

New Explosive Materials through Covalent and Non-Covalent Synthesis: Investigation of Explosive Properties of Trinitrotoluene: Acridine and Picric Acid: Acridine

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Abstract

Trinitrotoluene (TNT) and picric acid (PIC) suffer from suboptimal thermal and impact sensitivities, which severely hinder their real-world use. We here demonstrate how co-crystallization with acridine (ACR) can improve these properties of TNT and PIC without detrimentally affecting their explosive performance. Remarkably, while PIC:ACR formed readily, attempts to co-crystallise TNT with ACR led to formation of new covalent bonds between the co-formers, thereby creating a new molecular entity. The structure and energetic behaviour of both novel solid forms (PIC:ACR and TNT-ACR) were characterised using a range of experimental and computational tools, indicating that both materials have improved thermal and mechanical stability but explosive performance has decreased to some extent. These findings will increase the likelihood of rational energetic material design in the future and open a new chapter in this discipline.

Keywords: Energetic salts, Picric acid, Trinitrotoluene, Acridine, Non-covalent interactions, Carbanion adducts.

1. Introduction

Energetic materials (explosives, propellants, and pyrotechnics; EMs) are a class of substances that can rapidly release large amounts of energy and gas when initiated by external stimuli [1]. Despite the importance of EMs to a wide range of military (munitions, missiles) and civilian (mining, space exploration) technologies, new EMs are rarely introduced into circulation. This owes to the significant cost and stringent safety criteria that must be met before new chemical entities can be fielded. The energetic performance and power of EMs must always be balanced against safety aspects, including their sensitivity to initiation by heat, impact, shock, or friction [2, 3]. While significant work in the field is aimed directly at new molecule synthesis, the bar for development beyond the state of the art is very high, not only in terms of performance but also of the necessity for inexpensive and safe production [4]. It is unavoidably complicated to combine high heats of formation, desirable detonation performance, good thermal stabilities, and impact and shock insensitivity within a single crystalline material [5]. The synthesis of new EMs involves several reaction steps and a longer processing time, making this technology extremely complicated and time-consuming [6]. The co-crystallization technology for EMs has gotten a lot of attention as a very promising strategy. The intentional formation of multi-component organic compounds without the synthesis or breaking of covalent bonds (commonly referred to as co-crystal synthesis [7, 8] has discovered many applications in applied organic solid-state chemistry [9-11], most notably in pharmaceuticals [12-17] and agrochemicals [18, 19]. Throughout the previous decade, tremendous progress was made in the co-crystal synthesis of novel solid forms of existing energetics. Co-crystallization technology was used to change parameters such as melting temperatures, decomposition points, density, packing coefficient, sensitivity (impact, friction, and electric discharge), and energetic performance properties. The physical and energetic characteristics of several different co-crystal examples were compiled and contrasted with their constituents in order to clearly show the advantages of energetic co-crystals over their constituents (Table 1) [3, 20-32].

TNT was synthesized in 1863 and is now one of the most commonly used EMs. It is valuable in part because of its sensitivity to stress and friction. Energy property improvements are costly and time-consuming. As a result, new, environmentally friendly, non-toxic, and highly EMs that require safe handling and storage must be developed [33]. PIC was manufactured in 1742 and first utilized as an explosive in 1830. Given its tremendous explosive power, it has also emerged as a potential replacement for more prevalent EMs. It is also frequently utilized in the dye industry, rocket fuel manufacturing, and pharmaceutical manufacturing [34]. The relatively high chemical reactivity of PIC is one of the main reasons for its problems in utilization. Overly acidic compounds are often prone to chemical instability and hygroscopicity, which can create serious problems with transport, processing, and storage.

In this study, through solvent evaporation and leveraging the proton transfer process, a charge-transfer complex PIC:ACR was successfully synthesized between PIC and ACR. Similarly, TNT was subjected to solvent evaporation with ACR, resulting in the formation of a novel organic molecule, TNT:ACR. While the primary objective of the research was to investigate the formation of a new co-crystal structure by crystallizing TNT with ACR, the unexpected synthesis of TNT:ACR via covalent bonding and steric effects between the TNT and ACR rings

marks a milestone in crystal engineering, as this represents the first instance of such a novel organic molecule. Theoretical and experimental findings collectively suggest that the newly synthesized energetic compounds offer a viable trade-off between high impact sensitive properties and desirable thermal stabilities.

Table 1. Physical and explosive properties of known energetic compounds and selected cocrystals compared with those of their components

Entry ^a	T _m ^b (°C)	T _d ^c (°C)	ρ ^d (g.cm ⁻³)	D ^e (km.s ⁻¹)	P ^f (GPa)	IS ^g (J)	Ref.
TNT	80	283	1.65	6.88	19.5	15	[3, 24]
TNT: VANT	102	268.3	1.47	5.58	9.55	79.4	[25]
TNT: ATL	103	194	1.52	7.08	18.5	79.4	[20]
TNT: ACR	127	215	1.55	5.87	11.0	89.1	This work
ϵ-CL-20	145	227	2.03	9.40	44.6	4.0	[3, 26]
TNT: CL-20	136	205	1.84	-	-	55	[3]
HMX	-	280	1.91	9.32	39.5	55	[26, 27]
CL-20:HMX	-	235	1.51	9.48	-	55	[27]
BTF	198	289	1.90	8.42	34.3	-	[28]
CL-20:BTF	-	235	1.91	8.96	39.1	-	[28]
NTO	-	271	1.93	8.44	33.0	>40	[29]
TZTN	144	197	1.57	7.27	21.6	6	[29]
NTO:TZTN	157	178	1.66	7.45	23.5	11	[29]
PIC	121	>300	1.81	7.83	27.2	7.4	[30]
PIC: VANT	121.9	231.6	1.51	5.63	1.09	31.6	[25]
PIC:23DAT	58	287	1.56	6.06	14.7	70.8	[31]
PIC:ACR	266.5	319.3	1.60	6.03	12.0	70.8	This work
TATB	350	~360	1.94	8.54	32.1	50	[32]
RDX	205	210	1.80	8.79	34.9	7.5	[32]

^a [Abbreviated compounds] TNT: 2,4,6-trinitrotoluene, VANT: 9-vinylanthracene, ATL: 2,6-diaminotoluene, ACR: acridine, ϵ -CL-20: 2,4,6,8,10,12-hexanitro-2,4,6,8,10,12-hexaazaiso-wurtzitane, HMX: 1,3,5,7-Tetranitro-1,3,5,7-tetrazocane, BTF: benzotrifuroxan, NTO: 3-nitro-1,2,4-triazol-5-one, TZTN: 5,6,7,8-tetrahydrotetrazol[1,5-b][1,2,4]-triazine, PIC: picric acid, 23DAT: 2,3-diaminotoluene, TATB: 2,4,6-triamino-1,3,5-trinitrobenzene, RDX : 1,3,5-Trinitroperhydro-1,3,5-triazine. ^b Melting point. ^c Decomposition temperature (onset). ^d Density. ^e Detonation velocity. ^f Detonation pressure (calculated). ^g Impact sensitivity.

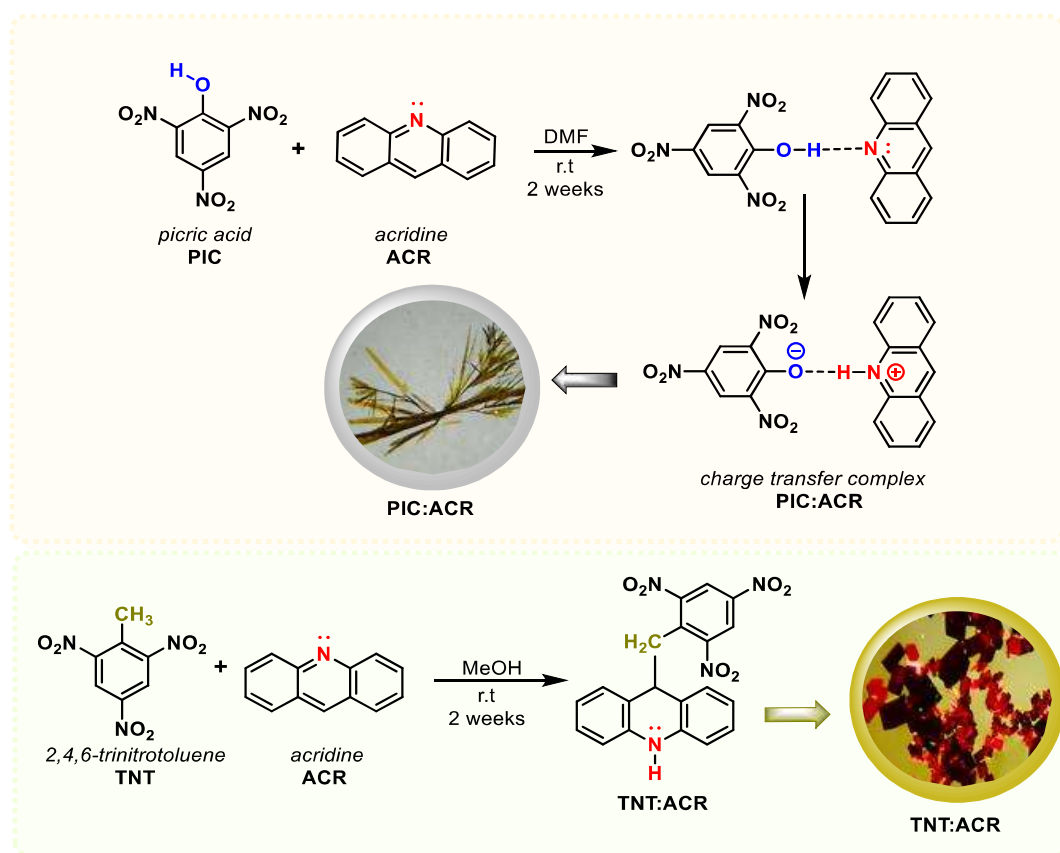
2. Experimental studies

Caution! Although we have had no difficulty handling these EMs, caution and appropriate safety procedures (leather gloves and face protection) are strongly advised! We synthesized all of these EMs on a milligram scale, and none of them exploded or detonated during this experiment. Wear safety shields, safety glasses, face shields, leather gloves, and protective clothing such as leather suits and earplugs.

2.1. Materials and sample preparation

PIC (moistened with water, $\geq 98\%$), ACR (97%) and 2,4-diaminotoluene (97%) were purchased from Sigma-Aldrich. In accordance with the literature, TNT was prepared from 2,4-dinitrotoluene [35]. Slow evaporation of a dimethylformamide (DMF) solution (4 mL) of PIC (93 mg, 1 equiv., at 50 °C) and ACR (71 mg, 1 equiv.) resulted in the formation of single

crystals of the salt (PIC:ACR) (**Scheme 1a**). Slow evaporation of a methanolic solution (4 mL) of TNT (90 mg, 1 equiv., at 70 °C) and ACR (142 mg, ~2 equiv.) resulted in the formation of single crystals of the new organic compound (TNT:ACR) (**Scheme 1b**).



Scheme 1. Synthetic routes and crystal formation of (*top, a*) PIC:ACR' charge-transfer complex and (*bottom, b*) TNT:ACR' host-guest type compound

2.2. Characterisation techniques

2.2.a. Optical Microscopy. Macroscopic images of select salts (PIC:ACR) and crystals (TNT:ACR) were obtained with an optical microscope (Olympus SZH) and camera (Olympus Q-color 3).

2.2.b. Single Crystal X-ray Diffraction (SCXRD). A suitable crystal was selected and mounted on a Mitigen holder in paratone oil on a Rigaku Oxford Diffraction SuperNova diffractometer. The crystal was kept at $T = 120.0$ K during data collection. Using Olex2 [36], the structure was solved with the ShelXT [37] structure solution program, using the intrinsic phasing solution method. The model was refined with version 2017/1 of ShelXL [38] using least squares minimization. Mercury CSD (v. 4.1) software was used to aid in the structural study of the co-crystal [39].

2.2.c. Nuclear Magnetic Resonance Spectroscopy (NMR) spectral studies. ^1H -NMR and ^{13}C -NMR spectra were recorded on a Bruker Ultrashield 300 MHz NMR spectrometer. The solvent was CDCl_3 .

