The Study of Co-Crystallization of Trinitrophenol (TNP) and Ammonium Nitrate (AN) As a Potential Method for Enhanced Stability

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DOI: https://doi.org/10.51584/IJRIAS.2025.100500035

Received: 16 April 2025; Accepted: 28 April 2025; Published: 05 June 2025

ABSTRACT

This study explores the co-crystallization of trinitrophenol (TNP) and ammonium nitrate (AN) using a slow solvent evaporation method at a 1:1 molar ratio. The co-crystal formation and its potential for improved explosive stability were investigated. Characterization techniques including Fourier-Transform Infrared Spectroscopy (FTIR), X-ray Diffraction (XRD), and Differential Scanning Calorimetry (DSC) were employed. FTIR analysis revealed new peaks corresponding to functional group interactions between TNP and AN, indicating co-crystal formation. XRD confirmed the presence of new diffraction peaks not observed in the individual components, further supporting co-crystallization. DSC analysis demonstrated a significant shift in thermal behaviour compared to TNP and AN. The co-crystal exhibited a glass transition, melting point, and decomposition temperature distinct from the single components. These observations suggest interactions between TNP's -OH groups and Ammonium NH_4^+ ions, leading to the formation of a more stable ammonium picrate co-crystal. The altered thermal profile indicates a potential improvement in the co-crystal's stability compared to the individual explosives.

Key words: co-crystal. Energetic material, trinitro phenol, ammonium nitrate, thermal profile.

INTRODUCTION

The quest to understand and control the behavior of energetic materials, which is the power houses behind explosives, propellants, and oxidizers, has been a continuous struggle for national defense sectors worldwide. Traditionally, advancements have relied on diverse synthesis techniques, leading to the discovery of iconic explosives like black powder, TNT, and RDX. However, this approach often comes at the cost of sacrificing stability or safety (e.g., nitroglycerine) (Ahmed *et al*.,2018).

One such example is trinitrophenol, also known as picric acid. While boasting explosive power comparable to TNT, its sensitivity to shock, heat, and friction in its dry state makes it a precarious proposition. Paradoxically, when wet, it becomes remarkably safe to handle. This inherent instability, coupled with its reactivity towards metals (forming salts), hinders its practical use. This research delves into the potential of subjecting trinitrophenol to co-crystallization with ammonium nitrate, aiming to create a more stable and explosively superior material with altered thermal properties (Zongwei *et al*., 2016).

The realm of energetic materials typically relies on established methods to enhance power and stability. These often involve modifying the chemical structure of existing compounds, searching for denser polymorphs (crystal structures), or formulating composite materials. However, co-crystallization offers a novel and potentially more systematic approach. This technique strategically combines existing molecules into a single crystal structure. Excitingly, the co-crystal can offer new and desirable properties based on the easily measurable solubility data of its individual components (Han *et al*.,2017).

This research explores the potential of co-crystallization as a path towards a new generation of energetic materials that not only pack a punch but also prioritize safety and stability. By harnessing the combined knowledge of existing energetic materials and the innovative power of co-crystallization, we can embark on a new chapter in the ongoing quest to unlock the secrets of these remarkable materials (Yadav *et al.*, 2015).

CHEMICALS AND METHOD

Chemicals

Ammonium nitrate, Trinitro phenol, acetone, methanol, ethanol, di-chloromethane all AR grade was obtained from CONSAT chemical shop Kaduna and Lagos, Nigeria.

Co-crystalization

Ammonium Nitrate and Picric Acid $NH_4NO_3/C_6H_3N_3O_7$ at a molar ratio of 1:1 (balanced stoichiometric equation) was prepared using slow evaporation method. A 0.259g of NH_4NO_3 and 0.74 of $C_6H_3N_3O_7$ was weighed and added into a 100ml beaker. 65ml of acetone was measured and also added into the 100 ml beaker containing the mixture of NH_4NO_3 and $C_6H_3N_3O_7$. The choice of acetone as a solvent is because it can dissolve both samples without using other solvent. Stirring commences using the stirrer and after 15 minutes during the process 15ml of distilled water was added to the mixture and the stirring continued till it dissolved completely. The beaker was removed from the water bath and covered with a filter paper which was kept in an oven for a week during which crystals was formed and dried at room temperature.

