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**Achieving balanced cocrystals of energetic materials
via coagglomeration**

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Abstract

Earlier reported methods for cocrystallization of EMs especially nitramines are lacking with selectivity and scalability. When it comes to adoption to industrial scale production of energetic-energetic cocrystals (EECCs) it's more difficult. We made thorough literature survey and developed method of coagglomeration for attractive nitramines via solvent mediated slurry method; in which Co-agglomeration of the co-precipitated micro-particles of nitramines themselves or with polynitroarenes by the slurry method is a unique crystal engineering approach to modify the energetic properties of attractive nitramines like CL20, HMX, BCHMX, RDX etc. The properties and structural modification in the 60+ co-agglomerated crystals (CACs) newly prepared in our laboratory. There are notable variations in the crystal morphologies and packing of crystals, including key properties like relatively high density, melting point, impact sensitivity, and detonation properties. These CACs are in the overwhelming majority showing properties like co-crystals. Apart from these aspects, co-agglomeration provides a huge opportunity to tune the key properties and performance of existing energetic materials and is easy to scale-up for the industrial level. These preliminary results also suggest that chemical engineering factors are involved in the preparation of CACs, as in conventional crystallization. The optimization of them should be a matter of downstream technological research.

Abstrakt

Dříve uváděné metody pro kokrytalizaci EM, zejména nitraminů, postrádají selektivitu a škálovatelnost. Pokud jde o přijetí do průmyslové výroby energeticko-energetických kokrytalů (EECCs) je to obtížnější. Provedli jsme důkladný průzkum literatury a vyvinuli metodu koaglomerace pro atraktivní nitraminy pomocí suspenzní metody zprostředkované rozpouštědlem; ve kterém ko-aglomerace společně vysrážených mikročástic nitraminů samotných nebo s polynitroareny suspenzní metodou je unikátní krystalový inženýrský přístup modifikovat energetické vlastnosti atraktivních nitraminů jako CL20, HMX, BCHMX, RDX atd. a strukturní modifikace v 60+ koaglomerovaných krystalech (CAC) nově připravených v naší laboratoři. Tam jsou pozoruhodné variace v morfologiích krystalů a uspořádání krystalů, včetně klíčových vlastností, jako je relativní vysoká hustota, bod tání, rázová citlivost a detonační vlastnosti. Těchto CACů je v drtivé většině většina vykazuje vlastnosti jako ko-krystaly. Kromě těchto aspektů poskytuje koaglomerace obrovské možnost vyladit klíčové vlastnosti a výkon stávajících energetických materiálů a lze je snadno škálovat průmyslovou úroveň. Tyto předběžné výsledky také naznačují, že se na tom podílejí faktory chemického inženýrství příprava CAC jako při konvenční krystalizaci. Jejich optimalizace by měla být otázkou následný technologický výzkum.

Keywords

Nitramines; Co-agglomeration; Co-crystals; Impact sensitivity; Detonation parameters

Klíčová slova

Nitraminy; Ko-aglomerace; Ko-krystaly; Citlivost na náraz; Detonační parametry

Table Content

Abbreviations.....	1
1. INTRODUCTION	2
1.1 Research background.....	2
1.2 Research & developments in cocrystallization of energetic materials.....	2
1.3 Preparation methods / techniques	3
1.4 Components shaping cocrystals - Intermolecular interactions.....	4
1.5 Thermochemical properties of cocrystals	5
1.6 Mechanical sensitivity of cocrystals – reaction towards external stimuli.....	6
1.7 Detonation properties of cocrystals.....	7
1.8 Technological challenges in preparation of cocrystals of EMs – Research objectives.....	7
2 MATERIALS AND METHODS.....	8
2.1 Preparation of co-crystals of attractive nitramines via Coagglomeration Method.....	9
2.2 Application of the CACs.....	9
3 RESULTS AND DISCUSSIONS	10
3.1 CACs of attractive nitramines with DATB and TATB.....	12
3.2 CACs of CL20 and BCHMX	13
3.3 CACs of attractive nitramines with HNS and HNAB	13
3.4 CACs of attractive nitramines with PANi	14
3.5 CACs of attractive nitramines with BTATz	15
4 APPLICATIONS OF CACs	15
4.1 HMX/BCHMX CACs in composite rocket propellant.....	15
4.2 CL20/BCHMX CACs in detonators	16
4.3 RDX/BCHMX CACs in gun powder.....	16
4.4 Applications Remaining CACs.....	17
5 CONCLUSIONS.....	17
5.1 Cocrystallization of attractive nitramines via coagglomeration	17
5.3 Impact sensitivity of CACs	19
5.4 Thermochemical and Detonation properties of CACs	20
5.5 Feasibility of co-agglomeration method.....	21
REFERENCES	22
LIST OF STUDENTS' PUBLISHED WORKS	28

Abbreviations

Codes	Chemical names
1, 4 DNI	1,4-dinitroimidazole
2, 4 DNI	2,4-dinitroimidazole
4, 5 MDNI	4,5-dinitro-1-methylimidazole
ADNP	4-amino-3,5-dinitropyrazole
AMTN	1-amino-3-methyl-1,2,3-triazoliumnitrate
ANPyO	2,6-diamino-3,5-dinitropyridine-1-oxide
AP	Ammonium per chlorate
aTRz	Azo-bis-1,2,4-triazole
BCHMX	1,3,4,6-Tetranitrooctahydroimidazo-[4,5-d]imidazole
BTF	Benzotrifuroxane
BTNEN	1,2,4-Butanetriol trinitrate
CAM	ϵ -caprolactone monomer
CL20 /HNIW	2,4,6,8,10,12 - Hexanitro - 2,4,6,8,10,12 - hexaazaisowurtzitane
DADP	Diacetone diperoxide
DAF	3,4-diaminofurazan
DATB	1,3-Diamino-2,4,6-trinitrobenzene
DMF	Dimethyl formaldehyde
DMSO	Dimethyl sulfoxide
DNB	Dinitrobenzene
DNBT	5,5'-dinitro-2 <i>H</i> ,2 <i>H'</i> -3,3'-bi-1,2,4-triazole
DNDAP	2,4-dinitro-2,4-diazapentane
DNI	dinitroimidazole
DNMT	1-methyl-3,5-dinitro-1,2,4-triazole
DNP	2,4-Dinitrophenol
DNT	1-Methyl-2,4-dinitrobenzene
H2O2	Hydrogen peroxide
HMPT	hexamethylphosphoramide
HMX	1,3,5,7-Tetranitro-1,3,5,7-tetraazacyclooctane
HNAB	2,2',4,4',6,6'-Hexanitroazobenzene
HNS	2,2',4,4',6,6'-Hexanitrostilbene
MDNT	1-methyl-3,5-dinitro-1,2,4-triazole
MTNI	1-methyl-3,5-dinitro-1,2,4-imidazole
MTNP	1-methyl-3,4,5-trinitropyrazole
n-K6 or Keto-RDX	2-oxo-1,3,5-trinitro-1,3,5-triazacyclohexane, K6
NM	Nitromethane
NMP	N-methyl-2-pyrrolidone
N-O···H	Hydrogen bonding
NT	Nitrotoluene
PANI	Polyaniline
PETN	Pentaerythritol tetranitrate
PVAc	Polyvinyl acetate
RDX	1,3,5-Trinitro-1,3,5-triazacyclohexane
TATB	1,3,5-Triamino-2,4,6-trinitrobenzene
TATP	triacetone triperoxide
TCTNB	1,3,5- trichloro-2,4,6-trinitrobenzene
TEX	4,10-dinitro-2,6,8,12,-tetraoxa-4,10-diazasowurtzitane
TFAZ	7 <i>H</i> -trifurazano[3,4- <i>b</i> :3',4'- <i>f</i> :3'',4''- <i>d</i>]azepine
TMS	tetramethylene sulfone
TNAZ	1,3,3 - Trinitroazetidide
TNP	1,3,5-Trinitro-1,3-diazacyclohexane
TNT	2, 4, 6,-Trinitrotoluene

1. INTRODUCTION

1.1 Research background

The energetic materials (EMs - explosives, propellants, and pyrotechnics) are used widely for military as well as civil applications[1]. Despite their production and handling risks, these materials proved indispensable in military and civilian uses. Evolution has been slow for over 1200 years; black powder prevailed until the early 20th century. Researchers synthesized various EMs based on the requirements; however, synthetic methods are slowly reaching saturation. More attractive energetic materials exhibit inherent impact sensitivity. To overcome this property, there are several efforts made by researchers to achieve energy-safety balanced EMs. Several methods came into existence, like improved crystallization, coating with insensitive materials to modification of surface morphology and shapes of the crystals [2], mixing with energetic/non-energetic materials, polymer coating [3] cocrystallization(Figure 1 & 2) etc.