2.2.d. Elemental analysis. C, H, and N elemental analyses were executed on an Elementar Vario Micro Cube instrument.

2.2.e. Infrared (IR) Spectroscopy. The IR spectra were obtained by Fourier transform techniques with a Perkin Elmer Spectrum 65 FT-IR spectrometer with ATR equipment. Each spectrum was acquired across the wavenumber range of 4000–400 cm^{-1} . The resolution ratio was 4 cm^{-1} .

2.2.f. Differential Scanning Calorimetry (DSC). DSC was performed on a NETZSCH STA 449 F1 Differential Scanning Calorimeter. 1.58 mg of sample was placed in an aluminum pan, and the thermal behavior of the samples was studied under a nitrogen purge (30.0 mL/min) at a heating rate of 10 $^{\circ}\text{C}/\text{min}$ over a range of 25–400 $^{\circ}\text{C}$. The TG curves were recorded with a heating rate of 5 $^{\circ}\text{C}/\text{min}$ using the same device operating between ambient and 600 $^{\circ}\text{C}$ under an N_2 atmosphere in Pt pans.

2.2.g. Mass spectrometry (MS). Mass spectra were obtained by a Shimadzu 2010 Plus equipped with a direct inlet (DI) unit and an electron impact ionizer. The DI temperature was changed between 35 and 110 $^{\circ}\text{C}$, and ionization was achieved with 70 electron volts (eV) of electrons. During the ionization interval between 5 and 10 minutes, 10 points were selected to read m/z values.

2.3. Impact sensitivity measurement test

The impact sensitivity was determined by using a BAM fall hammer device (BFH-12). Impact testing was conducted at the Cavendish Laboratory, Cambridge on the TNT, PIC, PIC:ACR, and TNT:ACR. A sample of 40 mm^3 was enclosed in an anvil device consisting of two coaxial steel cylinders. Anvil devices were disposed of along with the sample after the test. A load of 10 kg was dropped onto a sample from heights ranging from 10 cm to 100 cm. The ‘one-in-six’ test procedure was performed to obtain the limiting impact energy for both tested samples. The method conducted throughout is the 30-trial Bruceton method. The results are denoted by the abbreviation H_{50} (cm). The Bruceton analysis also provides a standard deviation (s.d.; on a logarithmic scale, related to the drop height increment) [40, 41].

2.4. Detonation performance analysis

All detonation parameters, such as detonation velocity, pressure, and oxygen balance, presented in this work were calculated using the EXPLO5 software package [42].

2.6. Hirshfeld surface analysis

Hirshfeld surface and 2D fingerprint calculations were calculated with Crystal Explorer software ver. 3.1 [43] on crystal structures imported from CIF files.

3. Theoretical Calculations

3.1. Theoretical calculation of heat of formation (HOF)

In this paper, all ab initio calculations were carried out using the program package Gaussian 09 (Revision-D.01) [44] and visualized by GaussView 5.0.8 [45]. Atomic coordinates were obtained from SCXRD data and used as the initial input data. The hybrid B3LYP density functional, corrected for dispersion interactions via the Grimme GD3 empirical term, with the def2-TVZP basis set in the gas phase, was utilized for these calculations. To determine the formation energy and detonation parameters of the analyzed compounds, enthalpy values in the

gas phase were initially calculated using the complete basis set method (CBS-4M; M refers to the method of using minimum population localization) as implemented in the Gaussian 09 software [46-48].

3.2. Investigation of frontier molecular orbitals (FMOs)

Contour plot visualization and energy value determination of the FMOs were performed using Gaussian 09 outputs obtained from geometry optimization studies carried out by B3LYP-D3/def2-TZVP [49]. Additionally, the FMO, ϵ_{HOMO} , and ϵ_{LUMO} were evaluated for TNT, PIC, ACR, TNT:ACR, and PIC:ACR.

3.3. Visualization of electrostatic potential (ESP) map

In this part, all the ESP surfaces were calculated by the Multiwfn program with the help of $0.001e \text{ Bohr}^{-3}$.

3.4. Reduced density gradient (RDG) analysis

The reduced density gradient (RDG) analysis was performed based on the electron density to further show the intermolecular interactions of the TNT:ACR and PIC:ACR compounds in real space [50, 51]. In the subsequent phase of the computational investigations, the non-covalent interaction (NCI) patterns were examined based on the output data obtained from the geometry optimization studies, carried out using Gaussian 09 at the B3LYP-D3/def2-TZVP level of theory. To achieve this, the Multiwfn software (v.3.8) [52] was employed to generate the essential density gradients. These gradients were subsequently used to develop the demonstration graphs using the VMD (Visual Molecular Dynamics) software (v.1.9.3) [53].

4. Results and Discussion

4.1. Experimental results

4.1.1. Synthesis of PIC:ACR and TNT:ACR

The crystal morphologies are indicated in **Fig. 1**. It can be seen that TNT:ACR crystals are dark red block-shaped crystals (like prism-shaped crystals) (**Fig. 1b**), and PIC:ACR salt crystals are yellow blade-shaped crystals (**Fig. 1d**). Both have a well-defined morphology, a regular structure and, a uniform size. The crystal shapes and colours differ from those of their co-formers (TNT in **Fig. 1a**, PIC in **Fig. 1c**). This difference in morphology shows that TNT:ACR and PIC:ACR crystals can have dissimilar crystal structures to those of their constituent co-formers.

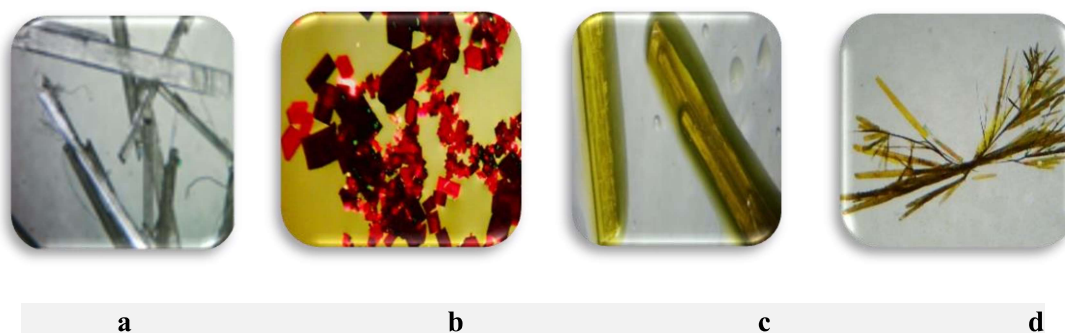


Fig. 1. Microscope images at 50X magnification of a) TNT, b) TNT:ACR, c) PIC, and d) PIC:ACR.

4.1.2. Determination of the PIC:ACR and TNT:ACR's crystal structure

SCXRD Analysis

The crystallographic data collected and the structural refinement results of TNT:ACR and PIC:ACR are summarized in **Table 2**. Cambridge crystallographic data centre under the CCDC numbers 1818116 and 1818115, respectively. ORTEP drawings of TNT:ACR and PIC:ACR are shown in **Figs. 2a-b**. The SCXRD analysis of compounds (TNT:ACR and PIC:ACR) is determined by selecting good-quality crystals of appropriate size ($0.17 \times 0.14 \times 0.10 \text{ mm}^3$ and $0.20 \times 0.11 \times 0.05 \text{ mm}^3$, respectively). There are some differences between TNT:ACR and PIC:ACR; TNT:ACR owns the monoclinic crystal system with the $P2_1/n$ space group and $1.552 \text{ g} \cdot \text{cm}^{-3}$ ($T = 120.0 \text{ K}$) density, while PIC:ACR owns the triclinic crystal system with the $P-1$ space group and $1.598 \text{ g} \cdot \text{cm}^{-3}$ ($T = 120.0 \text{ K}$) density.

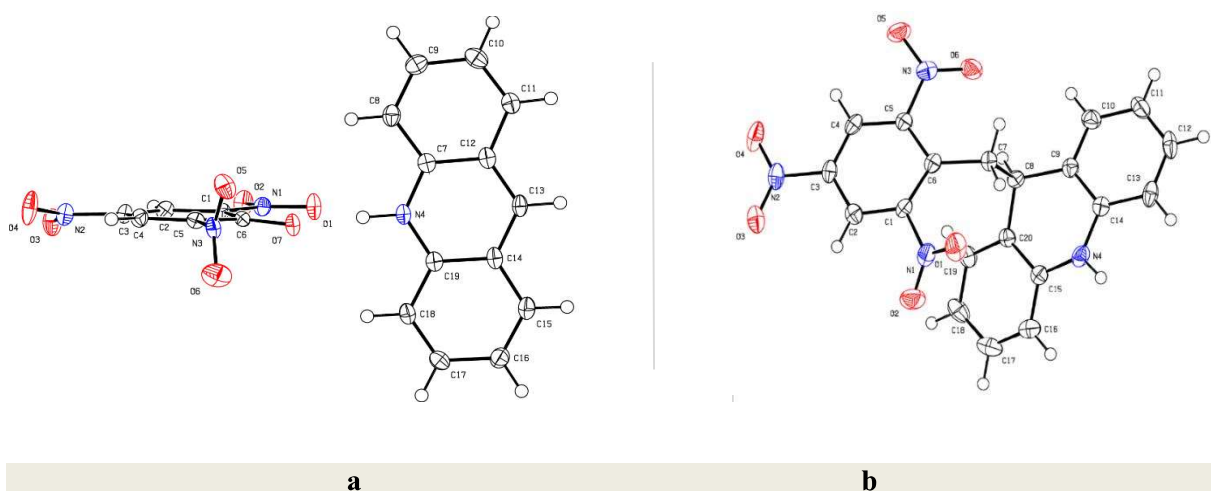


Fig. 2. ORTEP drawing of a) PIC:ACR and b) TNT:ACR (the asymmetric unit of the title compound, showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level).

a) SCXRD Analysis of PIC:ACR

Single yellow plate-shaped crystals of PIC: ACR were re-crystallized from DMF by a slow evaporation method. The ACR molecule is an aromatic amine with a pyridine structure; it has an aqueous pK_a of 5.58 and is a mildly basic substance. The aqueous pK_a value of PIC is 0.38, and it is a strong acid that is present in practically all amphiprotic solvents. Thus, PIC rapidly protonates ACR to form acridinium picrate salt (**Fig. 1a**). When the pK_a values of PIC and ACR are evaluated, it becomes clear that this transfer is possible [54]. The salt of PIC: ACR (acridinium picrate) has an asymmetric unit consisting of one PIC anion (PIC^-) and one ACR cation (ACR^+). The PIC is bonded with ACR by a set of bifurcated intermolecular hydrogen bonds, shown as $\text{N}_4\text{-H}_4 \dots \text{O}_7$ and $\text{N}_4\text{-H}_4 \dots \text{O}_1$ (**Table 3**), leading to a formation of an independent heterodimer (**Fig. 3b**). There is a strong hydrogen bond at the acridinium picrate crystal, that is, the bond between $\text{N}_4\text{-H}_4 \dots \text{O}_7$, and this hydrogen atom is the phenolic hydrogen of PIC, which is already transferred onto the nitrogen atom. Other interactions given in **Table 3** are not hydrogen bonds; they should be considered mandatory interactions that occur without stacking [55]. These interactions are extremely weak due to electrostatic interactions. The moderate π -stacking interaction between the nitro group on the ACR and the neighbouring PIC anion

(centroid to centroid distance of 3.55 Å), as well as that between two adjacent parallel PIC anion (centroid to centroid distance of 3.62 Å) hold the heterodimers together to form a molecular layer (**Fig. 3b**). Based on the NCI calculation results strong hydrogen bonds, Van der Waals and the steric effect have a considerable effect on PIC:ACR formation (**Figs. 14a-b**). N₄-H₄...O₇ interaction is also seen in the IR spectrum. The large peak observed at 2592 cm⁻¹ in the IR spectrum of acridinium picrate in **Fig. 7a** is the stretching vibration of $\nu_{(N-H)}$ in the acridinium cation. At 3200-3400 cm⁻¹, this signal indicates $\nu_{(N-H)}$ stretching vibration. Hydrogen bonds can shift this signal about 1000 cm⁻¹ to the low energy levels [56]. According to DSC curve, PIC:ACR melts at 266°C (T_d (ACR):107°C, T_d (PIC): 122°C). Salt compounds are projected to have a higher melting point and a lower impact sensitivity (safer) [5, 33, 48, 57]. The formation of PIC:ACR was also confirmed by the ¹H-NMR and ¹³C-NMR results (see section 4.1.3., **Fig. S1 and Fig S2**)

Table 2. Crystallographic data and structure refinement parameters for TNT:ACR and PIC:ACR.