FTIR Analyses

The Cocrystal, ammonium nitrate and tri -nitro phenol were characterized by Agilent technology Cary 630 FTIR. The scanning range of the IR spectra was 525-4000 cm^{-1}. Experiments were performed at room temperature.

XRD analysis

The Co-crystal, potassium chlorate and Ammonium nitrate samples were characterized by X-ray diffraction (XRD) using a Empeyrean Pan-Analytical Advance XRD. Each sample was scanned over the 2θ angular range 5°-80° with a sampling interval of 0.2°. The XRD reflections were obtained at room temperature (25 °C).

DSC analysis Differential Scanning Calorimetry

(DSC) analyses of the dried Co-crystal samples, ammonium nitrate and potassium chlorate were carried out using a METLER star (SW 13.00) and Chip DSC-10 Linseisinstrument at a heating rate of 10 K/min. The samples were heated from 30 °C to 150 °C. The mass of the samples used was 1.000 mg. The system was in a nitrogen atmosphere.

RESULT AND DISCUSSION

FTIR Analysis

The assignments for the major characteristic bands are listed in Table 1.0. The results indicated that several characteristic absorption peaks are highly sensitive to the structure changes of the co-crystal in the IR spectra. NH_4NO_3 has bands at 3231.6 cm-^{1}, 3045.2 cm-^{1}, 827.5 cm-^{1}, and 1289.7 cm-^{1} O-H stretching , C=C stretching , C=H bending and C=C bending and . However, these bands shifted to 3239.1 cm-^{1} and 3101.1 cm-^{1}, 1867.4 cm-^{1} and 827.5 cm-^{1}, 782.7 and 700.7, 916.9 cm-1, respectively in the co-crystal. Similarly, some characteristic absorption peaks of $C_6H_3N_3O_7$ 3104.9, 916.9, 831.2 and 700.7, 823.7, 1364.2 and 1763.0 cm-^{1} also shift after crystallization and also the co-crystal exhibited some bands of N-H stretching 3425.4 cm-^{1}, C≡C stretching 2113.4 cm-^{1}, C=C stretching 1628.8 cm-^{1}, O=H bending 1423.8 and 1312.0 cm-^{1}, N-H bending 1524.5 cm-^{1}, C-O stretching 1259.8 cm-^{1}, C-N stretching 1334.4 cm-^{1} which did not appear in the band of NH_4NO_3 and $C_6H_3N_3O_7$. Those shifts in phenomena may be caused by the hydrogen bond interactions involved in co-crystal formation which changes the symmetry characteristic which is similar when compared with the work Jin-ting *et al*, 2015 carried out on cocrystallization of 3- nitro- 1,2,4- triazol-5 –one (NTO) and 5,6,7,8-tetrahydroterazolo(1,5-b(1,2,4)-triazine(TZTN) at a molar ratio of 1:1.

Table 1 shows the FTIR bands, Assignments of NH_4NO_3, $C_6H_3N_3O_7$ and $NH_4NO_3/C_6H_3N_3O_7$

S/N	**ASSIGNMENT**	**NH_4 NO_3**	**$C_6H_3N_3O_7$**	**NH_4NO_4/ $C_6H_3N_3O_7$1:1 Slow**
1	N = H stretching			3425.4
2	C = C stretching			
3	C – H =bending	827.5	916.9 831.2 700.7	1867.4 827.5 782.7 700.7
4	C = C= bending	1289. 2		916.9
5	O – H= stretching	3231.6 3045.2 1408.9	3104.9	3239.1 3101.1
6	O – H= bending	715.6	1427.6	1423.8 1312.0
7	C – C = stretching			
8	N – O = stretching			
9	C – O = stretching	1755.6	1088.4	1259.8
10	C-H stretching		2870.1	
11	N-H bending		1606.5	1524.5
12	C-N stretching		1338.1	1334.4
13	C≡C stretching			2113.4