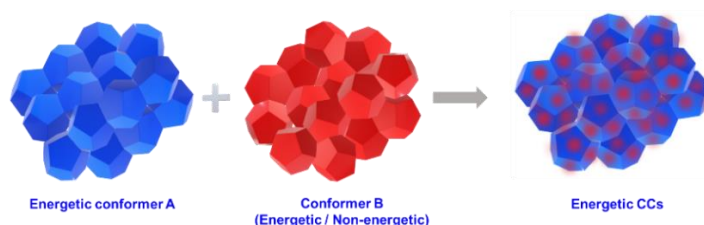


Figure 1. a) Schematic of Cocrystals(CCs) of energetic materials; if coformer B is energetic its known as Energetic-Energetic Cocrystals (EECCs) [4]

These efforts continued; however, approaches slowly focused along with sensitivity, the key research components thermal stability and detonation properties of EMs [5]. Later, cocrystallization with energetic-energetic materials begins. Initially, it did not much grab the attention from researchers, but gradually from 2010 onwards, it became a hot topic for researchers from both scientific as well as technological points of view. Current PhD research work made efforts to find compatible and easily scalable with a high-purity achievable approach, i.e., *via* coprecipitation followed by coagglomeration.

This is short summary of PhD thesis can be a reference to exploring high-performance cocrystals energetic materials in scalable approach in application in future application in all special activities of the space and military purposes [6]. Because there is plenty of potential in this approach that needs to be explored.

1.2 Research & developments in cocrystallization of energetic materials

The cocrystallization is beginning more attraction to researchers rather than synthesizing new materials as an alternative route in development of the novel properties with existing energetic materials [6, 7](Figure 2). This method also helps to alter the physical chemical as well as performance and strengthen safety of

the EMs[7]. Its most promising method to develop excellent energetic materials as it can achieve a favorable balance between high energy and low sensitivity for the energetic materials by tuning their components and ratios [4, 6, 7].

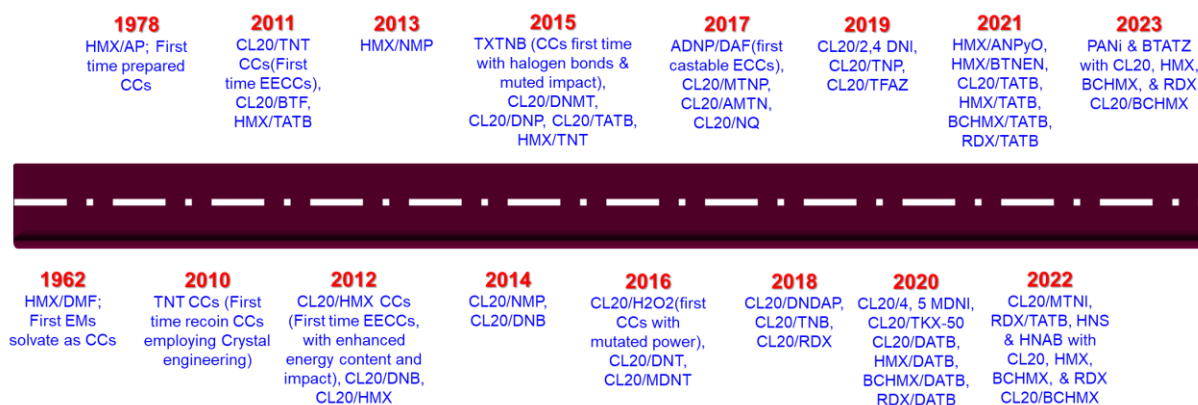


Figure 2. Schematic road map - evaluation of Cocrystals in attractive nitramines

Considering these aspects their huge research and development have been happening in cocrystallization of EMs, not only preparations there is huge research also happened in simulation to understand the intermolecular structural orientations and compatibility [7–9]. Cocrystallization of EMs mainly two ways; one cocrystallization with non-energetic material and another is cocrystallization with energetic molecule. Further, confirmation of cocrystallization; if single crystal grown successfully characterization is easier and otherwise bit challenging [11]. There are different methods of preparations (discussed in section 1.3) which varies with thermochemical and instrumental conditions [12].

1.3 Preparation methods / techniques

Preparation methods mainly categorized by four methods Evaporation crystallization, Spray drying/ vapour deposition, Slurry technique and Vacuum freeze drying. Selection of solvents is challenging in this method due to both conformers great difference in solubility[13]. The crystal free-growth shapes are not controllable in this method, yielded single crystals more beneficial to scientific studies than technological application viz. sometimes crystals appeared to be sharp needles possess mechanical sensitivity will be retained or increased [6, 11, 13]. In Spray drying / vapour deposition technique his process is quicker and easier to get nanosized crystals, more details of the obtained crystal morphological properties [15]. However, the safety aspect of the cocrystals preparation mainly with large-scale of this process is not very compatible certainty due to possibly formation of flakes if crystals not dried completely & designing spray nozzle, pressure maintenance (aspects of their sensitivity). Slurry technique is easily adaptable to larger scale productions the compatible to scale up. This method both cofomers undergo good reaction to each other in solvent medium with controlled size growth of the crystals. The risk of adulteration with external

materials is low, as the technique involves only physical bonding and the obtained cocrystals are also with structural homogeneity[16]. Vacuum freeze drying method is very helpful in achieving the ultrafine nano cocrystals of the EMs. In the vacuum freeze drying process, the solution was frozen quickly so that the process of particles of co-crystal growth and aggregation was very short which was helpful to form the nano-sized co-crystals [11, 41]. In this method need to maintain the continuous high vacuum otherwise cocrystallization ends up with slurry and wet crystals.

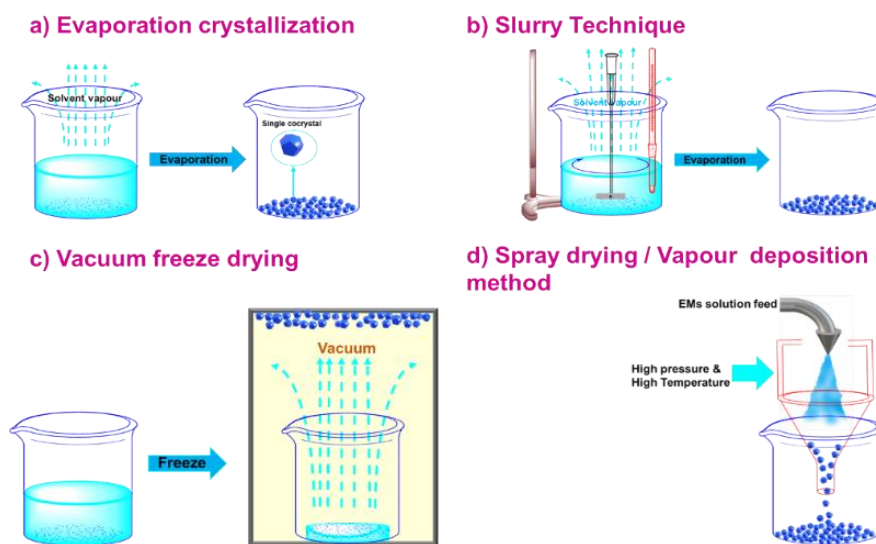


Figure 3. Schematic representation of different cocrystallization methods

1.4 Components shaping cocrystals - Intermolecular interactions

Intermolecular interactions stabilize both conformers in cocrystal form in the single crystal lattice (Figure 4). Intermolecular (noncovalent) interactions are classified into van der Waals (dispersion interaction) and electrostatic (Coulomb interaction). Chemically, they are also referred to as hydrogen bonding (HB), halogen bonding, or stacking [5, 7, 60]. A donor and acceptor with acidic and electronegative hydrogen atoms (N, O, F, etc.) form hydrogen bonds [19]. Hydrogen bonds are weak, moderate, or strong based on bond energy [20]. EMs lack active hydrogen atoms and cannot form strong hydrogen bonds [21]. Next comes, stacking changes due to these interactions actively influence intermolecular arrangement and respond to stimuli by converting mechanical to intermolecular interaction energy, which disperses throughout stacked layers of EECCs in ascending order: wavelike (layer-by-layer), crossed (caged), face-to-face (sandwich), and mixed stackings [22], [23]. With all these intermolecular changes finally packing of structures occurs and it plays an important role in defining sensitivity and performances of EECCs. The detonation properties, sensitivity, and other parameters of EMs are essentially determined by the packing configuration[74,79] [80, 82].