	TNT:ACR	PIC:ACR
Empirical formula	C ₂₀ H ₁₄ N ₄ O ₆	C ₁₉ H ₁₂ N ₄ O ₇
ρ_{calc} [g cm ⁻³]	1.552	1.598
m/mm^{-1}	0.118	0.125
Formula weight [g mol⁻¹]	406.35	408.33
Colour	dark red	yellow
Shape	block	plate
Size [mm³]	0.17×0.14×0.10	0.20×0.11×0.05
T[K]	120.0	120.0
Crystal System	monoclinic	triclinic
Space Group	<i>P2₁/n</i>	<i>P</i> -1
<i>a</i>/Å	10.2487(9)	8.1668(6)
<i>b</i>/Å	12.4491(8)	8.5961(7)
<i>c</i>/Å	14.0939(11)	12.9101(10)
<i>a</i>°	90	109.341(7)
<i>b</i>°	104.691(8)	96.105(6)
<i>g</i>°	90	91.543(6)
<i>V</i>[Å³]	1739.4(2)	848.46(12)
<i>Z</i>	4	2
<i>Z'</i>	1	1
Wavelength[Å]	0.71073	0.71073
Radiation type	MoK _α	MoK _α
2θ range for data collection[°]	6.54 to 50.696	6.386to 57.82
<i>Q</i>_{max}[°]	25.348	28.910
Measured Refl.	17747	17282
Independent Refl.	3178	3944
Reflections Used	2692	2856
<i>R</i>_{int}	0.0530	0.0851
Restraints	0	0
Largest Peak	0.286	0.278
Deepest Hole	-0.221	-0.265
GooF	1.257	1.097
Final R indexes [<i>I</i>≥2σ(<i>I</i>)]	R ₁ = 0.0674, wR ₂ = 0.1435	R ₁ = 0.0598, wR ₂ = 0.1164
Final R indexes [all data]	R ₁ = 0.0824, wR ₂ = 0.1493	R ₁ = 0.0913, wR ₂ = 0.1291
CCDC number	1818116	1818115

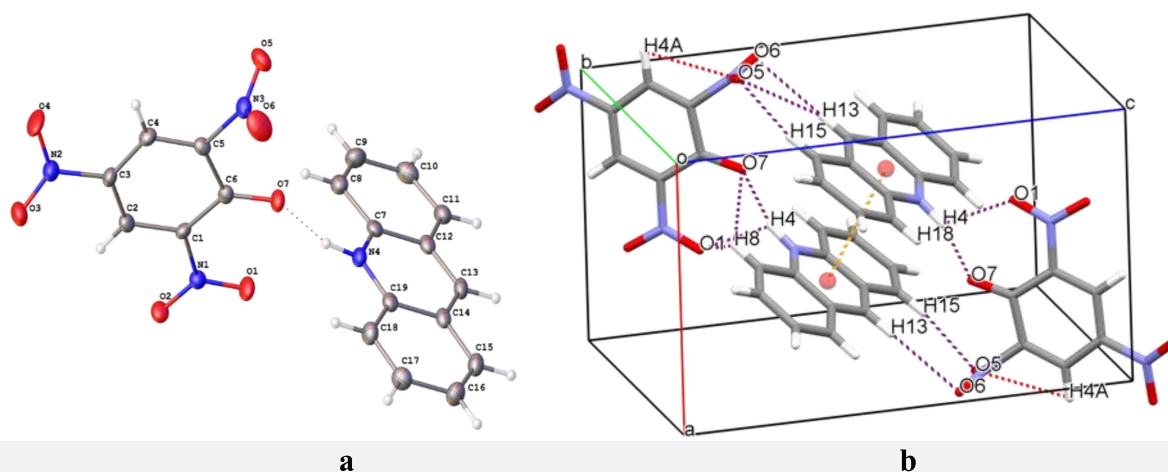


Fig. 3. a) Crystal structures of PIC:ACR and b) Crystal structure in unit cell of PIC:ACR (..... purple and red dashed lines represent intermolecular hydrogen bonds, orange dash lines indicate the π -stacking interactions between neighboring heterodimers).

PIC and ACR rings are almost vertical to each other. The dihedral angle between the planes of the rings in the cation (N4C7C12C13C14C19) and anion (C1C2C3C4C5C6) is 86.62° [41] (**Fig. S3**). Due to this special structural characteristic and the extensive 2D hydrogen bond networks of salt, its crystal packing assembles into a wave-like stacking as shown in **Fig. 4**. The wave-like stacking can usually be seen in those low-sensitivity and highly energetic materials; in this case, the stability of PIC:ACR salt should also be enhanced. It is suggested that these conformers are self-assembled into layers, enhancing the strength of crystal packing as well as the stability of energetic salt [25, 31, 58].

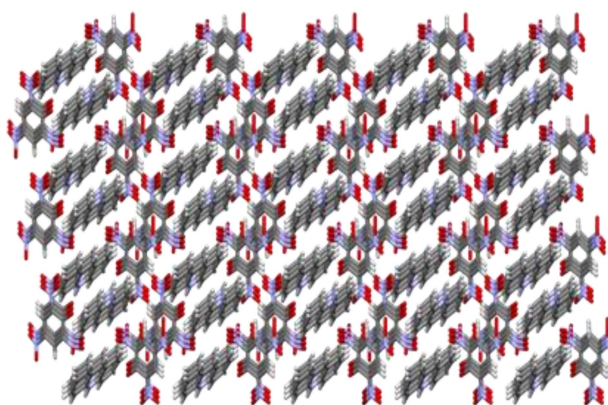


Fig. 4. Wave-like assembly form of energetic ionic salt of PIC:ACR

Table 3. Hydrogen bond geometries for PIC:ACR crystal structures [$\text{\AA}$, $^\circ$].

D (Donor)	H	A (Acceptor)	[ARU] ^a	D-H [$\text{\AA}$]	H...A [$\text{\AA}$]	D...A [$\text{\AA}$]	D-H...A [$^\circ$]
N (4)	H (4)	O (1)	[0]	0.95	2.261	2.815	116.21
N (4)	H (4)	O (7)	[0]	0.95	1.802	2.722	161.15
C (13)	H (13)	O (7)	[1]	0.95	2.818	3.247	108.44
C (13)	H (13)	O (6)	[1]	0.95	2.696	3.639	171.98
C (15)	H (15)	O (5)	[1]	0.95	2.454	3.362	159.81
C (4)	H (4A)	O (2)	[2]	0.95	2.458	3.392	167.50
C (8)	H (8)	O (4)	[3]	0.95	2.72	3.216	135.00
C (10)	H (10)	O (1)	[4]	0.95	2.569	3.407	147.24
C (10)	H (10)	N (1)	[4]	0.95	2.673	3.352	128.97
C (17)	H (17)	O (7)	[5]	0.95	2.777	3.677	158.45
C (15)	H (15)	O (3)	[6]	0.95	2.683	3.340	126.86

^a Translation of ARU-code to CIF and equivalent position code: [0] = x, y, z, [1] = -x+1, -y+1, -z+1, [2] = x+1, +y, +z, [3] = -x+2, -y+1, -z+2, [4] = x, +y+1, +z, [5] = -x+1, -y, -z+1, [6] = x-1, +y, +z-1. **Note 1:** Analysis of Potential Hydrogen Bonds and Schemes with $d(\text{D} \dots \text{A}) < R(\text{D})+R(\text{A})+0.50$, $d(\text{H} \dots \text{A}) < R(\text{H})+R(\text{A})-0.12$ Ang., $\text{D-H} \dots \text{A} > 100.0$ Deg. **Note 2:** *HBs lengths and angles are measured on Mercury 4.1.3 [39].

b) SCXRD Analysis of TNT:ACR

At room temperature, single dark red block-shaped crystals of TNT: ACR were re-crystallized from methanol using the slow evaporation method. The aim of the TNT: ACR study was to prepare a co-crystal based on the $\pi \dots \pi$ interaction between TNT and ACR. Nevertheless, as illustrated in **Fig. 5** and **Scheme 2**, combining these two co-formers results in the synthesis of a new organic molecule. TNT is a good candidate for hyperconjugation, and due to this ability, it is easy for TNT to give a proton out. The toluenic hydrogen atoms of the TNT molecule should behave as an acid. There are numerous examples in the literature that show TNT's acidic behavior [59-62]. As a result of the acidic behavior of TNT, a proton attacked to the basic region of ACR; a nitrogen atom on the ring, and acridinium cation formed (**Scheme 2**). C8 of the acridinium cation turns into a carbenium. The carbanion generated following hyperconjugation attacked this carbenium, resulting in the formation of a new compound, 9 (2,4,6-trinitrobenzyl)-9,10-dihydroacridine. While the ACR compound is an aromatic molecule that is planar, the dihydroacridine ring in TNT: ACR has an arch structure. The middle ring loses its aromatic nature as a result of the creation of one covalent bond (between C8 and C9) (**Fig. 5**).

The piperidine ring is not planar and has a low, deformed half-chair shape. Despite the fact that ACR has an aromatic structure, the middle ring of the ACR changed into an aliphatic form as a result of this addition process. The ring is shaped like an envelope (**Fig. 5**). The reason for such an elongation may lie in the steric effects, i.e., repulsion between the TNT and the ACR ring [63]. In order to verify this synthesis and aliphatic side, the most suitable method is actually the ^1H -NMR and ^{13}C -NMR spectral methods (**Fig. S4** and **Fig. S5**). The formation of the TNT:ACR molecule is confirmed by NMR findings (see section 4.1.3). The toluenic hydrogen atoms of the TNT molecule must behave like acids for this molecule to arise. The unexpected synthesis of TNT:ACR via covalent bond and steric effects between the TNT and ACR rings constitutes a significant milestone in crystal engineering because it is the first occurrence of such a new organic compound.

When **Table 4** is investigated, it is evident that several weak interactions are ($C_4-H_{4A}...O_1$, $C_{10}-H_{10}...O_4$ and $C_{11}-H_{11}...O_6$) are formed (**Fig.6.**). These interactions are extremely weak formed due to only electrostatic interactions. From NCI plots of TNT: ACR, it is clear that steric effects and Van der Waals forces make up a large proportion of intermolecular interactions. In addition, these theoretical calculation results support the experimental findings. TNT: ACR exhibits significant potential to develop energetic–nonenergetic crystals as there are no strong intermolecular HBs in their molecules [64].