Xrd Analysis

The XRD diffractogram of NH_4NO_3, $C_6H_3N_3O_7$ and co-crystal (NH_4NO_3/ $C_6H_3N_3O_7$ 1:1 SLOW) are presented in Table 2 . The diffractogram of NH_4NO_3 exhibited characteristic peak of 2Ө with some selected values at 18.0881, 24.5084, 26.3488, 28.2676 29.2147 and 31.2757 which are not present in the co-crystal pattern while $C_6H_3N_3O_7$ exhibited characteristics peak of 2Ө with some selected values at 9.3970, 14.0291, 16.2646, 18.6813, 19.0188, 19.2708 which are also not present in the co-crystal pattern. The co-crystal exhibited new peak of 2Ө values at 13.9970 and 17.8743 13.9970 17.8743, 19.4140, 23.7984, 23.9260, 32.9365, 37.9099, 41.2689, 46.9912, 48.5101, 48.9905, 57.2375, 59.7379 , 65.7211 which are not in the pattern of the co-formers, that indicates a new peak have been formed after crystallization. The work shows some similarities when compared with the work of Chongwei *et al*, 2017 worked on Nano-CL-20/HMX Cocrystal Explosive for Significantly Reduced Mechanical Sensitivity. The XRD shows all diffraction peaks of raw HMX appeared in CL-20/HMX cocrystals pattern. However, diffraction peaks of raw CL-20 did not appear in pattern of CL-20/HMX cocrystal explosive at 12.5° and 13.8°. Compared with patterns of raw CL-20 and raw HMX, at 11.4° and 13.2°, respectively, new diffraction peaks appeared on CL-20/HMX cocrystals pattern. Changes showed that prepared samples did not simply mix with CL-20 and HMX, but they interacted to form new cocrystals.

Table 2 shows the XRD 2Θ peaks values of NH_4NO_3, $C_6H_3N_3O_7$ and $NH_4NO_3/C_6H_3N_3O_7$1:1

S/No	**NH_4NO_3 POSITION ^{0}2Theta**	**$C_6H_3N_3O_7$ POSITION ^{0}2Theta**	**Co crystal POSITION ^{0}2Theta**
1.	18.0881	9.3970	13.9970
2.	24.5084	14.0291	17.8743
3.	26.3488	16.2646	19.4140,
4.	28.2676	18.6813	23.7984,
5.	29.2147	19.0188	23.9260,
6.	31.2757	19.2708	32.9365,
7.	33.2142	21.0540	37.9099,
8.	36.4891	21.4222	41.2689,
9.	39.9551	21.9292	46.9912,
10	40.3346	22.9786	48.5101,
11	40.5234	23.3623	48.9905,
12	45.9789	23.7754	57.2375,
13	49.5297	25.0811	59.7379
14	50.4936	25.5759	
15	51.2239	26.1857	65.7211
16	51.3901	26.8925	
17	56.3408	28.4902	
18	58.7243	29.7664	
19	61.1872	30.3573	
20	61.3912	31.3682	
21	62.3027	31.9353	
22	62.5165	32.2652	
23	63.6356	32.8803	
24	63.8214	33.6147	
25	68.7415	34.2617	
26	68.9644	35.1026	

27	71.1838	35.9150	
28		37.8007	
29		38.3578	
30		38.9774	
31		40.1196	
32		42.5934	
33		43.6596	

DSC Analysis

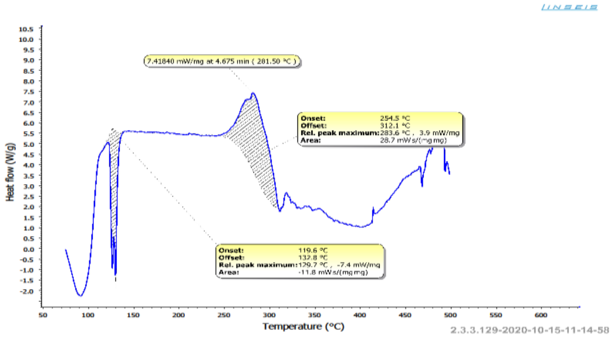
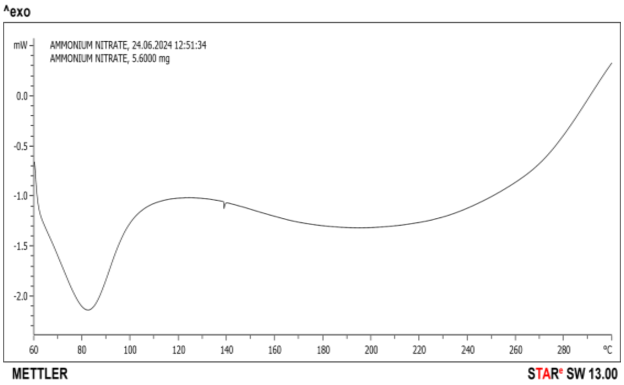