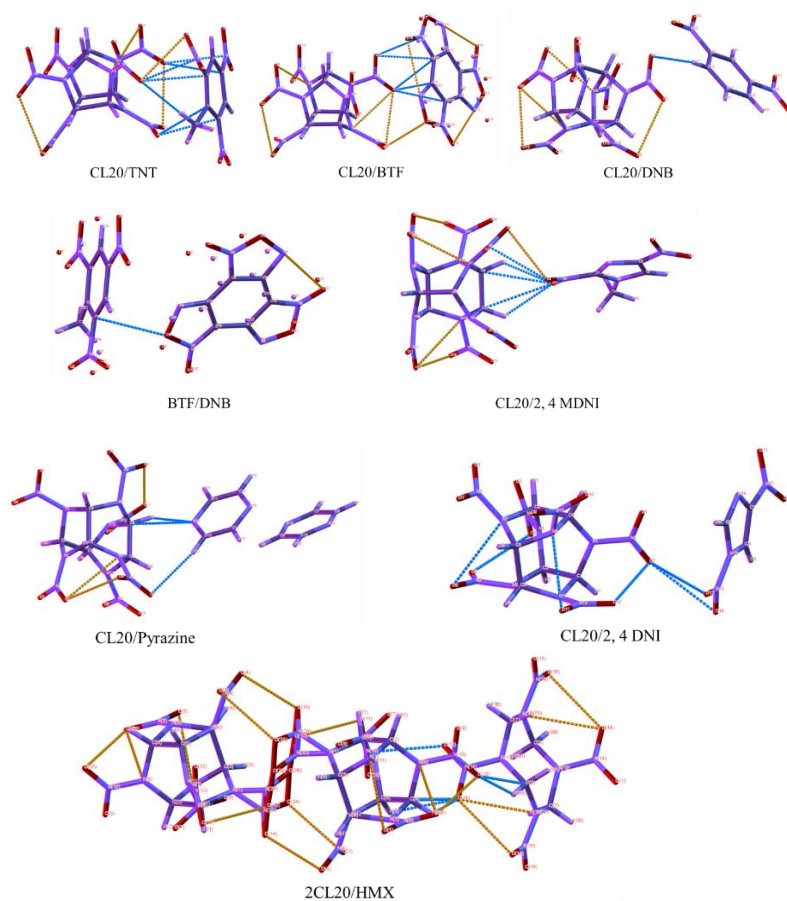


Figure 4. A) 3D Single crystal XRD molecular structures of EECCs of nitramines, here, orange coloured bonds indicates pure hydrogen bonds whereas blue coloured bonds indicates electrostatic intermolecular short contacts developed between both coformers during cocrystallization. CL20/TNT[28]; CL20/BTF[29]; CL20/DNB[30]; BTF/DNB[31]; CL20/2,4 MDNI[32]; CL20/Pyrazine[33]; CL20/2,4 DNI[34] and 2CL20/HMX[35]

1.5 Thermochemical properties of cocrystals

Thermal behaviour changes due on EECC crystal packing and lattice energy[40]. Thus, thermal data distinguishes it as a physical combination and shows no cocrystallization-related thermal stability differences [36]. Inconsistency between impact sensitivity and thermal stability, or strong thermal stability does not necessarily imply low impact sensitivity [6]. Thermal stability research must focus on EECCs breakdown temperatures and compare them to pure coformer EMs. To avoid self-accelerating decomposition temperature (SADT), new storage and transit conditions are needed [37]. CCs usually decompose at lower temperatures than pure coformers[43]. Some cases small increases occur [38]. Intermolecular interactions and crystal packing change melting and decomposition temperatures (5–10 C) during cocrystallization [39]. As thermal breakdown temperature rises, decomposition products increase but equilibrium time and potential energy decrease [40].

Heat release rate affects EECC combustion and detonation performance, as does coformer stoichiometry and reaction circumstances [54, 100]. The enthalpy of formation (ΔH_{form}) shows the energetic content of EECCs. Higher heat of combustion suggests lower energetic content, while oxygen balance affects heat of detonation [13, 101]. Also verified is a direct extremely excellent linear link between heat of combustion and experimental relative explosive strength of explosives [44].

Most importantly, co-crystal density exceeds 99% of the predicted maximum density of beginning nitramines [45]. Density and crystal packing of energetic materials affect explosive detonation [46]. Cocrystallization increases density in HMX/NTO [47] and BTF with different cofomers[48]. EECCs increase crystal density, which reduces explosive volume and cavities-defects and boosts detonation pressure [34, 46, 105].

1.6 Mechanical sensitivity of cocrystals – reaction towards external stimuli

In cocrystallization sensitivity of EECCs depends on the coformer EMs molecule selected to modify the targeted EMs, molar ratio, and their intermolecular interactions (Section 1.4), crystallization method (Section 1.3) as well as the obtained EECCs crystal morphology and are discussed briefly as follows.

Impact sensitivity relies on several aspects, including measuring method and human error. These factors make it difficult to quantitatively connect outputs with lattice parameters, according to theoretical and synthetic chemists [129]. The important relationship between impact sensitivity and energetic material performance (volumetric explosive heat or detonation energy) or energy content (enthalpy of formation or heat of combustion). Licht's rule that high power usually increases sensitivity and that an insensitive explosion does not perform well applies here (with many exceptions) and is not yet supported by theory[133, 134]. Impact sensitivity of EECC can be "tun-on" or "turn off" depending on factors such as HNIW/TNT [53], which had an 87% decrease in impact with [54] and increased in other cases [55]. Effect of crystal packing-stacking pattern on impact is proven, with π - π stacking contributing to low impact in EECCs [5, 116].

Secondly Friction sensitivity, EMs are sensitive to friction, especially energetic salts, but sometimes insensitive. FS is affected by CC shape and size, such as β HMX and nano-CCs [56]. HMX/CL20 and CL20/RDX impact and friction sensitivity dropped significantly [11, 42, 50]. Similar to IS, EECCs had lower FS than their pure cofomers, which had many hydrogen bonds and π - π stacking [6].

Third electric spark sensitivity, the morphologically porous crystals with air gaps, like porous RDX, can exhaust more ESD spark energy and drop with particle size [58]. Researchers also studied the external electric field's effect on EECCs and found that $-\text{NO}_2$ groups trigger bonds on the molecular surface field,

so as the electric field increases, the nitro groups charge increases, indicating that the EECCs sensitivity increases [67, 119]. Applied electric fields trigger bonds by causing N to \rightarrow NO₂ and NO₂ to \rightarrow N [60].

1.7 Detonation properties of cocrystals

Detonation parameters detonation velocity (D), detonation pressure (P), and detonation energy (E) are key parameters to evaluate the performance of EECCs. This key parameter decides the EECCs alteration of their detonation power and effectiveness as like its initial cofomers. D and P will be affected by cocrystallization, packing density of EECCs lower further it directly influences viz., higher density more promising EMs D and also it varies with molar ratios of the cofomers chosen for EECCs preparations [64, 105]. However, the detonation velocities of mixture of the explosives would be generally higher than what would correspond to the percentage of the components in these mixtures [63] which often valid for EECCs also [109, 124, 125], in some cases these properties are increased [29]. Another way it can described it achieve safety and morphological suitability of EECCs needed to adjust with detonation properties slightly, however its negligible. It occurs due to the binding energy, trigger bond energy, trigger bond length, cohesive energy density of EECCs [66]. Earlier reported results showed that difference in detonation velocities between the EECCs and physical mix, the crystal structure and resultant cofomer bond energy contribute to the observed difference in detonation velocities [67].

1.8 Technological challenges in preparation of cocrystals of EMs – Research objectives

The cocrystallization technique is widely used in EMs, however several studies are still in the exploratory phase, leaving some critical difficulties unsolved [11, 81]. Cocrystallization is a reliable and cost-effective approach to tune the energetic characteristics of existing EMs without synthesizing new molecules. Crystal engineering techniques are difficult to prepare for military and civic use. As described in Section 1.3, each preparation method has merits and disadvantages, but due of EM availability and processing laboratory capability, researchers focus on the scientific aspect at the laboratory scale.

The bigger challenge is scalability. Large-scale production methods can produce high-quality crystals, but they may nucleate and make it hard to maintain uniform crystalline sizes for traditional applications [69]. Efficient EECCs with the right energy density (bulk energy content), safety, and performance for the application are similarly difficult [11, 90, 130]. EECCs' high sensitivity and reactivity contribute to a disparity between energy content and safety of EMs, requiring stabilization [47, 48, 126, 131]. Solubility of cofomers can cause two types of crystals with recrystallization without cocrystallization during cocrystal preparation [11]. Rod- or needle-like EECC morphology makes them useless in applications [74]. Crystal

engineering faces several challenges, yet cocrystallization technology will be important for the latest EM, pyrotechnics, and fuel additives [68]. Due to these factors, preparing EECC to current application requirements is difficult and time-consuming. This led us to search for an optimized approach or modification of an existing method for large-scale EECC production.

At Institute of Energetic Materials, University of Pardubice, we tried shaped and optimized method to modify the EMs; finally developed universal strategy up with slurry based coagglomeration in solvent (in which coformers are very little soluble) state which is more acceptable safety wise as well to more effective in tuning energy – safety parameters with controlling their morphology too. Structure property relationships needed to address as point of the EECCs preparation with respect their conformers, and it will play very crucial role as backup data and justification to scale up [80, 97]. The coagglomeration method (section 2) fulfilled all these challenges successfully developed around 60+ agglomerated crystals (CACs) which form EECCs, and some interesting results have been briefly presented in upcoming next section 3.