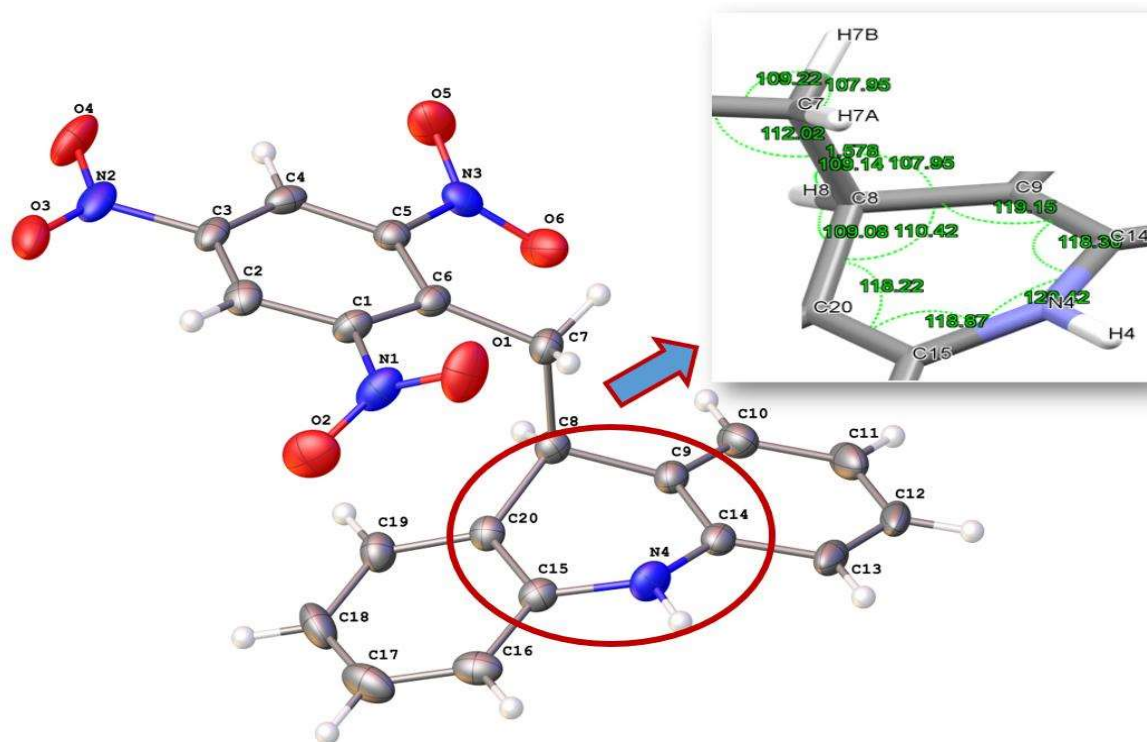
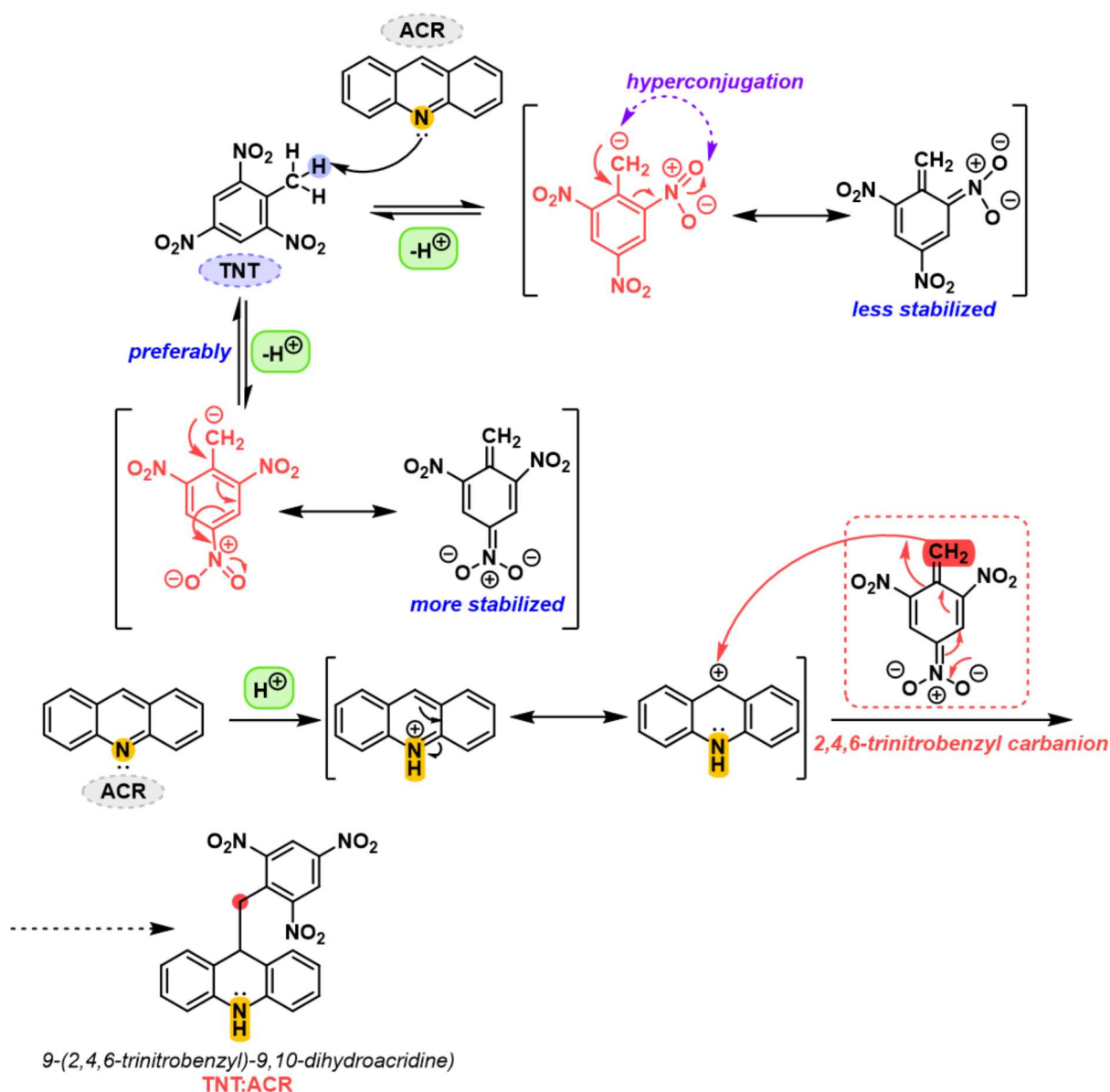


Fig. 5. Crystal structure of TNT:ACR and bond angles of ACR central ring

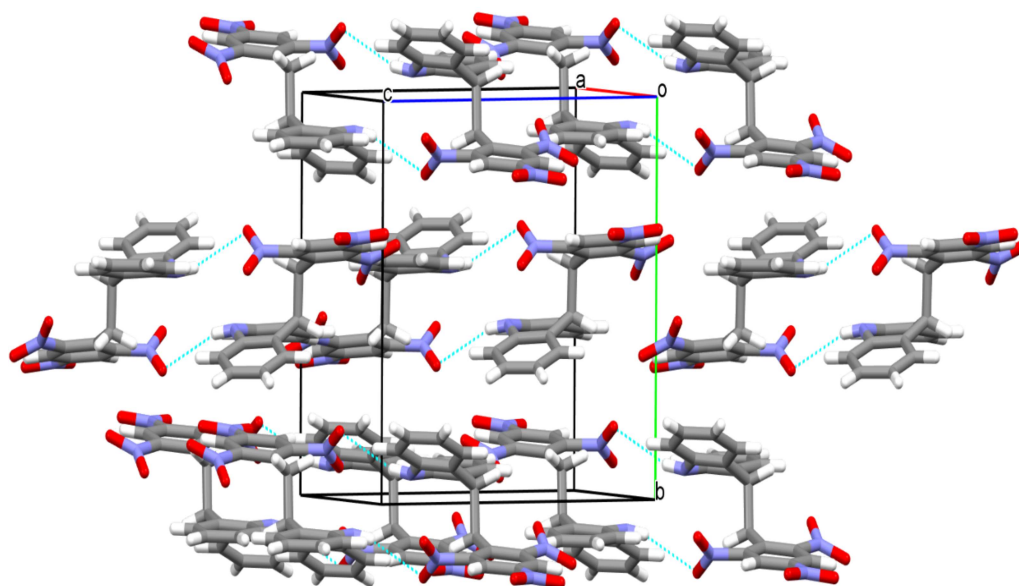


Scheme 2. A plausible mechanism for the formation of TNT:ACR

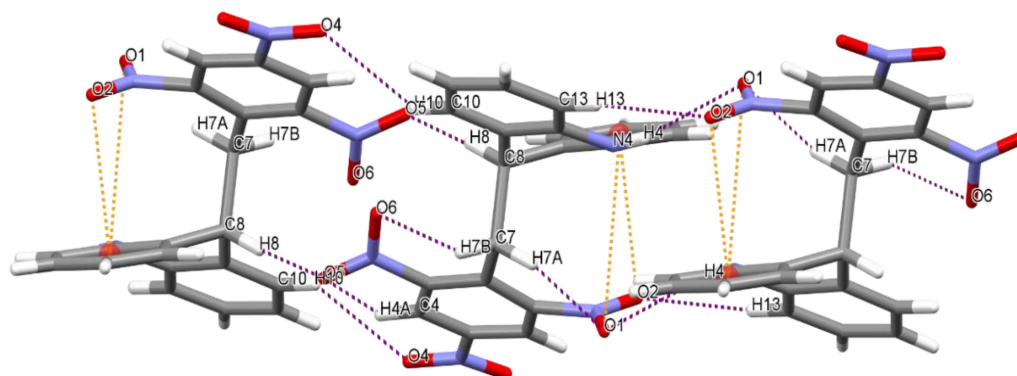
Table 4. Hydrogen bond geometries for TNT:ACR crystal structures [$\text{\AA}$, $^\circ$].

D (Donor)	H	A (Acceptor)	[ARU] ^a	D-H [$\text{\AA}$]	H...A [$\text{\AA}$]	D...A [$\text{\AA}$]	D-H...A [$^\circ$]
C (8)	H (8)	O (6)	[0]	1	2.479	3.005	112.31
C (4)	H (4A)	O (1)	[1]	0.95	2.835	3.574	135.37
C (8)	H (8)	O (5)	[2]	1	2.698	3.635	156.03
C (10)	H (10)	O (4)	[2]	0.95	2.559	3.324	137.75
C (11)	H (11)	O (6)	[3]	0.95	2.544	3.335	140.84
N (4)	H (4)	O (1)	[4]	0.813	2.545	3.321	160.23
C (13)	H (13)	O (2)	[4]	0.95	2.613	3.528	161.74
C (13)	H (18)	O (4)	[5]	0.95	2.451	3.352	158.36

^a Translation of ARU-code to CIF and equivalent position code: [0] = x, y, z, [1] = x+1/2, -y+1/2+1, +z+1/2, [2] = -x+2, -y+1, -z+2, [3] = -x+1, -y+1, -z+2, [4] = -x+1, -y+1, -z+1, [5] = -x+1/2+2, +y-1/2, -z+1/2+1. **Note 1:** Analysis of Potential Hydrogen Bonds and Schemes with d (D... A) < R (D)+R(A) + 0.50, d (H... A) < R(H)+R(A)-0.12 Ang., D-H... A > 100.0 Deg. **Note 2:** *HBs lengths and angles are measured on Mercury 4.1.3 [39].



a



b

Fig. 6. a) Blue dash lines are shown as the intermolecular hydrogen bonds the crystallographic packing behaviors and intermolecular hydrogen bonds b) a view of the layer structure, orange dash lines indicate edge to face T-shaped N-H $\cdots\pi$ interactions between TNT and ACR; Purple dash lines are shown as the intermolecular hydrogen bonds

4.1.3. Nuclear Magnetic Resonance Spectroscopy (NMR) spectral studies

^1H -NMR and ^{13}C -NMR study results of PIC:ACR and TNT:ACR are given below (**Fig.S1**, **Fig. S2**, **Fig. S4**, and **Fig. S5**).

TNT:ACR

^1H -NMR (DMSO *d*₆, d): 9.02 (1H, brs, NH), 8.92 (2H, s), 7.12-7.16 (2H, m), 6.86-6.88 (2H, m), 6.68-6.77 (4H, m), 4.31 (1H, t, $J=7.3$ Hz), 3.33 (2H, d, $J=7.3$ Hz).

^{13}C -NMR (DMSO *d*₆, d): 151.5, 146.3, 140.7, 133.4, 128.3, 128.3, 123.4, 120.7, 120.5, 114.4, 43.8, 35.5.

PIC:ACR

^1H -NMR (DMSO d_6 , d): 7.91 (2H, t, $J=7.6$ Hz), 8.25 (2H, t, $J=7.6$ Hz), 8.32 (2H, d, $J=8.5$ Hz), 8.49 (2H, d, $J=8.5$ Hz), 8.58 (1H, s), 9.89 (1H, brs).

^{13}C -NMR (DMSO d_6 , d): 161.24, 146.98, 142.32, 141.92, 136.83, 130.30, 128.03, 126.44, 125.63, 124.60, 122.16.

4.1.4. Elemental analysis. C, H, and N elemental analyses were executed on an Elemantar Vario Micro Cube instrument. Experimental and calculated results were found to be in agreement with each other (**Table 5**).