Fig 1.a: DSC spectra of trinitro Phenol ($C_6H_3N_3O_7$)Fig .



1.b: DSC spectra of ammonium nitrate

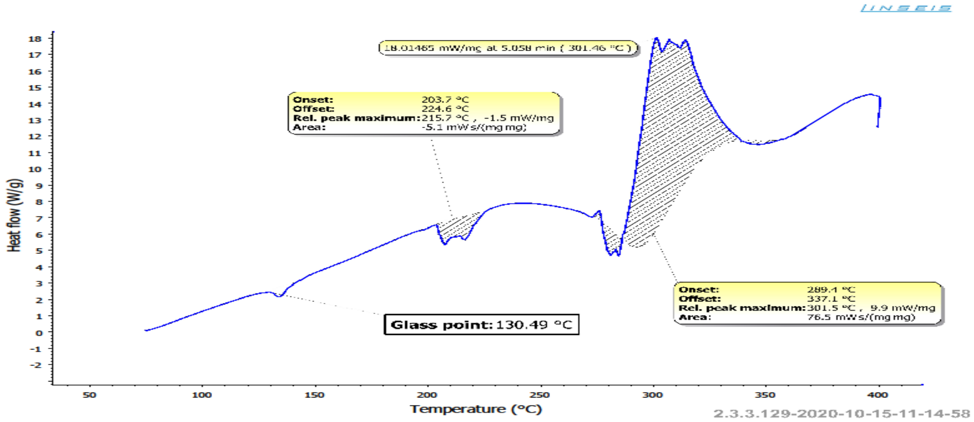


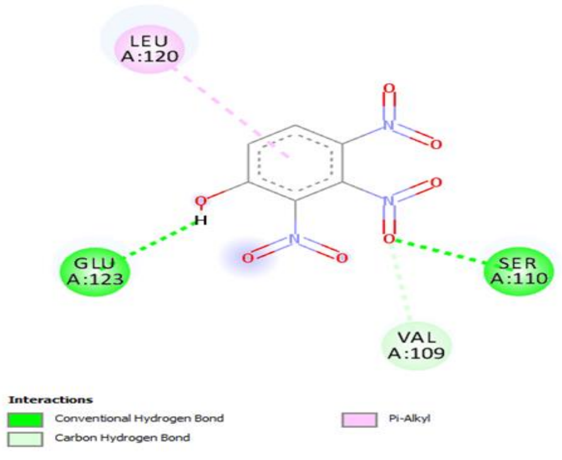
Fig 1.c: DSC spectra of $C_6H_3N_3O_7/NH_4NO_3$cocrystal 1:1 slow

Table 3. endothermic, exothermic peak values and melting point for $C_6H_3N_3O_7$, NH_4NO_3, 1:1 cocrystal slow

S/N	SAMPLE	ENDOTHERMIC ^0C	ENDOTHERMIC ^0C	EXOTHERMIC ^0C	MELTING POINT ^0C
1	$C_6H_3N_3O_7$	129.7		291.5	122.5
2	NH_4NO_3	127.9	170.5	237.5	169.6
3	$C_6H_3N_3O_7/NH_4NO_3$ 1:1	215.7		301.45	281.5