2 MATERIALS AND METHODS

In this coagglomeration method used coformers DATB, TATB, HNS, HNAB and BTATz influence the four attractive nitramines RDX, HMX, BCHMX and CL20 (as shown in Figure 5).

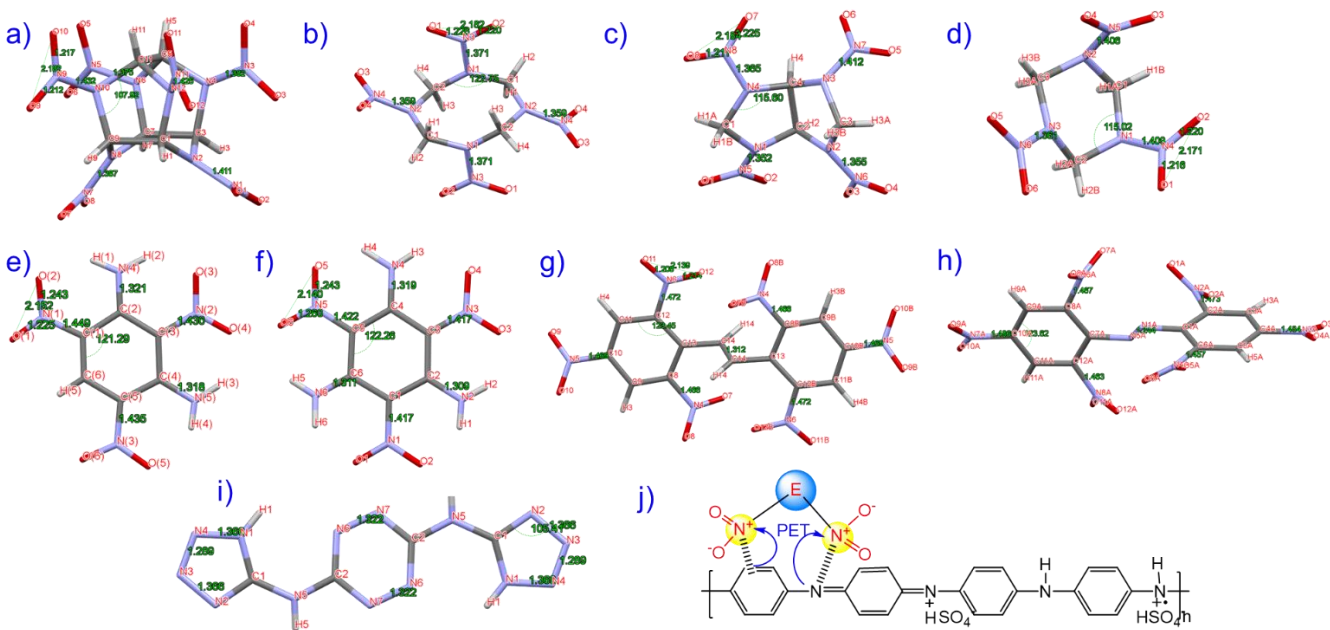


Figure 5. 3D molecular structures of attractive nitramines(a-d) and coformers used in CACs preparations. a) CL20, b) HMX, c) BCHMX, d) RDX and coformers used for CACs e) DATB, f) TATB, g) HNS, h) HNAB i)BTATz [45], [75], [76], [77], [78], [79], [80] and j) 2D Emeraldine salt of PANi “E” – attractive cyclic nitramine i.e., it denotes formation of charge transfer complex with a, b, c, and d [25, 26].

Also, the found relationships between impact sensitivity, thermochemical, and detonation performance characteristics, on the one hand, and some FTIR and Raman outputs, to confirm the formation of co-crystals during co-agglomeration. All these mentioned relationships represent a new insight into the co-crystals investigation. These instrumental insights are very helpful for analyzing the cocrystals which are below 100 μm and not measurable by single crystal X-ray [45], [75], [76], [78], [83], [84], [85].

2.1 Preparation of co-crystals of attractive nitramines via Coagglomeration Method

The preparation of co-agglomerated crystals (CACs) with specific energetic cofomers (shown Figure 2a to d) and the aforementioned attractive nitramines (shown Figure 2c to h) was conducted using a primarily two-step procedure [15].

- First step - the co-precipitates are prepared by employing the rapid solvent-antisolvent method. This method involves introducing a solution containing co-formers, which do not necessarily possess a defined crystallography and can be obtained directly from their production after stabilization (E.g., introducing water into the acetonic solution).
- Second step - Co-agglomeration strategy involves combining a small quantity of solvent with a co-precipitate, resulting in a well-mixed slurry (in which components exhibit low solubility in the solvent). Subsequently, the slurry is subjected to heating for a specific duration, reaching a temperature around the boiling point of the solvent.

The acquired CACs were dried, subsequently labeled, and subjected to a comprehensive analysis for morphology and phase purity, and also underlying intermolecular changes in both cofomers after undergoing coagglomeration were described. The coagglomeration method works as controlled cocrystallization as compared to earlier literature reported methods.

2.2 Application of the CACs

Propellant compositions are prepared in a total of nine batches (P1–P9), each with a batch size of 700 gm, with each batch being inserted in proportions of 10%, 220%, and 30% of pure HHMX (P1–3), HMX/BCHMX physical mixture (P4–P6), and MX/BBCHMX (P7–9) replacement for AP.

Secondly, the test of the initiation strength of coagglomerates (CACs) of CL20 with BCHMX was carried out according to standard [86] with weights ranging from 51 to 300 mg of selected CACs in aluminium shells of 7.5 mm diameter, with a pressure of 60 kg per pressing pin and a secondary charge of 720 mg pentaerythritol tetranitrate (PETN), pressed by a pressure of 180 kg per pressing pin.

Third one, the gun propellant's nitrocellulose content was replaced by RDX, RDX/HMX, and RDX/HMX CACs, approximately 10% of which were pure RDX (S10.1). We replaced 89% NC and 10% of the physical mixture RDX/BCHMX (S10.2) with a sample containing CACs (S10.3). To further stabilize the samples,

we added 1% diphenylamine. Further performance was evaluated to check the effects of CACs, comparing pure and physical mixtures.

BCHMX suitability as a physical mixture and CACs with HMX for the respective applications can be effectively evaluated in Chapter 4. This can help design new combinations of nitramines for applications in propellants.

3 RESULTS AND DISCUSSIONS

As compared to traditional methods of cocrystallization coagglomeration method shown improvements in particle sizes of cocrystals, with enhancements in their surface areas. Almost all CACs are smoothed surfaces with disappearance of their crystal defects which further influenced improving their impact insensitivity (Figure 6 & 7). From the obtained particle size analysis its clearly observed coagglomeration method yielded fine particles almost trend is uniform in all cofomers, except in case crowded molecules BCHMX and CL20. Angular / clipped of BCHMX and globular molecular environments also play crucial role in crystal growth, and its logically proven [76]. A few selective top three highly impact insensitive cocrystals shown in Figure 9, which clearly shown at particular molar ratios the nitramines with energetic cofomers possibility to achieve desired impact sensitivity.

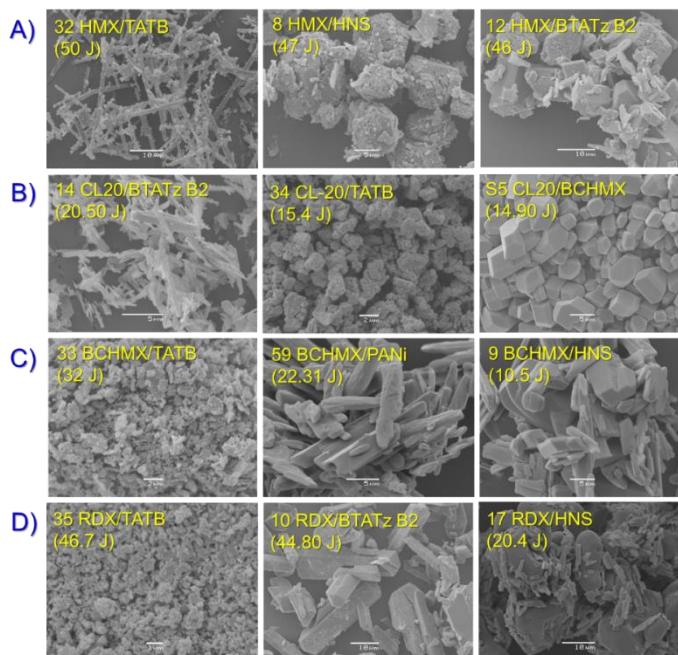


Figure 6. FESEM images with sample IDs top 3 highly impact insensitive left to right; A) HMX CACs, B) CL20 CACs, C) BCHMX CACs, and D) RDX CACs, (images regenerated from Ref. [45], [75], [76], [77], [78], [84]).