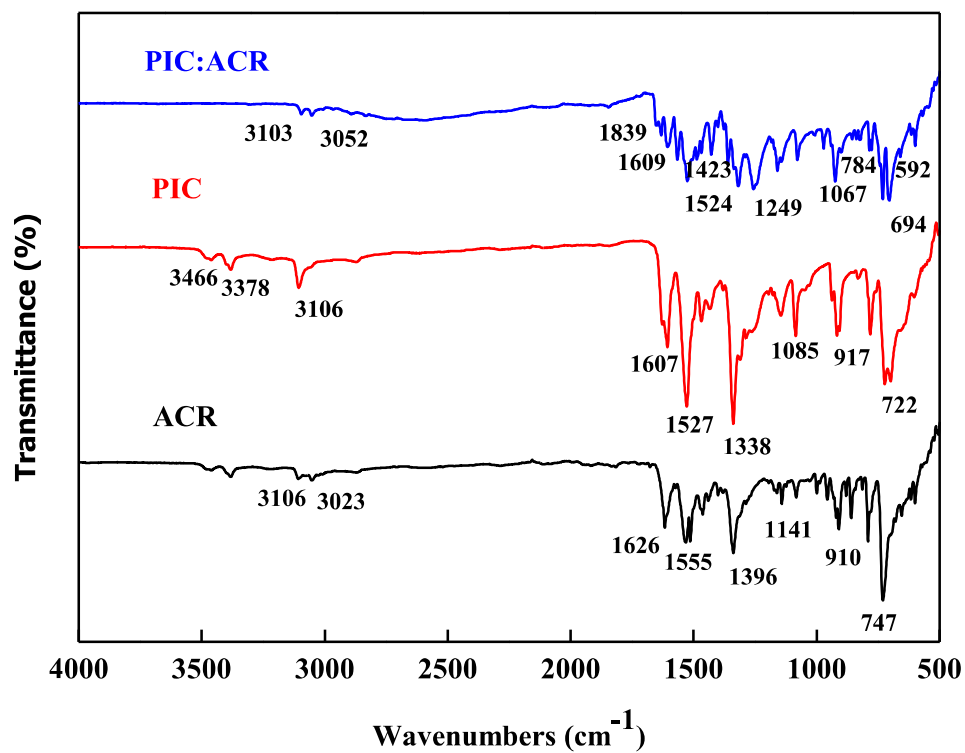
Table 5. Elemental analysis results of PIC:ACR and TNT:ACR

Compounds	Calculated results (%)			Analysis results (%)		
	C	H	N	C	H	N
PIC:ACR	55.89	2.96	13.71	56.17	3.08	13.67
TNT:ACR	59.12	3.47	13.78	59.41	3.38	13.91

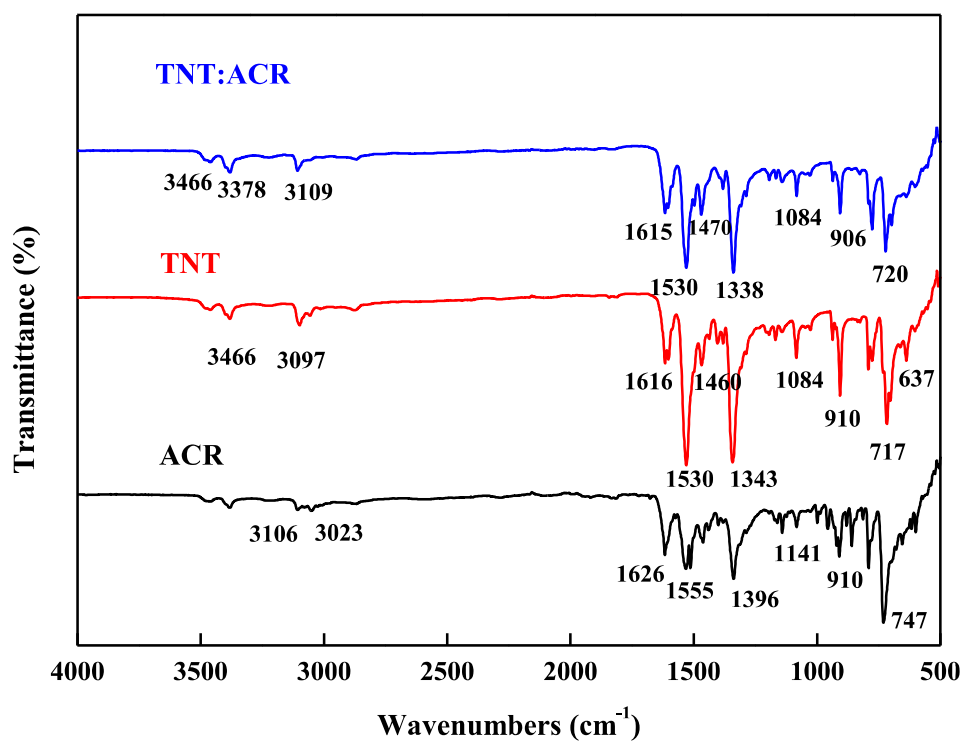
4.1.5. Infrared (IR) Spectroscopy

Stretching vibrations of aromatic hydrogens of ACR and PIC ($\nu_{(\text{C-H})_{(\text{Ar})}}$) provide two weak signals at 3103 and 3052 cm^{-1} . The spectrum shows a broad signal at 2591 cm^{-1} . This signal likely indicates the $\nu_{(\text{N-H})}$ stretching vibration at the acridinium ring. At 3200-3400 cm^{-1} , this signal indicates $\nu_{(\text{N-H})}$ stretching vibration. Hydrogen bonds can shift this signal about 1000 cm^{-1} to the low energy levels [56]. Lower energy level signals are as expected; signals at 1640-1609 cm^{-1} belong to $\nu_{(\text{C=N})}$ stretching at ACR rings, and signals at 1566-1525 cm^{-1} belongs to $\nu_{\text{C=C}}$ aromatic rings. Symmetric and asymmetric vibration bands of the $\nu_{(\text{N=O})}$ ($-\text{NO}_2$) group of PIC:ACR appear at 1318 cm^{-1} and 1524 cm^{-1} respectively, and the signals at 731-734 cm^{-1} are bending vibrations of hydrogens attached to aromatic rings, ($\delta_{(\text{C-H})_{(\text{Ar})}}$) (**Fig. 7a**, PIC: ACR).

Two sharp signals at 3482 and 3368 cm^{-1} show the typical stretching vibrations of $\nu_{(\text{N-H})}$ bonds (**Fig. 7b**, TNT: ACR). Weak signals around 3103 cm^{-1} are also caused by $\nu_{(\text{C-H})_{(\text{Ar})}}$ stretching vibrations. As a difference from the PIC spectrum, an aliphatic $\nu_{(\text{C-H})_{(\text{Aliph})}}$ stretching is observed at 2857 cm^{-1} . The signal at 1525 cm^{-1} represents the aromatic ring deformation stretching $\nu_{(\text{C=C})}$. The 1459 cm^{-1} signal represents the bending and stretching of the aliphatic methylene group. The symmetric and asymmetric vibration bands of the N=O ($-\text{NO}_2$) group of TNT: ACR appear at 1318 cm^{-1} and 1524 cm^{-1} , respectively, whereas the signal at 721 cm^{-1} indicates the bending vibrations of $\nu_{(\text{C-H})_{(\text{Ar})}}$.



a



b

Fig. 7. Comparison of IR patterns for a) TNT: ACR and b) PIC: ACR

4.1.6. Mass spectra (MS) analysis

The fundamental peak, which corresponds to the ACR molecule, can be seen in **Fig. S6** at m/z 179.1 [$C_{13}H_9N$]. Peaks at m/z 89 are the $[C_6H_4CH]^+$ fragment of the ACR. Peaks at m/z 229 and 199 represent PIC; $[C_6H_3N_3O_7]^+$ and $[C_7H_6N_2O_5]^+$. The peak m/z values of the TNT-ACR are 406.1 (molecular peak), 210, 193, 179.1 (base peak), and 89.1. At m/z 179.1 [$C_{13}H_9N$], the basic peak of the ACR molecule can be detected in **Fig. S7** and. Peaks at m/z 89 are the $[C_6H_4CH]^+$ fragment of the ACR. The signal at m/z 316 is most likely the $[C_6H_2(NO_2)_3-CH_2-CH-C_6H_4]^+$ fragment, and the peak at m/z 193 is the $[C_{13}H_9N-CH_2]^+$ fragment from the ACR ring.

4.1.7. Hirshfeld surface analysis

The Crystal Explorer 3.1 software tool was used to thoroughly evaluate the strength and importance of the hydrogen bonds and other intermolecular interactions, as well as their influence on crystal shape, 2D fingerprints, and the corresponding Hirshfeld surface [65]. It was performed in accordance with the guidelines established in the literature and the instances described [66], revealing the presence of the interactions detected by Mercury software [39] and listed in **Table 3** and **Table 4**. The color scale is used to identify the various regions of intermolecular interactions on the Hirshfeld surface. The red, white, and blue colours related to d_{norm} Hirshfeld surfaces are highlighted by the shorter contact, contact around the VdW separation, and longer contacts, respectively. Hirshfeld surface analysis was utilized to investigate all of the intermolecular forces and non-covalent interactions calculated for the TNT:ACR and PIC:ACR crystal structures. The Hirshfeld surface analyses for PIC:ACR and TNT:ACR are indicated in **Fig. 8a** and **Fig. 10a**, which display surfaces that have been mapped over d_{norm} (-0.2086 to 1.2365 $\text{\AA}^\circ$ and -0.2085 to 1.1411 $\text{\AA}^\circ$ for TNT:ACR and PIC:ACR, respectively). The consequences of the information indicated in **Fig. 9a** and **Fig. 11a** can be easily seen in these areas, with significant circular depressions (deep red) visible on the surface indicating strong N-H...O, weak C-H...O interactions. The red colour points in the two-dimensional fingerprint plots are indicative of short contacts for the O...H, H...H, N...H, C...H, O...O, and C...C interactions (**Fig. 9a** and **Fig. 11**), demonstrating their significant roles in the molecular packing of the new compounds. In **Fig. 8b** and **Fig. 10b**, the fingerprint plots show two sharp “tails” corresponding to N-H...O, C-H...O hydrogen bonds extending down to around $d_i=1.05 \text{ \AA}^\circ$, $d_e=1.1 \text{ \AA}^\circ$ for PIC:ACR and $d_i=1.1 \text{ \AA}^\circ$, $d_e=1.1 \text{ \AA}^\circ$ for TNT:ACR. These account for about 26% (H...H) of the total TNT:ACR Hirshfeld surface, whereas PIC:ACR accounts for approximately 16% (H...H) of the total PIC:ACR Hirshfeld surface. The O...H interactions are still the main contribution to the total Hirshfeld surfaces (43% for TNT:ACR and 39% for PIC:ACR) and can be viewed as the “ridge” of the 2-D fingerprint plots, indicated in **Fig. 8c** and **Fig. 10c**. The $\pi \dots \pi$ (C...C) interactions possess a comparable contribution (7% for TNT:ACR and 7% for PIC:ACR) to the total Hirshfeld surface of the compounds, and appear as the large spikes in the middle of the 2-D fingerprint plots. As presented in **Fig.3** and **Fig.6**, strong N-H...O (PIC:ACR) and weak C-H...O (TNT:ACR) interactions were some of the most important intermolecular interactions; this was in good consistent with the Hirshfeld surface calculations and the crystal structure data.

Moreover, O $\cdots$ O interactions make up a large proportion of the intermolecular contacts in the PIC:ACR and TNT:ACR. It can be confirmed from **Figs. 8b-c**, **Fig. 9**, **Figs. 10b-c**, and **Fig. 11**, the contributions of O $\cdots$ O contacts to the Hirshfeld surfaces of PIC:ACR and TNT:ACR found 5%, 3%, respectively. According to studies, the intensity of O $\cdots$ O interactions is inversely related to the intermolecular distance. The distances of intermolecular O $\cdots$ O interactions are typically less than 3.3 Å [67]. It was found that the O $\cdots$ O distances in TNT:ACR were beyond this interaction range (**Fig. S8**). These results suggest that the O $\cdots$ O interactions in the PIC:ACR are weak but numerous (**Fig. S9**). It can be concluded that the O $\cdots$ O interactions contribute more to the stabilization of the TNT:ACR than the PIC:ACR.