The DSC curve as shown in Fig. 1a-c and thermal values in table 3, displayed a curve of single component of $C_6H_3N_3O_7$, NH_4NO_3 and co-crystal of $C_6H_3N_3O_7/NH_4NO_3$ 1:1 which are different from each other. The $C_6H_3N_3O_7/NH_4NO_3$ co-crystal presents a unique thermal property by exhibiting a shift of the base line indicating a glass point peak at 130.49 ^0C, an endothermic peak value of 215.7 ^0C was observed which signify the melting point of the crystal before decompose and also an exothermic peak values of 301.45 ^0C was displayed indicating the temperature at which it decompose which is different from the value of single component $C_6H_3N_3O_7$ and NH_4NO_3 , where $C_6H_3N_3O_7$ displayed an endothermic peak of 129.7 ^0C indicating a melting stage of the crystal while an exothermic peak of 291.50 ^0C was displayed which indicate the decompose temperature without undergoing co-crystallizaation, while NH_4NO_3 displayed an endothermic peak of 54.7 ^0C as a phase change and an endothermic peak of 127.9 and 170.5 ^0C, indicating the melting of the crystal leading to an endothermic peak value of 237.5 ^0C which decompose without heat. The endothermic peak value displayed by the single component indicate to be lower for $C_6H_3N_3O_7$ compared to the co-crystal value while NH_4NO_3 gave a value higher than the co-crystal and also the co-crystal displayed an exothermic peak value that did not appear on the single component and indicated to be higher than the single components this behavior observed could be as a result of the interaction between NH_4ClO_4 and NH_4NO_3 which altered the phase change resulting to co-crystallization thereby altering the thermal property resulting to the values obtained. This behaviuor was observed to be in line with the work of Dong *et al* 2015 were they cocrystalize picric acid and trinitrotoluene and the work of Zhi *et al*.,2016.

Molecular Modeling of Picric acid and Ammonium nitrate



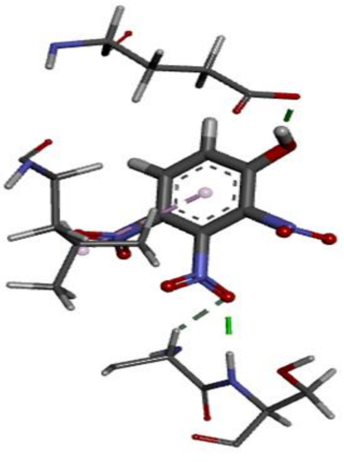


Fig. 2 and 3 show 2d, and 3d view of Hydrogen bond interaction of the picric acid (TNP) - $C_6H_3N_3O_7$ trinitrophenol and NH_4NO_3 ammonium nitrate using discovery studio virtualizer.

The stability and characteristics of the co-crystallized compounds are greatly influenced by the hydrogen bond interactions between $C_6H_3N_3O_7$ (trinitrophenol) and NH_4NO_3 (ammonium nitrate). Discovery Studio Virtualizer was used in this work to display the hydrogen bond interactions, which shed light on the molecular connections between these oxidizer and explosive compounds. The complex nature of molecular interactions in these systems is highlighted by the hydrophobic pi-alkyl interactions and hydrogen bonding between TNP $C_6H_3N_3O_7$ and AN

NH_4NO_3 with particular amino acid residues, including SER110, LIG1, and VAL109. The observed hydrogen bond distances, which range from 1.76269 Å to 5.28963 Å, indicate different interaction strengths; stronger bonds are generally indicated by shorter distances.

At a distance of 1.94802 Å, as seen in Fig 2 and 3 the hydrogen bond interactions between $C_6H_3N_3O_7$ and NH_4NO_3 with SER110 is very significant because it represents a stable connection that adds to the overall stability of the co-crystallized compounds. The structural integrity of the co-crystallized system is further improved by the hydrophobic pi-alkyl contact with LIG1 and the carbon-hydrogen bond interaction with VAL109. The significance of hydrogen bonding interactions in stabilizing energetic materials is shown by the production of ammonium picrate as a result of these interactions between $C_6H_3N_3O_7$ and NH_4NO_3. The hydrogen bond interactions found in this study provide insight into the underlying molecular mechanisms controlling the creation and stability of ammonium picrate, which is well-known for its explosive and stable characteristics.

Furthermore, knowing the precise chemical interactions that exist between $C_6H_3N_3O_7$ and NH_4NO_3 not only helps to explain how they co-crystallize, but it also provides important information for the creation of new energy materials with specific characteristics.