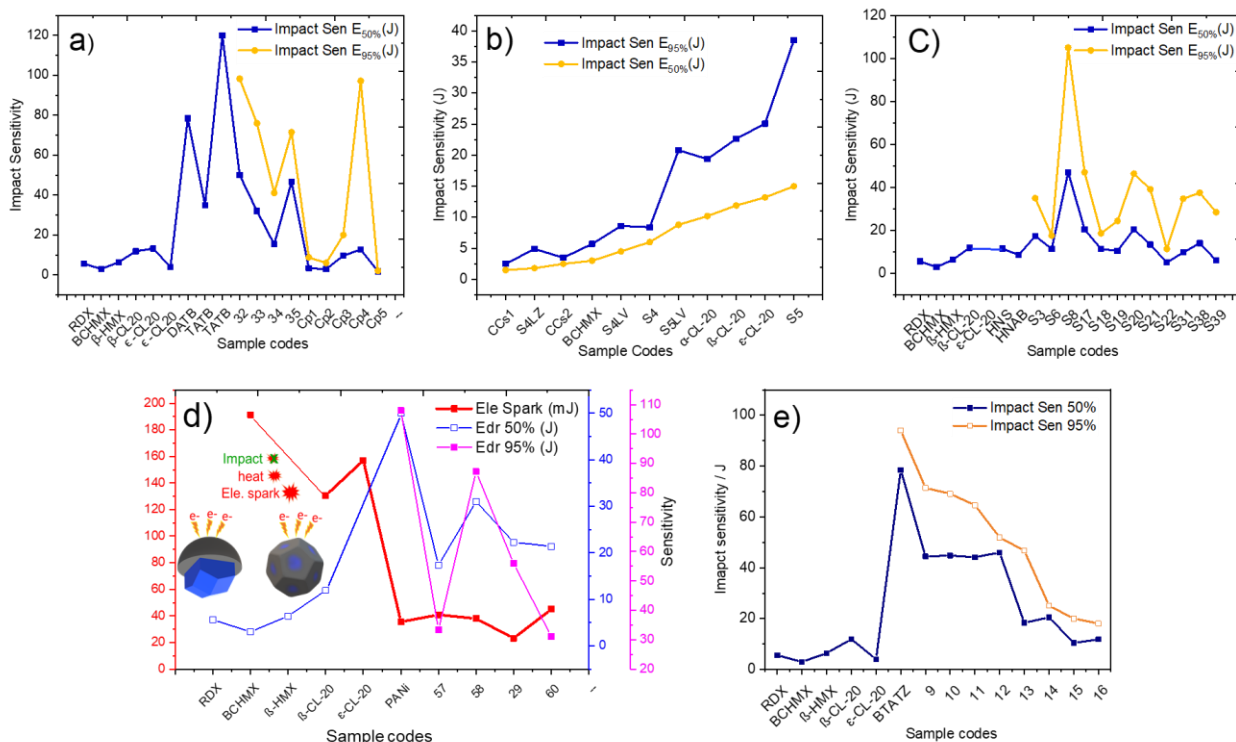


Figure 7. A comparative graphical representation of impact sensitivities (For sample codes details as follows [1 – 6]; **CACs of DATB and TATB:** BCHMX/DATB (Cp1); BCHMX/DATB (Cp2); RDX/DATB (Cp3) ; δ -HMX/ DATB (Cp4); β -CL-20/DATB (Cp5); δ -HMX/TATB (32); BCHMX/TATB (33); β -CL-20/TATB (34); RDX/TATB (35). **CACs of CL20/BCHMX:** CCs1 [0.60/1.00]; CCs2 [0.63/1.00]; S4 [1.10/1.00]; S5 [1.80/1.00]; S4LV [1.53/1.00]; S4LZ [1.52/1.00]; S5LV [1.57/1.00]. **CACs of HNS and HNAB:** 3 HMX/HNS; 6 HMX/HNS; 8 HMX/HNS; 17 RDX/HNS; 18 CL-20/HNS; 19 BCHMX/HNS; 20 RDX/HNAB; 21 BCHMX/HNAB; 22 CL-20/HNAB; 31 HMX/HNAB; 38 HMX/HNAB; & 39 CL-20/HNAB. **CACs of BTATz:** 9) RDX/BTATz B1, 10) RDX/BTATz B2, 11) HMX/BTATz B1, 12) HMX/BTATz B2, 13) CL20/BTATz B1, 14) CL20/BTATz B2, 15) BCHMX/BTATz B1 and 16) BCHMX/BTATz B2 **CACs of PANi:** 57 CL20/ PANi, 58 HMX/PANi, 59 BCHMX/PANi and 60 RDX/PANi

All cofomers shown very good compatibility with HMX and also true for RDX, for these both nitramines particles sizes within expectations. In case of the BTATz CACs it's interesting to see that crossed stirrer given lower particle sizes compared to linear stirrer, which is used during coagglomeration process [45], [75], [76], [77], [78], [84]. Spectral and powder X-ray diffraction measurements have demonstrated the creation of short contacts of the N-O---H type, including stacking of benzene rings with selected cofomers, hydrogen bonding, and van der Waals forces of attraction (which primarily occur between NO₂, N-N

(nitramines), and C-H). The stability of the crystal lattice is increased by these intra- and intermolecular interactions (for the PANi cofomer see a charge transfer complex type of interaction in Figure 2i).

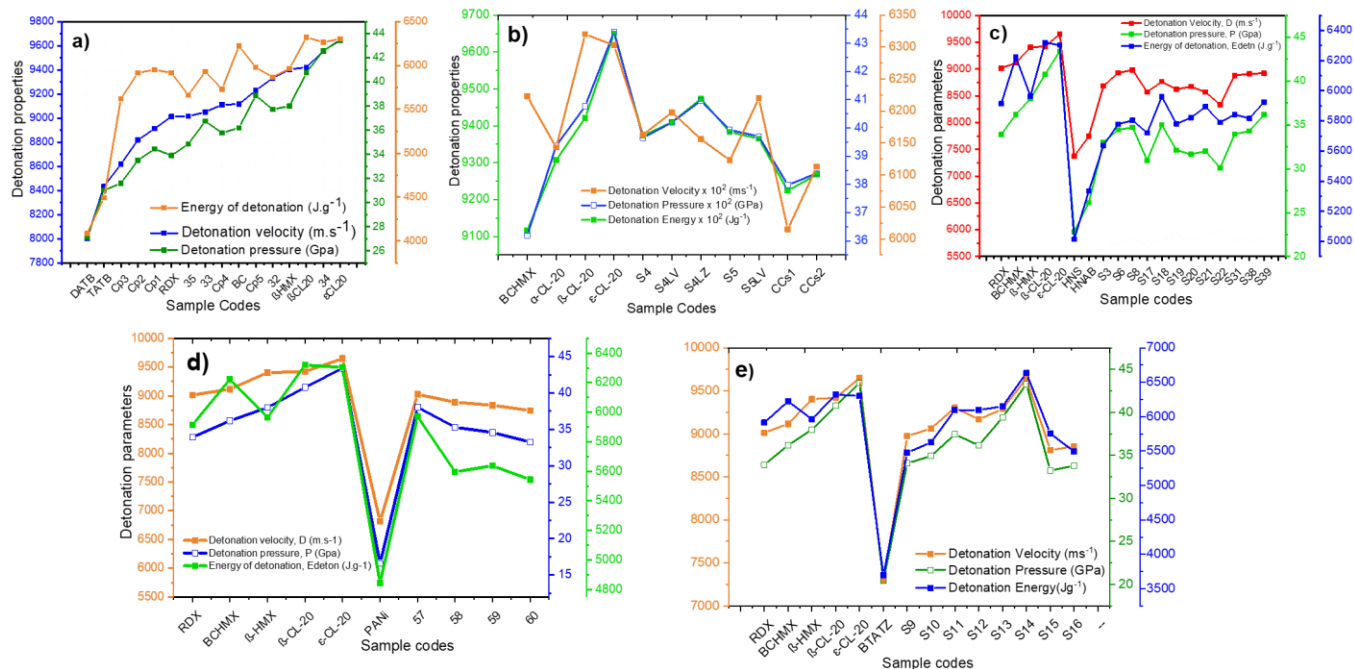


Figure 8. A comparative graphical representation of detonation properties (For sample codes details see caption Figure 3)

As a result of these intra and intermolecular interactions between cofomers and nitramines (structures shown in Figure 2 for pure cofomers) exhibited observable above mentioned changes, which suggests that molecules of cofomers at particular molar ratio enter into the nitramines crystal lattice. These changes are described in detail in recent publications [45], [75], [76], [77], [78], [79], [80], [85] and results summarized briefly as follows.