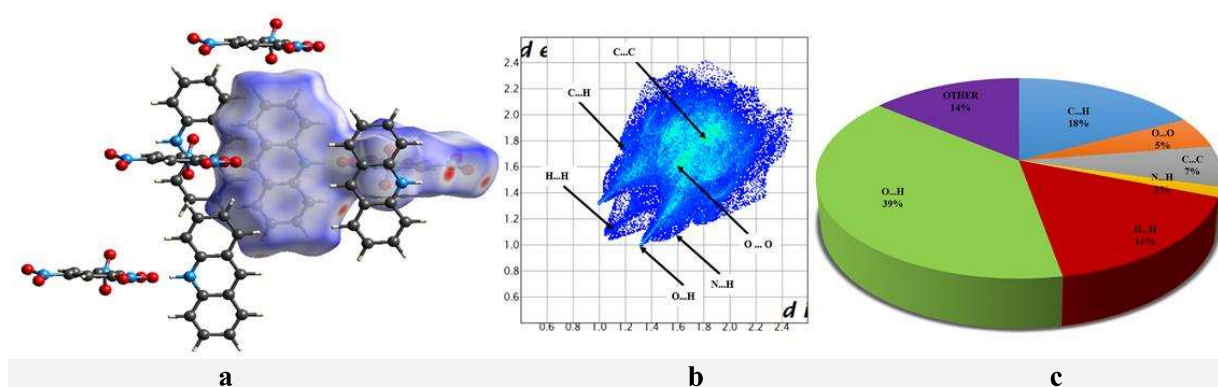


Fig. 8. a) Hirshfeld surface mapped with d_{norm} b) 2D-fingerprint plots c) Populations of close intermolecular and interatomic contacts of PIC:ACR.

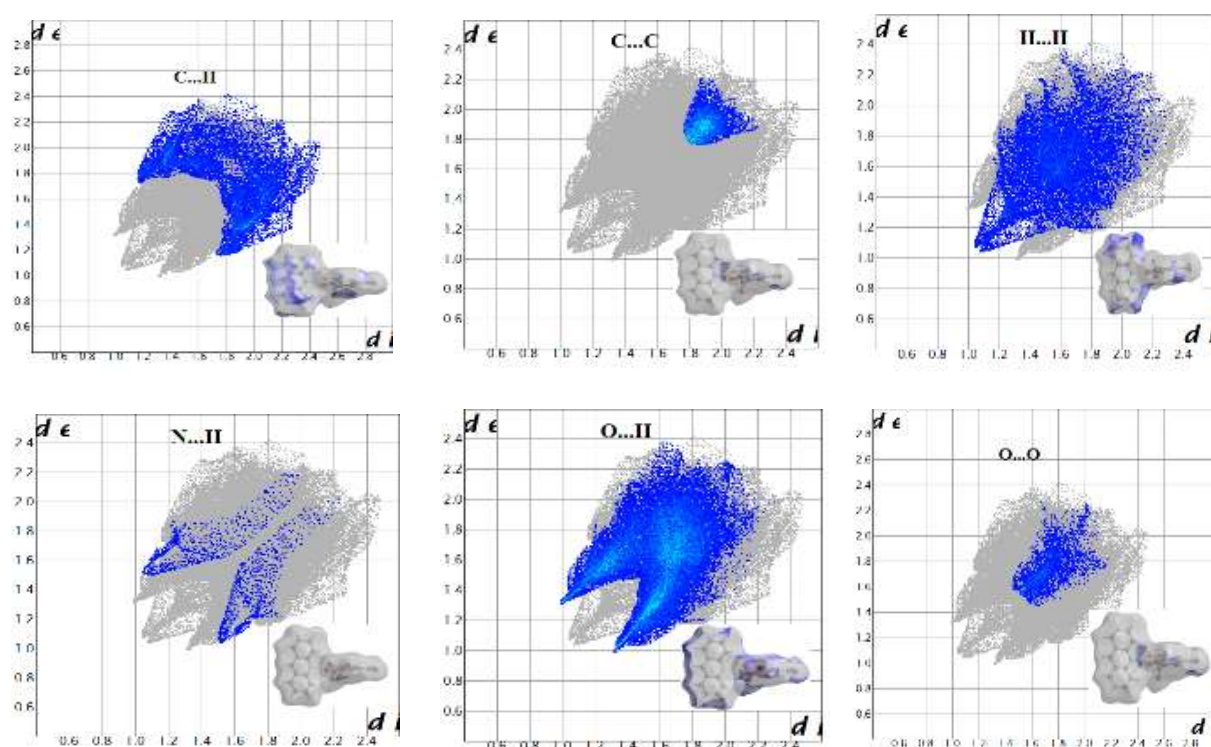


Fig. 9. Two-dimensional fingerprint plots for PIC:ACR, showing contributions from different contacts.

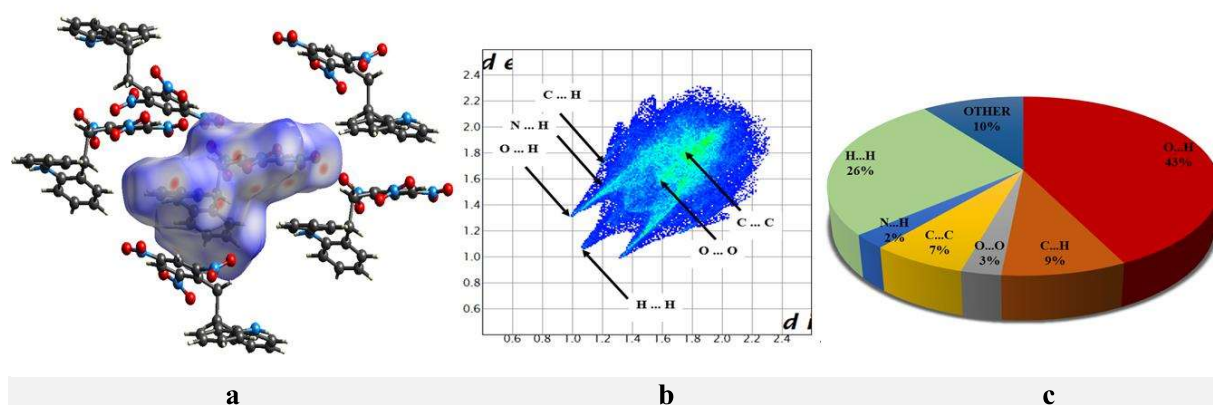


Fig. 10. a) Hirshfeld surface mapped with d_{norm} b) 2D-fingerprint plots c) Populations of close intermolecular and interatomic contacts of TNT:ACR.

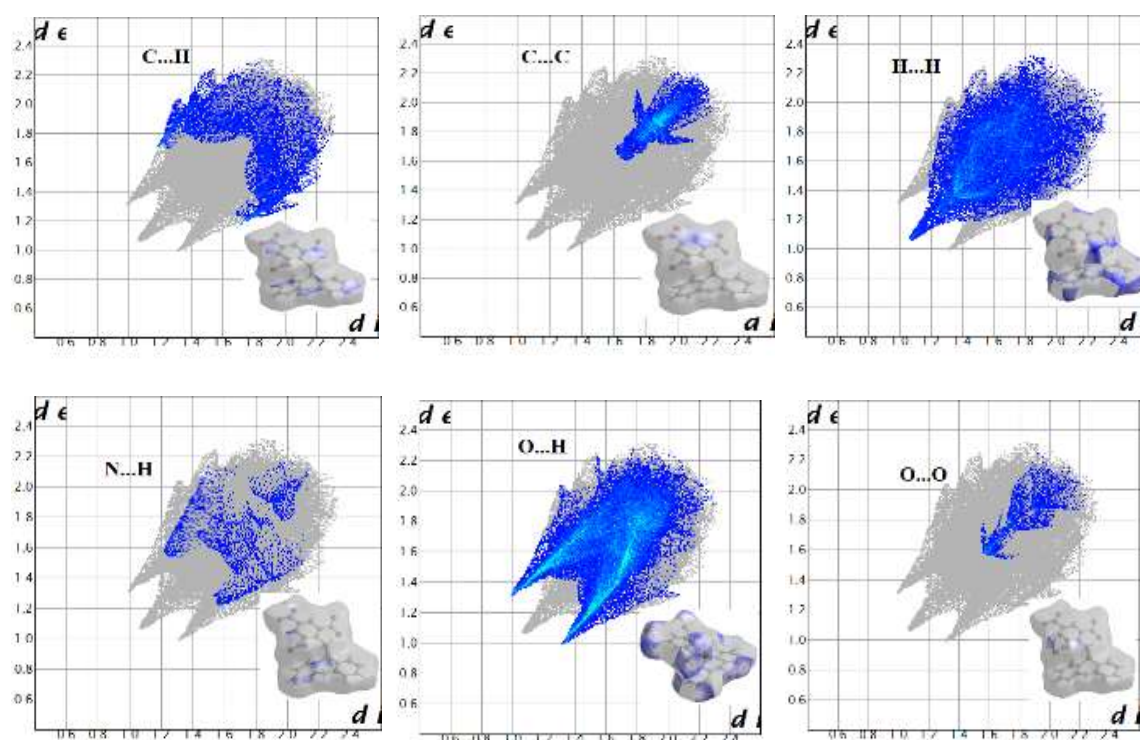


Fig. 11. Two-dimensional fingerprint plots for TNT:ACR, showing contributions from different contacts.

4.1.8. Differential Scanning Calorimetry (DSC)

Thermal stability is a vital factor in EMs since an unacceptable thermal stability noticeably restricts these materials' applications. The endothermic reaction commences at around 266.5 °C, indicating the high purity of PIC:ACR (**Fig.S13**). The melting point and decomposition temperature of PIC:ACR are higher than those of PIC and ACR (**Fig.S10**, **Fig.S12** and **Table 6**). The underlying reason for the higher melting point is unknown, although a reasonable explanation could be the substantial involvement of weak interactions in salt packing [33]. Increasing the melting point can aid in the development of explosives that resist deformation prior to explosion, thereby broadening their uses [68]. The formation of new salt might result in inter-and intramolecular hydrogen bonds, which aid in stabilizing the system. Intermolecular hydrogen bonding has also been shown to improve thermal conductivity, thereby increasing hot spot energy transmission and dissipation [58]. The higher thermal stability and greater

insensitivity may be caused by the strong hydrogen bonds and π - π stacking between cations and anions in the salts [69]. As illustrated by the DSC curve (**Fig. S13**), which features two endothermic and one exothermic TNT: ACR peaks. At the first endotherm, which is 89.9 °C, it is supposed that TNT originated from the impurity. The TNT:ACR crystal was measured at a melting point of 127.6 °C, which is a higher melting point compared to TNT (**Fig. S11 and Table 6**). The melting point is determined by the lattice energy, or the total intermolecular interaction that occurs in a crystal cell [70]. The increase in melting point indicates intermolecular interactions, while the TNT:ACR new compound a formed covalent bond, which led the lattice energy to be much higher than TNT. The unexpected situation here is that the decomposition temperature, i.e., thermal stability, of the TNT:ACR molecule decreases. While the decomposition temperature of the TNT molecule is above 240 °C, the TNT:ACR compound was thermally decomposed at 215 °C. Furthermore, mass losses for PIC:ACR and TNT:ACR were measured to be 77.59 % and 59.92 %, respectively (**Fig. S14-16 and Table 6**).

Table 6. Melting point, decomposition temperature and weight loss of TNT, PIC, ACR, TNT: ACR, and PIC:ACR.