CONCLUSION

The investigation into co-crystallization as a method to modify the properties of trinitrophenol (TNP) yielded promising results. Utilizing slow solvent evaporation, a co-crystal with ammonium nitrate was successfully formed. FTIR analysis confirmed interactions between the hydroxyl groups of TNP and the ammonium ion (NH_4^+), suggesting hydrogen bond formation. Differential Scanning Calorimetry (DSC) revealed a significant alteration in thermal behavior.

The co-crystal exhibited a glass transition temperature of 130.49 °C, a melting point of 215.7 °C, and a decomposition temperature of 301.45 °C. These values were all notably higher compared to those observed for the individual components, indicating enhanced stability of the co-crystal. X-ray Diffraction (XRD) further corroborated the formation of a new crystalline phase, potentially an ammonium picrate co-crystal, resulting from the interaction between TNP's hydroxyl groups and $NH4^+$. Also the Discovery Studio Virtualize corroborated the formation of hydrogen bonding leading to the formation of a new crystalline phase by displaying a molecular model of trinitrophenol TNP and ammonium nitrate. The model shows angle formation showing the hydrogen bonding through cocrystallization. These findings highlight the potential of co-crystallization as a technique to not only modify TNP's thermal properties but also potentially reduce its corrosive nature, paving the way for its safer future applications.

REFERENCES

1. Ahmed, K, H., Svalopluk, Z., Ahmed, E., (2018). Promising new insensitive cocrystal. Paper presented at conference of new trends in research of energetic material. 1-30
2. Braga, D., Grepioni, F., Maini, L., Polito, M., (2009). Crystal Polymorphism and Multiple Crystal Forms. 132: 25
3. Changyan, G., Haobin, Z., Xiaochuan, W., Jinjiang, X., Yu, L., Xiaofeng, L., Hui, H., and Jie, S., (2013). Crystal Structure and Explosive Performance of a new CL-20 and Caprolactam Co-crystal. Journal of Molecular Structure. 1048: 267-273
4. Chongwei A. N., Hegun L, Baoyun, Y. E., and Jingyu, W., (2017). New Cl-20/HMX cocrystal explosive for significantly reduced mechanical sensitivity. Journal of Nano materials. 10: 1155
5. Gorbovskiy, K.G., Kazakov, A.I., and Mikhaylichenko, A. I. (2021). Ammonium nitrate Thermal Decomposition Kinetics under Nonisothermalconditindons in Open system. Journal of technology of inorganic substances and materials, 55, 742-747
6. Han Gao, Wei Jiang*, Jie Liu, Gazi Hao, Lei Xiao, Xiang Ke, and Teng Chen. (2017). Study of an Energetic-oxidant Co-crystal: Preparation, Characterisation, and Crystallisation Mechanism defence science journal. 67: 510-517.

7. Jin-Ting, W., Jian-guo, Z., Tong, L., Zhi-min, L and Tong- lai, Z., (2015). A Novel Co-crystal Explosive NTO/TZTN with Good Comprehensive Properties. Journal of the royal society of chemistry. , 5: 28354
8. Prafulla, P., Shingekar, A. P., Suyog, A., Adrian, L. K., Elaine, C. B., and Anant, P. (2017). Synthesis of Caffeine and Maleic Acid Co-crystal by Ultrasound Assisted Slurry Co-crystallization. Journal of Pharmaceutical Sciences. (106): 66-70.
9. Yadav, A. V., Shete, A. S., Dabke, A. P., Kulkarn, P. V., and Sakhare, S. S. (2009). Co-crystal, a Novel Approach to Modify Physiochemical Properties of Active Pharmaceutical Ingredients. Indian Journal of Pharmaceutical, (4), 359-370.
10. Zhi-Xiang, X., Xiao, Q. F., Quiang, W., (2016). Phase stability of Ammonium nitrate with Organic Pottassium salts. Central European Journal of Energetic material. 13(3). 756-754
11. Zongwei Yang, Qun Zeng, Xiaoqing Zhou, Qi Zhang, Fude Nie, Hui Huang, Hongzhen Li*(2016). Cocrystal explosive hydrate of a powerful explosive, HNIW, with enhancing safety. Journal of the royal society of chemistry., 5: 28354