3.1 CACs of attractive nitramines with DATB and TATB

Both 1,3-diamino-2,4,6-trinitrobenzene (DATB) and 1,3,5-triamino-1,3,5-trinitro benzene (TATB) lead to the formation of co-agglomerates (CACs) with the nitramines (shown Figure 2e & f), in which HMX presents in its δ -form and CL-20 in its β -form [14, 15]; the δ -HMX stabilization in these CACs is particularly interesting, since the lifetime of this pure isomer is only 12 hours [87]. Whereas using DATB yielded CACs with a density of at most 99 % of the theoretical density of the mixed crystal, the TATB CACs densities are higher than those using the pure nitramines (including β -CL-20). The sensitivity is quite strongly reduced in the TATB CACs (15 – 50 J) compared to their DATB analogues (4 – 12 J)(See Figure

7a). Detonation parameters of CACs containing DATB and TATB are logically lower than those of the starting nitramines. The detonation energies of these mixed crystals are higher than would be expected from the respective percentage of the co-formers. The most interesting of the CACs studied appears to be HMX/TATB ($D = 9332 \text{ m.s}^{-1}$) which in the formulation used here, has a slightly increased density ($\rho = 1.909 \text{ g.cm}^{-3}$) with only slightly reduced detonation parameters compared to pure HMX ($\rho = 1.902 \text{ g.cm}^{-3}$, $D = 9404 \text{ m.s}^{-1}$)(See Figure 8a), while its impact resistance is extremely high (50 J). This CACs, together with RDX/TATB co-agglomerate, could be suitable filler for ammunition objects with high vulnerability resistance.

3.2 CACs of CL20 and BCHMX

The CACs of sterically crowded molecules CL20/BCHMX (shown Figure 2c & d) took long time efforts finally stabilized form obtained [76], here most important things are used medium of co-agglomeration and the molar ratio of cofomers. This can yield a co-crystal with clearly lower impact sensitivity (14.9 J for the β -CL-20/BCHMX molar ratio = 1.8) than that of pure ϵ -CL-20 (13.2 J) and of pure BCHMX (3 J) (See Figure 7b). The density of the studied co-agglomerates (CACs) achieves 99.5 % of the theoretically calculated ones and the density of the cofomers at the molar ratios used reaches 99.6 % of the β -CL-20 crystal density. The CACs has shown that CL-20 is present in them as its β -modification; in one sample, obtained by classical co-crystallization, have both α - and β -modifications.

The CACs studied have lower detonation energies than would be consistent with the percentage of individual cofomers in these crystals; this is a new finding (See Figure 8b), which does not correspond to the general view about the detonation parameters of explosive mixtures. The application of the most sensitive CACs (1.2 J) as a detonator primer did not exhibit the required acceleration capabilities in the given detonator design. However, a comparison with literature data showed that the CACs and CCs of this type could have advantageous applications in propellants because β -CL-20 is morphologically stable in these co-mixed crystals.

3.3 CACs of attractive nitramines with HNS and HNAB

The CACs with the 2,2',4,4',6,6'-hexanitro-2,2',4,4',6,6'-stilbene (HNS) cofomer are finer grained than those with the 2,2',4,4',6,6'-hexanitro-2,2',4,4',6,6'-azobenzene (HNAB) one (shown Figure 2g & h). CACs containing HNAB seem to be more perfect than CACs containing HNS [78]. However, impact sensitivity of the second mentioned ones is generally lower; the dominant sample is HMX/HNS with the molar ratio of 1.00/0.11 and the impact sensitivity of 47 J (See Figure 7c). The study of the surface morphology of these crystals has shown their microporous structure, which is not significantly reflected

into their crystal density. These CACs probably contain porous micro/nano crystalline clusters of HNS (for the pure HNS recently similar structure described in [88]). Three other CACs (RDX/HNS, RDX/HNAB and BCHMX/HNAB) had higher impact resistance than that exhibited by their original pure cofomers. For CL20, however, the entry of HNS or HNAB into its crystal lattice is destabilizing.

In these CACs the HMX is present in its δ -form, CL-20 in its β -form and the trans-HNS molecule changes its conformation to cis-form. On the basis of FTIR and Raman spectral studies shown there are more intense intermolecular interaction between HNS and nitramines (especially through the hydrogen bonds formed by the hydrogen atoms of the $-\text{CH}=\text{CH}-$ bridge) and in the case of δ -HMX also thanks to its spatial compatibility with cis-HNS molecules. The most interesting CAC from those studied appears to be the already-mentioned HMX/HNS with the molar ratio of 1.00/0.11 and the microporous structure of its crystals, whose calculated detonation velocity is of 8.98 km.s^{-1} for $\rho = 1.8778 \text{ g.cm}^{-3}$ (compare with 9.40 km.s^{-1} for β - HMX) (See Figure 8c). The combination of HMX and HNS molecules thus appears to be advantageous. The CACs studied, with the exception of the ones containing CL-20, may be applied as secondary fillers of special detonators and, after the verification of their pressability, also as fillers of various ammunition objects.

3.4 CACs of attractive nitramines with PANi

After successfully preparing the CACs of the Energetic-Energetic molecules category, coagglomeration extended to check feasibility of the method nonenergetic polymeric moiety with these attractive nitramines [79]. Obtained results are interesting with polyaniline (PANi), which shown effective influence in these attractive nitramines (shown Figure 2i). As usual the polymorphic changes observed exhibited α -HMX and β -CL20 after interacting with polymer chain. These attractive nitramines formed a charge transfer complex with PANi chain [25, 26], its interesting changes further confirmed by fluorescence quenching and quantum yield. In crystalline form the PANi moiety coated on surface of the nitramines crystals which further leads to thermal, mechanical/impact stability in corresponding CACs, however due to conductive nature PANi electric they are spark sensitive. In all these nitramine complexes showed an increased sensitivity to electrical spark, 20 - 40 mJ (See Figure 7d). Also found laser (29 mV with 10x/0.25 grating) sensitive in Raman measurements. From the point of view of performance in the studied nitramines is more interesting RDX/PANi complex ($D = 8744 \text{ m.s}^{-1}$) with a slightly increased density ($\rho = 1.8295 \text{ g.cm}^{-3}$), slightly reduced calculated detonation parameters compared to pure RDX ($\rho = 1.810 \text{ g.cm}^{-3}$, $D = 9014 \text{ m.s}^{-1}$), with also a good impact resistance of 21 J (See Figure 8d). The most resistant against impact is α -HMX/PANi (31.01 J), followed by remaining CACs. These PANi coagglomerates could be suitable primary components for electrical initiators.

3.5 CACs of attractive nitramines with BTATz

This case CACs produced parallelly in two batches with a linear stirrer (- B1) and a cross stirrer (+ B2); the B2 approach yielding better crystal morphology, quality of surface and higher density[89]. HMX in the corresponding CACs as its α -modification, which is highly sensitive in the pure state (1.9 J). The coagglomerate of α -HMX with BTATz, obtained by coagglomeration under mixing by cross stirrer, was found to be the least sensitive (46 J) (See Figure 7e) from the studied CACs and should have a detonation energy slightly better than that of β -HMX (6097 against 5864 J.g⁻¹) (See Figure 8e). Similarly, during the coagglomeration process, the ϵ -CL20 was converted to its β -modification in CL20/BTATZ. The cyclic nitramines CACs with nitrogen rich BTATZ as a cofomer are exergonic and could provide energy for self-propagating reactions, making them

4 APPLICATIONS OF CACs

4.1 HMX/BCHMX CACs in composite rocket propellant

Coagglomerated crystals (CACs) of and Physical mixture (PM) HMX/BCHMX were prepared, thoroughly characterized. The pure HMX (P1-P3) and these both [PM (P4-P6) & CACs (P7-P9)] are employed in composite rocket propellant separately (P1-P3; P4-P6 & P7-P9) at different proportions (10 – 30%). The experimental results obtained from PXRD, FTIR, Raman, and DTA analyses provide compelling evidence of robust intra- and intermolecular interactions between the cofomers in the CACs. These findings unequivocally demonstrate the formation of cocrystals. In order to assess the impact of CACs on the properties of propellant particles, a comprehensive characterization was conducted. The results revealed significant enhancements in the performance of propellant particles when CACs were incorporated. The examination of morphology and particle size indicates that CACs exhibit consistent sizes, well-distributed characteristics, and possess microcrystal edges that have undergone softening. This results in a homogeneous distribution over the propellant coarse, which is compared to a physical mixture. The location of these particles has a significant impact on thermal characterization.