Entry	T _m	T _d	Δ Mass
TNT	80	234	96
PIC	123	260	93
ACR	112	-	-
TNT:ACR	127	215	59
PIC:ACR	266	319	77

T_m: melting point, T_d: decomposition temperature, Δ Mass: weight loss was measured by DSC

4.2. Outputs of the quantum chemical calculations

4.2.1. Theoretical calculation of heat of formation (HOF)

The heat of formation (HOF) is an important parameter to determine the performance of the potent energetic materials, and it can be calculated according to Equation 4.2 [71–73].

$$\Delta H_f^\circ(\text{g}, \text{M}) = H_{(molecule)}^\circ - \Sigma H_{(atoms)}^\circ + \Sigma \Delta H_f^\circ(\text{atoms}) \quad \text{Equation 4.1}$$

where $\Delta H_f^\circ(\text{g}, \text{M})$ represents the enthalpy of formation of the investigated molecule (M) in gas phase; $H_{(molecule)}^\circ$ stands for the calculated enthalpy value of the molecule M with the CBS-4M method (H^{298} in **Table 7**); $\Sigma H_{(atoms)}^\circ$ denotes the summary of calculated enthalpies for the individual atoms (H, C, N, O) and $\Sigma \Delta H_f^\circ(\text{atoms})$ stands for experimental values of the enthalpy of formation (ΔH_f°) for the corresponding atoms H, C, N, and O to be 217.100, 716.682, 472.679, and 249.178 kJ.mol⁻¹, respectively [74]. On the other hand, it is well known that in order to calculate more accurately the detonation properties of TNT: ACR and PIC:ACR, the prediction of the solid-phase heat of formation $\Delta H_f^\circ(\text{s}, \text{M})$ is crucial and it can be done by using Hess's law (**Equation 4.2**) [75, 76].

$$\Delta H_f^\circ(\text{s}, \text{M}) = \Delta H_f^\circ(\text{g}, \text{M}) - \Delta H_f^\circ(\text{sub}, \text{M}) \quad \text{Equation 4.2}$$

where $\Delta H_f^\circ(\text{sub}, \text{M})$ stands for the heat of sublimation which can be calculated by using the Trouton's rule 1 (**Equation 4.3**)

$$\Delta H_f^\circ(\text{sub}) \approx 0.188 \cdot T_m \text{ (kJ.mol}^{-1}\text{K}^{-1}) \quad \text{Equation 4.3}$$

where T_m represents melting points of compounds [77].

Table 7. Calculated $\Delta H_f^\circ(\text{sub}, \text{M})$, $\Delta H_f^\circ(\text{s}, \text{M})$, and $\Delta H_f^\circ(\text{g}, \text{M})$ values of investigated compounds

Compound	Gas phase	Solid phase	
	$-\Delta H_f^\circ(\text{g}, \text{M})$	$-\Delta H_f^\circ(\text{s}, \text{M})$	$\Delta H_f^\circ(\text{sub}, \text{M})$
PIC:ACR	34	134	101
TNT:ACR	123	198	75.2

$\Delta H_f^\circ(\text{g}, \text{M})$ gas-state heat of formation [kJ.mol⁻¹] was calculated by using Equation 4.1

$\Delta H_f^\circ(\text{s}, \text{M})$ solid-state heat of formation [kJ.mol⁻¹] was calculated by using Equation 4.2

$\Delta H_f^\circ(\text{sub}, \text{M})$ sublimation of enthalpy [kJ.mol⁻¹] was calculated by using Equation 4.3

4.2.2. Frontier molecular orbital (FMO) analysis

Molecular orbital analysis, which is commonly employed in chemical reactions, can provide useful information about the electronic structure. The ability to donate electrons is defined by the eigenvalue of the highest occupied molecular orbital (HOMO), and the ability to accept electrons is defined by the eigenvalue of the lowest unoccupied molecular orbital (LUMO). The energy gap (ΔE), which is the difference between HOMO and LUMO, provides detailed information on the wavelength that a molecule can absorb and indicates the ability of electrons to transition from occupied to unoccupied orbitals. The calculated HOMO and LUMO energies and the energy gaps ($\Delta E_{(\text{LUMO-HOMO})}$) are shown in **Table 8**. The energy gap between HOMO and LUMO is related to a molecule's kinetic stability, chemical reactivity, and optical polarizability. According to certain research on the excitonic mechanism of detonation initiation, pressure inside the impact wave front enhances the HOMO $\rightarrow$ LUMO transition within a molecule [77, 78]. The smaller the energy gap, the easier is HOMO $\rightarrow$ LUMO electron transfer, the shorter the wavelength required for electronic excitation, and the easier is explosive decomposition of the EMs.

The HOMO energy levels of TNT, ACR, PIC:ACR are elevated, while the $\Delta E_{(\text{LUMO-HOMO})}$ energy differences (PIC= 4.52, TNT=3.98, ACR= 3.58, PIC:ACR=2.08, and TNT:ACR=2.10 eV) are reduced (**Fig.12** and **Table 8**). The smaller $\Delta E_{(\text{LUMO-HOMO})}$ value for this difference in PIC: ACR makes it more sensitive than TNT:ACR. BAM fall hammer experimental values verify this conclusion.

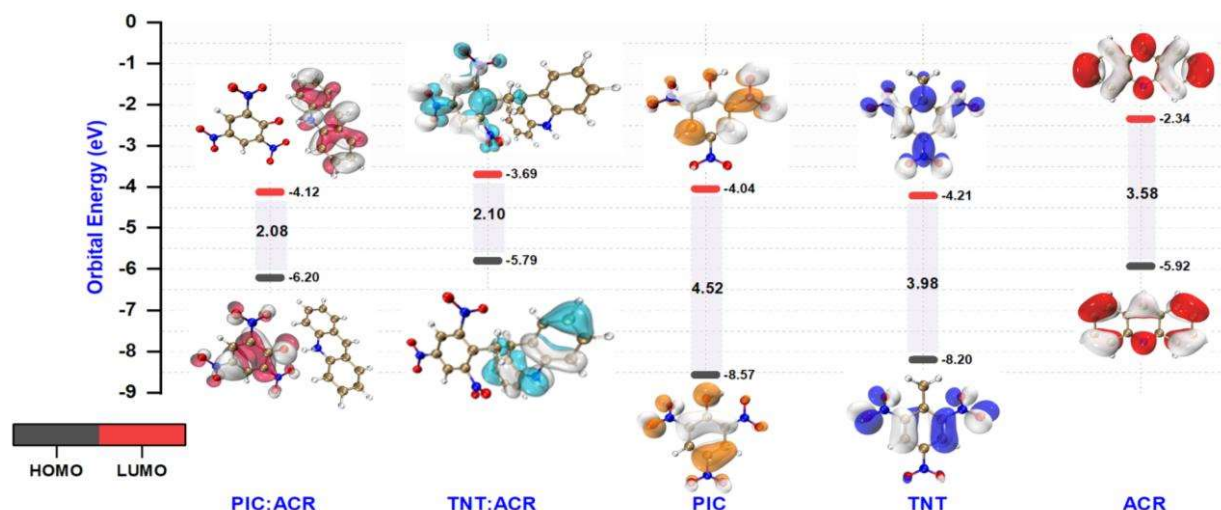


Fig. 12. Frontier orbital energy values and corresponding contour plots of PIC, TNT, ACR, PIC:ACR, and TNT:ACR.

Table 8. Optimization parameters found with the help of algorithms in Gaussian 09 using DFT/ B3LYP-D3/def2-TZVP

	PIC:ACR	TNT:ACR	PIC	TNT	ACR
Empirical formula	C ₁₉ H ₁₂ N ₄ O ₇	C ₂₀ H ₁₄ N ₄ O ₆	C ₆ H ₃ N ₃ O ₇	C ₇ H ₅ N ₃ O ₆	C ₁₃ H ₉ N
E (au)	-920.649	-884.705	-921.362	-885.433	-555.785
E_{HOMO} (eV)	-6.204	-5.788	-8.565	-8.197	-5.923
E_{LUMO} (eV)	-4.124	-3.691	-4.042	-4.212	-2.342
ΔE_{LUMO-HOMO} (eV)	2.080	2.097	4.523	3.985	3.581
μ (D, Debye)	18.234	3.799	1.483	1.135	1.989

4.2.3. Electrostatic potential (ESP) maps

Electrostatic potential (ESP) maps are extensively used to estimate a molecule's total charge distribution across the isodensity surface, with different colours corresponding to positive and negative electrostatic potential regions. Intermolecular interactions between the maximum and minimum locations on ESP maps that are strong and complimentary could favour the co-crystallization process [80]. The ESP mapped surfaces and the surface areas of the PIC, TNT, ACR, TNT:ACR, PIC:ACR are indicated in **Fig. 13**, where important surface local minimum and maximum of ESP are showed in blue and red, respectively. It can be seen from **Fig. 13** that the strongly positive ESPs distribute in the central regions of the TNT and PIC, whereas ACR had a negative ESP. Besides, the negative ones concentrate on the edges of the TNT, PIC molecules, especially on the oxygen atoms of nitro groups. The nitro group of the TNT and PIC molecules has more negative potential than the nitro group of the TNT:ACR and PIC:ACR molecules. This will cause variations in the ESP distribution in different crystals. As shown in **Fig. 13**, the ESPs of the TNT:ACR and PIC:ACR distribute unevenly compared with the pure crystals. The TNT:ACR and PIC:ACR have a more positive ESP, whereas the TNT and PIC have a more negative ESP. It is noteworthy to note that the connections TNT:ACR and PIC:ACR are colored white, indicating that the electrical charges are neutral and that significant intermolecular interactions might be predicted. It was first suggested by Politzer et al. [81] and comprehensively developed by later researchers [82, 83] that the impact sensitivities of explosives are increased by the presence of strongly positive surface potential maxima and by

high degrees of internal charge separation. As expected, the global $V_{s,max}$ of TNT:ACR (66.87 kcal mol⁻¹) and PIC:ACR (61.22 kcal mol⁻¹) are lower than that of pure TNT (60.53 kcal mol⁻¹) and PIC (51.23 kcal mol⁻¹), indicating that the impact sensitivity of ACR molecules is reduced in the two compounds. The result is dramatic as a unique example of the formation of TNT:ACR and PIC:ACR with higher sensitivity (safer) than the pure components. The mapped ESP results imply that TNT:ACR (h_{50} =89.1 cm), PIC:ACR (70.8 cm) is less sensitive than TNT (h_{50} =25.1 cm), PIC (15.1 cm) by impact. It is consistent with the experimental results, demonstrating once more that electrostatic potential is a reliable criterion for assessing the impact sensitivity of explosives.

