also it can greatly reduce the loss of material and financial resources during the experiment, and it can also help researchers to understand the relevant mechanisms from a microscopic perspective, so it has very important scientific significance and application value. Molecular dynamics simulation has been widely used by researchers to study the properties of macro materials. Compared with other simulation methods, molecular dynamics possesses correct physical criteria and theoretical basis, which can ensure the accuracy of the calculation results. Molecular dynamics simulation can not only observe the structure and change details of materials from the micro
level, but also it will predict the macro characteristics of materials, which effectively supplements the deficiency of theoretical system and experimental means.

For example, Li et al. [14] studied the mechanical properties and binding energy of specific crystal planes of cyclotetramethylenehexanitramine/nitroguanidine (HMX/NQ) through molecular dynamics simulations. The result showed that these two explosives were easiest to form a cocryystal explosive with a molar ratio of 1:1. Ding et al. [15] constructed hexanitrohexaazaaisowurtzitane/nitroguanidine (CL-20/NQ) cocryystal models with different molar ratios, and the binding energy and mechanical properties of cocryystal explosives were studied by the method of combining molecular dynamics simulation and density functional theory. Wei et al. [16] theoretically predicted the structure and characteristics of the cocryystal of cyclotetramethylenehexanitramine/triaminotrinitrobenezene (HMX/TATB). On the basis of Wei, Shen et al. [17] synthesized the HMX/TATB cocryystal explosive by the solvent-nonsolvent method, and it was found that the cocryystal morphology was significantly changed through scanning electron microscopy.

Xiong et al. [18] established a 5,5-bistetrazole-1,1-diol dihydroxyammonium salt/cyclotrimethylenetrinitramine (TKX-50/RDX) cocryystal model, and it was found that with the increase of temperature, the binding energy and thermodynamic stability of the cocryystal system decrease gradually, and the TKX-50/RDX cocryystal structure significantly reduced the sensitivity by molecular dynamics simulations. In order to study the effect of solvent effect on crystal growth, Liu et al. [19] constructed 3-nitro-1,2,4-triazol-5-one/5,6,7,8-tetrahydrotriazole [1,5-b] [1,2,4]-triazine (NTO/TZTN) cocryystal model in three solvents of methanol, ethyl acetate and acetone, and utilized quantum chemistry (QC) calculations and molecular Dynamics (MD) simulation to predict several properties. The result showed that the combination of NTO and TZTN possessed a positive synergistic effect in methanol solvents. According to this theoretical result, researchers have successfully prepared NTO/TZTN cocryystal explosives from methanol. Han et al. [20] used molecular dynamics (MD) to study the effect of molar ratio on the structure and properties of cyclotetramethylenehexanitramine/1-methyl-4,5-dinitroimidazole (HMX/MDNI) cocryystal explosive, the result indicated that in all molar ratios of the HMX/MDNI cocryystal model, the binding energy at the 1:1 ratio was the largest and the elastic modulus was the smallest, indicating that the eutectic explosive was most likely to be synthesized at the ratio of 1:1. Xie et al. [21] employed molecular dynamics methods to study the cocryystal model of cyclotetramethylenehexanitramine/2-methylpyridine-N-oxide with different molar ratios, and the binding energy, mechanical properties, oxygen balance and explosion velocity of the selected surface were predicted, which revealed that the cocryystal explosive had a higher binding energy and better ductility at the molar ratio of 1:1. Wei et al. [22] studied the cyclotetramethylenehexanitramine/1,1-diamino-2,2-dinitroethylene (HMX/FOX-7) cocryystal model at different molecular molar ratios via molecular dynamics methods, and estimated their binding energy, mechanical properties, density and detonation velocity. The result showed that the cocryystal model at 1:1 molar ratio had the largest binding energy and the best mechanical properties, and it also could be inferred theoretically that acetone might be a suitable solvent to prepare the HMX-FOX-7 cocryystal explosives in the laboratory.

Liu et al. [23] utilised molecular dynamics to study the cocryystal model of 3,4-dinitrofurzanyl oxyfurazan/1,3,3-trinitroazetidine (DNTF/TNAZ), and the melting point and detonation parameters of DNTF/TNAZ cocryystal explosives were predicted. It has been found that the cocryystal explosive with a mass ratio of 4:6 possessed high energy and low melting point, making it an ideal choice for new melt-cast explosives. Hang et al. [24] established hexanitrohexaazaisowurtzitane/trimethylene trinitroamine (CL-20/RDX) cocryystal models with different molar ratios by substitution method, and applied the MD simulation method to study the effects of molar ratio on the mechanical properties, stability and explosive properties of eutectic explosives. The result showed that 1:1 cocryystal explosive has the best mechanical properties, the highest binding energy and better explosive properties, so it was a high-energy composite with good stability and compatibility for the cocryystal explosive with the molar ratio of 1:1.
According to the above theoretical research, researchers mainly utilise molecular dynamics simulation method to study the properties of different cocrystal explosives, which provides feasible support for the preparation of cocrystal explosives. Moreover, some researchers have successfully prepared cocrystal explosives through theoretical results, which demonstrates that it is very necessary for us to conduct theoretical research.

3. Conclusion
In summary, cocrystal technology can effectively improve the properties of traditional explosives. Researchers actively apply supramolecular cocrystallization to the field of energetic materials, and explore the designing, characterization, prediction and synthesis of new high-energy insensitive explosives from the perspective of theoretical calculations and experiments. It is expected that through the combination of theoretical research and experimental exploration, composite high-energy density materials with excellent properties in all aspects will be obtained.