Specifically, in the third category (P7-P9), the carbonaceous aerosol composites (CACs) exhibited more pronounced variations in decomposition for all three concentrations. In the thermal decomposition test, it was shown that both CACs and PM exhibited higher reactivity compared to batches containing pure HMX. This can be attributed to the reduction in ammonium perchlorate (AP) content and the greater reactivity of the binder-cured HMX with BCHMX. Moreover, the response of prepared propellants to mechanical stimuli is mostly determined by the composition and concentration of nitramines present inside them. The sensitivity of the combination is not significantly affected by the amount of pure HMX, with the exception

of when it reaches a weight percentage of 30%. However, the sensitivity is influenced by the presence of PM and CACs. The use of CACs exclusively influences the sensitivity to impact, but the application of PM has a dual effect by negatively impacting both sensitivity to impact and another factor. The correlation between the sensitivity of these propellants and their performance, as well as their energy content, plays a pivotal role in ensuring safety during their manufacturing, handling, and storage processes. The experimental correlation is predominantly grounded on Licht's rule[51]. CACs propellants (P7, P8 & P9) showed relatively good burning rates (7- 9 mm.s⁻¹) compared earlier studies, especially propellant P8 with 20% CACs content showed highest burning rate (9.07 mm.s⁻¹) and propellant composition of CACs shown overall better performance in morphologically and other thermochemical properties.

4.2 CL20/BCHMX CACs in detonators

In the same way, the utilization of sensitive CACs is used in detonators. In order to assess their capacity for commencement. The utilization of the most sensitive CACs (1.2 J) as a detonator primer in this particular detonator design did not demonstrate the necessary acceleration capabilities. However, a thorough examination of existing literature reveals that co-crystals containing CACs and co-crystals of this nature possess potential benefits for usage in propellants due to the morphological stability of β -CL-20 within these co-mixed crystals.

4.3 RDX/BCHMX CACs in gun powder

RDX and BCHMX gun propellant efficiency and compatibility were tested. Three samples were taken for study control (S00), RDX (S10.1), Phy Mix (S10.2), and CACs (S10.3). Nitramines in ammunition are of legitimate interest, as shown by past research. Nitramines can qualitatively replace nitroglycerin in binary powders. Sample S10.3 can be tentatively compared; results for the two-component powder D063 with the same charge and barrel length. The samples also reveal that adding 10% RDX to the propellant does not boost the powder's specific energy compared to pure nitrocellulose. Based on ballistic bomb measurements, Prof. Kusák's intra-ballistic model [138, 139] calculated the theoretically feasible projectile velocity and powder gas pressure for comparison. Compared computed features of samples S00 and S10.1. In sample S10.1, the projectile velocity is 10 m.s⁻¹ lower due to the consolidation of pressure to the same level, where both the pressure and the percentage of burnt charge are about the same. This means that adding this much RDX alone does not improve propellant performance. Instead, it failed; burning RDX particles during powder function may explain it. Higher RDX concentrations, like in ECI powders, or a proper combustion moderator may improve performance.

The computational model directs adding 2% BCHMX to solve the powder mass's RDX shortage. This very small quantity addition of BCHMX not only compensated for the drop in values but also significantly

boosted them, despite a bigger weighting and less powder mass burned at the shot than in samples S00 and S10.1. Sample S10.2 values; if not all of the powder in the barrel is burned at the shot, some grains afterburn, causing a greater flash-off in front of the barrel. This is nearly unacceptable in military usage.

Sample S10.3, with the same amount of RDX and BCHMX as sample S10.2, is best appraised since its nitramines have been technologically processed to create coprecipitates. The 7.62x39 cartridge assembly with this propellant has the best projectile velocity and powder gas pressure calculations, even though the KP preparation process has not been completely successful. Thus, cis-1,3,4,6-tetranitrooctahydro[4,5-d]imidazole (BCHMX) positively affects the combustion of RDX powder mass even at a tiny two percent amount. It would also be helpful to show if this powder is stable at other operating temperatures and if temperature fluctuations effect ammunition ballistics. Real bullet assemblies must be used to verify 7.62x39 mm cartridge theoretical calculations.

4.4 Applications Remaining CACs

The individual cofomers chosen for preparation of CACs of attractive nitramines, the futuristic applications are addressed basis of their interesting characteristic thermochemical and energetic properties. Especially, PANi and BTATZ CACs are ideal combinations space craft carrier separate loads and initiating next stage by PANi CACs. PANi CACs are better as initiators and BTATZ CACs as main propulsion part. Also, PANi CACs can be used as catapulting charges with combination of other CACs as main charges i.e., application of electromagnetic launch technology in the field of missile.

5 CONCLUSIONS

In essence, every practical-technological procedure for cocrystallization of energetic materials relies on a bottom-up approach; energy-safety balanced energetic materials (with desirable thermochemical as well as stability characteristics) can be achievable. In cocrystallization, both energetic conformers undergo noncovalent self-assembly with supramolecular interactions, like hydrogen bonding, pi-pi stacking, von der Waals forces, etc., kind of short interactions. These interactions play a key role in influencing the above-mentioned energetic properties of cocrystals. This way, cocrystallization can increase their applicability in various types of military and civilian technical applications. Key highlights of the present summarized report of theses as below section-wise.

5.1 Cocrystallization of attractive nitramines via coagglomeration

This method is practically an innovated co-crystallization in suspension, generally classified in the literature as the "Slurry method", which considerably reduces the processing time and decreases the quantity of solvents compared to a solvent co-crystallization. It provides fine co-crystals of very good quality. The co-

crystals of cyclic nitramines with 1,3-diamino- and 1,3,5-triamino-2,4,6-trinitrobenzene with δ -HMX are intriguing, with TATB acting as an anti-caking additive (molar ratio 1.00/0.12, IS = 50 J, calculated D = 9.3 km/s) [1, 2,5]. The co-crystal of cyclic nitramines with cis-2,2',4,4',6,6'-hexanitrostilbene (HNS) and 2',4,4',6,6'-hexanitroazobenzene (HNAB) exhibits higher impact resistance than its coformers, with δ -HMX/cis-HNS having a molar ratio of 1.00/0.11 and IS = 47 J (TNT has 39.4 J) and calculated D = 8.9 km/s [4]. The co-agglomeration of sterically crowded nitramines ϵ -CL20 and BCHMX yielded a β -CL20/BCHMX product with a molar ratio of 1.8/1.0, IS = 14.9 J, and calculated D = 9.4 km/s. The product's impact resistance exceeds that of its coformers, mainly BCHMX with IS of 3 J [3]. The molar ratio of coformers and the continuous phase significantly impacts co-agglomeration. Proteogenic solvents often yield better morphology than aprotic mediums, but HNAB decomposes in them [4].

The co-crystal types studied had HMX in its δ -modification, CL20 in its β -modification, and HNS in its cis-conformation. The spatially similar orientation of the δ -HMX and cis-HNS molecules may explain the low sensitivity of the δ -HMX/cis-HNS co-crystal for the molar ratio of coformers 1.00/0.11 [4]. The phenomenon of explosive mixtures having higher detonation parameters than calculated based on component percentages is observed in co-crystals with DATB and TATB, but not in co-crystals with cis-HNS and HNAB. The opposite was found for co-crystals β -CL20/BCHMX [1-5]. The β -HMX converted in α -HMX/BTATz coagglomerate, which was formed via slurry cocrystallization with mixing using a cross stirrer, had the lowest sensitivity (46 J) among the CACs that were studied. It is expected to have a somewhat better detonation energy than β -HMX (6097 against 5864 J.g⁻¹) [6].

5.2 Applications of CACs

Prepared employed in composite rocket propellant HMX/BCHMX CACs in three compositions 10, 20, 30 % results compared with pure HMX and Physical mixture insertion at same compositions. Similarly, CL20/BCHMX in detonator, and last one RDX/BCHMX in gun propellant. Except in detonators remaining cases CACs shown positive results. In case of HMX/BCHMX CACs shown very good morphological compatibility, thermochemical properties and at 20% shown optimum burning rate compared to both pure HMX and Physical mixture. Also, compared with earlier literature reported composite propellants HMX/BCHMX CACs showed relatively good burning rates (7- 9 mm.s⁻¹). In cases of gun propellant addition of 2% of BCHMX in the from RDX/BCHMX CACs shown impactful results compared to pure RDX compositions.

Futuristic applications in military, civil and space applications are all based on their interesting stability, thermochemical and energetic properties of cocrystals of attractive nitramines. This thesis considers the impacts of various traditional preparation methods and characteristics compared with the coagglomeration

method. The coagglomeration process is promising, is expected to continue advancing and will keep advancing at the Technology level in upcoming years. ideal combination for propulsion applications.

5.3 Impact sensitivity of CACs

The well-known observation of Dr. Licht [51] that high-performance explosives usually have high sensitivity was developed over time into a semilogarithmic relationship [92] between impact sensitivity and the energy content of explosives and the enthalpy of formation, which is presented in Figure 10.