References
[1] Steed J W. (2013) The role of co-crystals in pharmaceutical design[J]. Trends in Pharmacological Sciences, 34:185-193.
[2] Luu V, Jona J, Stanton M K, et al. (2013) High-throughput 96-well solvent mediated sonic blending synthesis and on-plate solid/solution stability characterization of pharmaceutical cocrystals[J]. International Journal of Pharmaceutics, 44:356-364.
[3] Bolton O, Matzger A J. (2011) Improved stability and smart-material functionality realized in an energetic cocrystal[J]. Angewandte Chemie. International Ed. in English, 50:8960-8963.
[4] Levinthal M L.(1978) Propellant made with co-crystals of cyclotetramethylenetetranitramine and ammonium perchlorate[P]. US Patent, 40816110.
[5] Ma Y, Huang Q, Li H Z, et al. (2017) Preparation and Characterization of TNT/TNCB Cocrystal Explosive[J]. Chinese Journal of Energetic Materials, 25:86-88.
[6] Guo C, Zhang H, Wang X, et al. (2013) Study on a novel energetic cocrystal of TNT/TNB[J]. Journal of Material Science, 48:1351-1357.
[7] Lin H, Chen P Y, Zhu S G, et al. (2013) Computational study of pyrazine-based derivatives and their N-oxides as high energy materials[J]. Journal of Physical Organic Chemistry, 26:484-491.
[8] Lin H, Chen P Y, Zhu S G, et al. (2013) Theoretical design of pyrazine-based high energy materials[J]. Computational and Theoretical Chemistry, 1013:25-31.
[9] Lin H, Chen P Y, Zhu S G, et al. (2013) Structure and detonation performance of a novel HMX/LLM-105 cocrystal explosive[J]. Journal of Physical Organic Chemistry, 26:898-907.
[10] Lin H, Chen P Y, Zhu S G, et al. (2013) Synthesis, characterization, AIM and NBO analysis of HMX/DMI cocrystal explosive[J]. Journal of molecular structure, 2013, 1048:339-348.
[11] Song X L, Wang Y, Song C Y, et al. (2016) Preparation of CL-20/DNT cocrystal explosive and study on its performance[J]. Chinese Journal of Explosive & Propellants, 39:23-27.
[12] Zhang H B, Guo C Y, Wang X C, et al. (2013) Five energetic cocrystals of BTF by intermolecular hydrogen bond and π-stacking interactions[J]. Crystal Growth & Design, 13:679-687.
[13] Guo C, Zhang H, Wang X, et al. (2013) Crystal structure and explosive performance of a new CL-20/caprolactam cocrystal[J]. Journal of molecular structure, 1048:267-273.
[14] Li Y, Chen S. (2015) Theoretical insights into the structures and mechanical properties of HMX/NQ cocrystal explosives and their complexes, and the influence of molecular ratios on their bonding energies[J]. Journal of molecular modeling, 21:245.
[15] Ding X, Gou R J, Ren F D, et al. (2016) Molecular dynamics simulation and density function theory insight into the cocrystal explosive of hexaazaisowurtzitane/nitroguanidine[J]. International Journal of Quantum Chemistry, 116:88-96.
[16] Wei C X, Duan X H, Liu C J, et al. (2009) Molecular Simulation on Co-crystal Structure of HMX/TATB[J]. Acta Chmica Sinica, 67:2822-2826.

[17] Shen J P, Duan X H, Luo Q P, et al. (2011) Preparation and characterization of a novel cocrystal explosive[J]. Crystal Growth & Design, 11:1759-1765.

[18] Xiong S L, Chen S S, Jin S H. (2017) Molecular dynamic simulations on TKX-50/RDX cocrystal[J]. Journal of Molecular Graphics and Modeling, 74:171-176.

[19] Liu Y, Gou R J, Zhang S H, et al. (2019) Solvent effect on the formation of NTO/TZTN cocrystal explosives[J]. Computational Materials Science, 163: 308-314.

[20] Han G, Gou R J, Ren F D, et al. (2017) Theoretical investigation into the influence of molar ratio on binding energy, mechanical property and detonation performance of 1,3,5,7-tetranitro-1,3,5,7-tetrazacyclonane (HMX)/1-methyl-4,5-dinitroimidazole (MDNI) cocrystal explosive[J]. Computational and Theoretical Chemistry, 1109:27–35.

[21] Xie Z B, Hu S Q, Cao X. (2016) Theoretical insight into the influence of molecular ratio on the binding energy and mechanical property of HMX/2-picoline-N-oxide cocrystal, cooperativity effect and surface electrostatic potential[J]. Molecular Physics, 114:2164-2176.

[22] Wei Y J, Ren F D, Shi W J, et al. (2016) Theoretical Insight into the Influences of Molecular Ratios on Stabilities and Mechanical Properties, Solvent Effect of HMX/FOX-7 Cocrystal Explosive[J]. Journal of Energetic Materials, 34:426-439.

[23] Liu N, Shu Y J, Wu Z K, et al. (2016) Comparative study of melting points of 3, 4-bis (3-nitrofurazan-4-yl) furoxan (DNTF)/1,3,3,3-trinitroazetidine (TNAZ) eutectic compositions using molecular dynamic simulations[J]. RSC Advances, 6:59141-59149.

[24] Hang G Y, Yu W L, Wang T, et al. (2017) Theoretical insights into effects of molar ratios on stabilities, mechanical properties and detonation performance of CL-20/RDX cocrystal explosives by molecular dynamics simulation[J]. Journal of Molecular Structure, 1141:577-583.