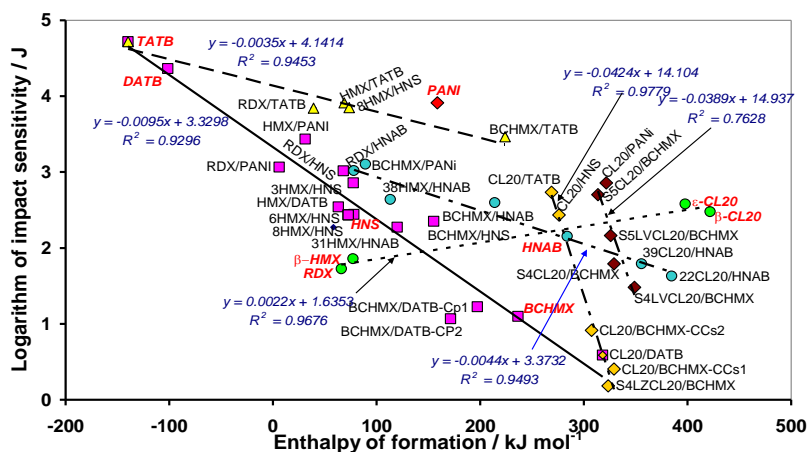


Figure 9. The semi-logarithmic relationships between the impact sensitivity and energy content (represented by the enthalpy of formation) of the CACs prepared (data taken from papers [45], [75], [76], [77], [78], [93]).

It clears that all coformers are stabilized and effectively reduced impact sensitivity of attractive nitramines (as shown in Figure 7). Especially, HMX shown more compatibility with all coformers, followed by RDX, BCHMX, and CL20. In both CL20 and BCHMX as mentioned earlier due to their crowded molecular environments it is not easy to interact with selected coformers. However, coagglomeration helped to resolve this problem. In the case of TATB and HNS SEM images shown by the outlook they are imperfect crystals, but they are highly impact insensitive. It may be due to their flexibility of crystals to withstand impact and forming pallets instead decomposition. To summarize these coagglomeration method effect and output CACs properties plotted dependency graphs using Licht's rule (Figure 9). The flow of dependencies is consistent, except that their exceptions for pure RDX, HMX and CL20 needed to find an explanation [94].

The coformers ratios also play a key role in the variation of impact sensitivity of cocrystals, viz., CL20/BCHMX being both sterically crowded at particular molar ratio (1:1.8) shown higher impact insensitive [76]. Also, in the case of HNS and HNAB slight variation of molar ratios impact sensitivity

varied [78]. Similarly, crystallization process during coprecipitation quick addition of solvent, or slow addition of solvent and more importantly shape of stirrer all factor well documented [84].

5.4 Thermochemical and Detonation properties of CACs

The well-known fact that mixing two explosives frequently produces a mixture with a higher detonation rate than would match the amount of components in this mixture is overlooked by researchers studying energetic cocrystals. [95].

It is evident from DTA studies that the onsets of the thermal disintegration of CACs are consistently slightly lower than those of pure nitramines. It makes sense that their exothermic decomposition peak temperatures would also be somewhat lower. The mechanism by which the composites interact with the Coformers structural components, intermolecular interactions between both coformers as depicted by spectroscopic analysis, may be the cause of the CACs decreased thermal stability when compared to pure nitramines(also the effect of the mixed melting point is appeared here, which is removing the stabilizing effect of the crystalline lattice). This interaction mode is expected to promote the homolysis of the --N-N-- in nitramines, and -N---O---H- bonds in plynitroarenes with hydrogen atom in gamma-position towards nitro group. Exothermic decomposition occurs in the original thermal range of the CL20 polymorphic transition not only due to the extreme degree of contact in the composite. Likewise, the decomposition of a composite containing HMX also initiates in the vicinity of its $\alpha - \delta$ - transition (in both cases, the movement of molecules in the crystal lattice at the polymorphic transition damages its stabilizing effect). Illustrates how coformers , bound to the nitramines, started to break down in this CACs solid form, which is significantly different from how its CACs thermolyzed with polynitro compounds.

The data in Figure 11, the present instance, shows that group A's brisant explosives (primarily CL20 and partially BCHMX) have the least impact on the increase in E_{deton} values for the CACs, group B's CACs of RDX and HMX with coformers have highly increases in these values. Group C PANi coformer has the largest effect ever observed.

The partial dependencies of the nitramine CACs form a single intersection (see Figure 10). According to Professor Urbanski, mixtures of explosives have higher detonation parameters than would be consistent with their percentage in the mixture; this is due to the higher entropy of the mixture than is present in the components entering it [95]. However, we found the opposite for pure nitramine CACs, due to molecules with different structures but although with the same chemical entities entering the cocrystal [76].

The coagglomeration generally categorized theoretically as the "slurry method" of co-crystallization, which involves preparing co-crystals, yields highly intriguing energetic materials with a relatively high crystal density. You can use components straight from production, after isolating them from reaction mixes and stabilizing them, thus there is no need for initial cofomers with defined granulometry. Cofomers can be co-precipitated to purify themselves in solution.

Our initial findings imply that [80], similar to traditional crystallization, chemical engineering considerations play a role in the CAC preparation process. This technology can be used for industrial scale cocrystal manufacturing with the help of technical and technological optimization.

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LIST OF STUDENTS' PUBLISHED WORKS

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- 10) Initiation Reactivity of Cyclic Nitramines Mixed Crystals from the Perspective of XPS Application, V. B. Patil, R-P, Jhonatan S. Zeman, [Defense Technology, under communication]
- 11) Towards to some published misconceptions about TNT and ϵ -CL20, S. Zeman, V. B. Patil, [FirePhysChem, Under review]
- 12) Technological frontiers in cocrystallization of four attractive cyclic nitramines, V. B. Patil, S. Zeman [Chemical Engineering Journal, Manuscript under communication]
- 13) Application of BCHMX/HMX CACs in composite rocket propellant [Manuscript under preparation]

➤ **Research articles in international conference proceedings**

• **Poster presentations at conferences**

- 1) Innovative coagglomeration method for producing the energy-safety balanced cocrystals of attractive nitramines; V. B. Patil, S. Zeman, NTREM2024; organized by Institute of Energetic Materials, Faculty of Chemical Technology, University of Pardubice, Pardubice Czech Republic in April 2024.
- 2) Coagglomerated Crystals of Attractive Nitramines in Nitrocellulose Gunpowder: A Technological Application; M. Novak, V. B. Patil, L. Velehradský, K. Kubát, S. Zeman, NTREM2024; organized by Institute of Energetic Materials, Faculty of Chemical Technology, University of Pardubice, Pardubice Czech Republic in April 2024.
- 3) Thermal studies of attractive nitramines/polyaniline composite crystals prepared via co-agglomeration; V. B. Patil, R Svoboda, P Bělina, S Zeman, NTREM2023; organized by Institute of Energetic Materials, Faculty of Chemical Technology, University of Pardubice, Pardubice Czech Republic in April 2023.
- 4) Preparation and emphasized study of TATB/nitramines co-mixed crystals via coagglomeration method, V. B. Patil, P Bělina, S Zeman, 24th New Trends in Energetic Materials (NTREM 2022), organized by Institute of Energetic Materials, Faculty of Chemical Technology, University of Pardubice, Pardubice Czech Republic on April 6 - 8, 2022. Received BEST POSTER PRIZE.
- 5) A new insight into the energetic co-agglomerate structures of attractive nitramines; V. B. Patil, K. Zalewski, J. Schuster, P. Bělina, W. A. Trzciński, and S. Zeman, Nobel laureate s&t seminar series 11th India-Japan Science And Technology Seminar, (Virtual Conference); This was co-organized by Sree Chitra Tirunal Institute for Medical Sciences & Technology (Dept. of Science and Technology, Govt. of India) and Indian JSPS Alumni Association (IJAA) on 6-7 December 2021.

• **Oral presentations at conferences**

- 6) Novel approach for preparation of the energy-safety balanced cocrystals of attractive nitramines via coagglomeration, V. B. Patil, S. Zeman, 14th International High Energy Materials Conference & Exhibits (HEMCE-2024), organized by High energy materials society of India in collaboration with Indian Space Research Organization (ISRO) & Defense Research & Development Organization (DRDO), INDIA; February 1-3, 2024; Vikram Sarabhai Space Centre, Thiruvananthapuram, Kerala, INDIA, Received BEST ORAL PRESENTATION prize.

- 7) Successful journey in preparation of the energy-safety balanced cocrystals of attractive nitramines via coagglomeration, V. B. Patil, S. Zeman, 46th International Pyrotechnical Society Seminar, EUROPYRO2023, September 11-14, 2023, Saint Malo, FRANCE.
- 8) Thermal studies on performance of DATB and TATB coagglomerated crystals, V B Patil, R Svoboda, S Zeman, 13th International High Energy Materials Conference and Exhibits (HEMCE-2022), organized by High energy materials society of India in collaboration with TRBL, Development Organization (DRDO) Chandigarh, May 26-28, 2022, Chandigarh, INDIA.