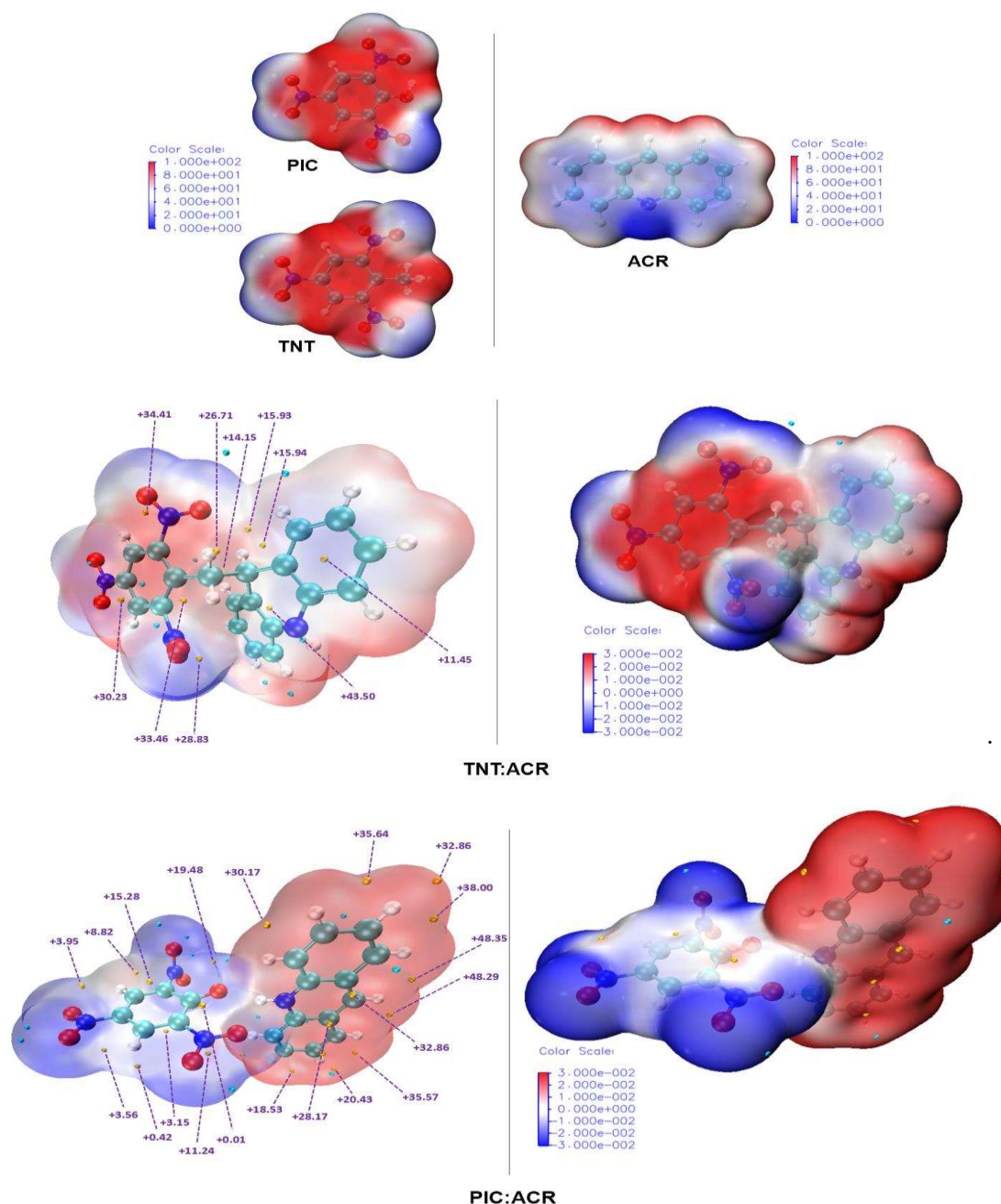


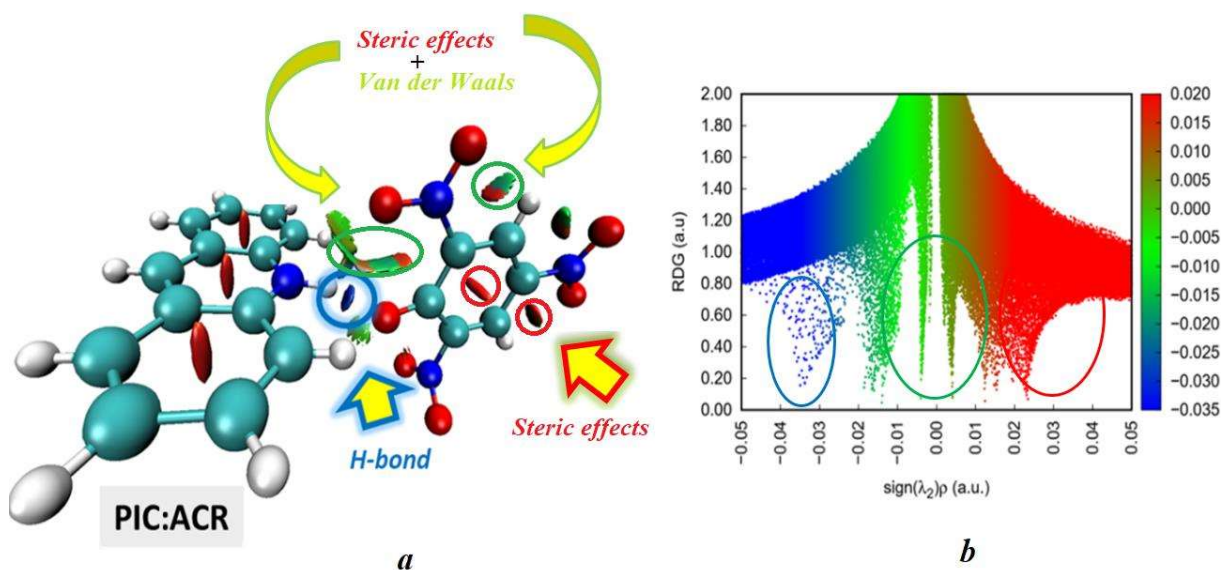
Fig.13. Electrostatic potential surfaces representing charge density distributions of PIC, TNT, ACR, TNT:ACR, PIC:ACR [B3LYP-D3/def2-TZVP]. Prominent surface local maxima of the electrostatic potential (ESP) are depicted as orange spheres, with corresponding values indicated in red text. The units for these values are in kcal.mol⁻¹, and the associated counter surfaces are based on the Van der Waals surface with an isodensity of 0.001e/Bohr³

4.2.4. Non-covalent interaction (NCI) plots

To further reveal the intermolecular interactions of the TNT:ACR and PIC:ACR crystals in real space, a reduced density gradient (RDG) analysis was carried out based on the electron density. RDG is powerful in detecting non-covalent interactions (NCIs), which can also provide valuable information in terms of the origin of molecular transformation, crystal packing, and stability [84–86]. There are a few spikes in the RDG maps. Blue represents strong attractive interactions (HBs), and red indicates substantial non-bonded overlap [steric repulsion stacking (SRs) in the middle of a molecule]. Also, green indicates weak vdW (Van der Waals) interactions (**Figs. 16b, d, e**). In each region, more scatter points indicate stronger electron density, i.e., a greater contribution to the total interactions. Furthermore, the strength of intermolecular interaction has a positive correlation with the electron density in the corresponding region. The bigger the intermolecular connection in each location, the higher the electron density.

Firstly, we investigate the case with ρ ranging from -0.04 to -0.03 a.u., which corresponds to the strong HBs region (**Figs. 14a-b**). It is clear that the crystal structure of PIC:ACR salt is formed by interactions involving $N_4-H_4...O_7$ and $N_4-H_4...O_1$. There are many weak NCIs propagating through the crystal, and large area of green (-0.01 to 0.01 a.u.) appear between PIC and ACR molecules. Then, turning to the v dW interaction region with ρ ranging from -0.02 to 0.005 a.u., it is seen that three possesses stronger spikes and more points, indicating notable v dW interactions (**Figs. 14a-b**). However, as can be seen from **Figs. 14a-b**, the scatter points and the electron density of PIC:ACR in the steric region (ρ ranging from 0.01 to 0.03 a.u.) are seen two possesses stronger spikes and more points, indicating notable SRs interactions. It is straight forward to conclude that the strong hydrogen bonding, vdW forces and steric effects make up a large proportion of PIC:ACR intermolecular interactions.

There are many weak NCIs interactions propagating through the crystal, and a large area of green (ρ ranging from -0.02 to 0.005 a.u.) appears on the TNT:ACR molecule (**Fig. 14d**). We can see easily that there are no strong HBs in the TNT:ACR molecule (**Figs. 14c-d**). Finally, we can conclude that it is possible to develop EMs from "energetic non-energetic co-crystals", since this does not necessarily require relatively strong interactions (strong HBs) in co-crystal design [87].



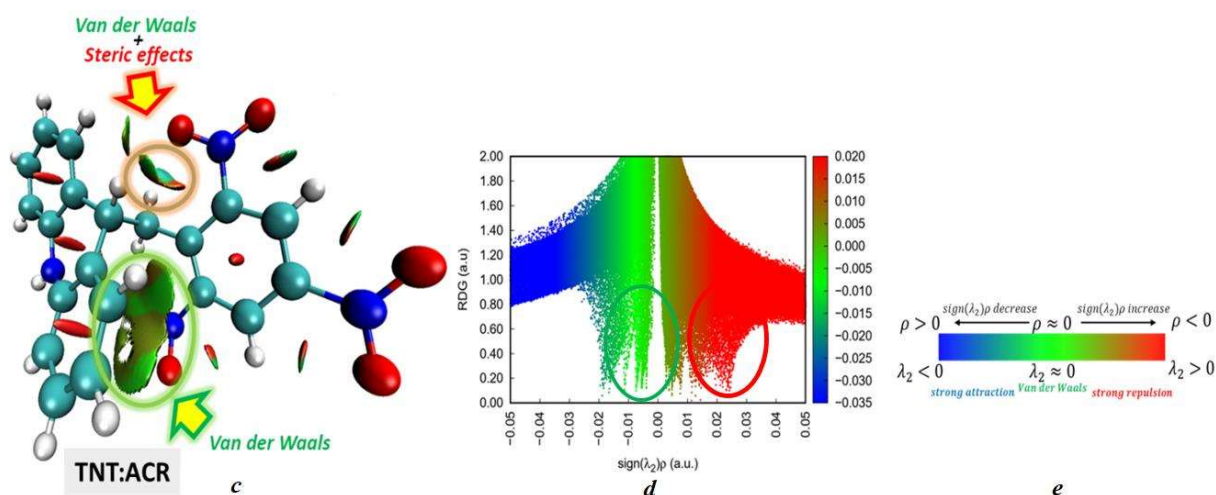


Fig. 14. NCI plots of (a) PIC:ACR and (d) TNT:ACR from different perspectives. Representative plot of reduced density gradient (RDG) vs. sign of the second Hessian eigenvalue ($\text{sign}(\lambda_2)$) multiplied by the electron density (ρ).

4.2.5. Evaluations of Explosive Parameters

Sensitivity is governed by various factors, including the physical, molecular, and crystal properties of the material, the nature of external stimuli, and environmental circumstances. We will assess the data in five categories in this study: intermolecular O...O interactions, crystal-packing effect, molecular electrostatic potentials, BAM fall hammer testing, and free space in the crystal lattice.

a) Intermolecular O...O interactions

We investigated the O...O interactions to understand the precise cause of the disparity in sensitivity between two crystals whose molecular structures are almost similar. Obviously, the intermolecular O...O interactions become of interest since the intermolecular contacts occur through the O...O contacts. The O...O interaction percentages of TNT: ACR and PIC: ACR compounds were calculated as 3% and 5%, respectively (**Fig.8c** and **Fig.10c**). It indicates that TNT:ACR could be more sensitive than PIC:ACR. The decrease in O...O interactions makes the molecule more insensitive (safer). In addition, the results were found to be consistent with the impact sensitivity results.

b) Impact sensitivity

The impact sensitivity of an EMs is highly dependent on its chemical and physical properties. A 10 kg drop weight was used in the BAM fall hammer equipment, and the outcomes are listed in Table 7. The h_{50} values of TNT, PIC, TNT:ACR, and PIC:ACR were found to be 25.1 cm (impact energy 25.1 J), 15.8 cm (impact energy 15.8 J), 89.1 cm (impact energy 89.1 J), and 70.8 cm (impact energy 70.8 J), respectively. The result further indicates that TNT:ACR and PIC:ACR have impact sensitivity superior to that of TNT, PIC, and low-sensitivity explosives. The impact sensitivity of energetic compounds was reduced by the formation of a new salt and a new organic matter.

c) Free space in the crystal lattice and packing coefficient

The free space, i.e., voids, and packing coefficient values of TNT, PIC, TNT:ACR, and PIC:ACR were calculated using Mercury CSD Ver. 4.1 [39]. Though TNT:ACR and PIC:ACR are not denser than TNT and PIC, the formation of novel chemicals increased the packing coefficient and voids. These two newly formed compounds also emphasize the possibility of higher free volumes in solid forms using ACR and other EMs (Table 9). Furthermore, higher compactness implies less free volume in the crystal, which favors molecular degradation and hotspot formation, contributing to greater insensitivity [58, 88, 89]. According to Table 9 and Fig. S17 and Fig. S18, the calculated free space values are consistent with the impact sensitivity, indicating that TNT:ACR and PIC:ACR are less sensitive than PIC and TNT.

Table 9. Comparison of the packing coefficient and free space of the unit cell of the PIC, PIC:ACR, TNT, and TNT:ACR.

Compound	ρ [g.cm ⁻³]	Packing Coefficient [%]	Free space ,voids [%]	Impact sensitivity [J]
PIC	1.81	71.7	11.6	15.8
PIC:ACR	1.6	74.2	11.2	70.8
TNT	1.7	72.1	13.1	25.1
TNT:ACR	1.55	73.1	12.9	89.1

ρ , density was calculated by using SCXRD data

Packing coefficient and free space were calculated by using SCXRD data

Impact sensitivity was measured by using BAM fall hammer method

PIC and TNT data were taken from CCDC data base and calculated by using SCXRD data

d) Calculation of detonation velocity, pressure, and oxygen balance

All detonation parameters calculated using using the program EXPLO5 V6.0. The software is based on the chemical equilibrium, steady-state model of detonation, and uses the Becker-Kistiakowsky-Wilson (BKW) equation of state for solid carbon [42]. The detonation parameters were calculated at the CJ (Chapman-Jouguet condition) point, which is found from the Hugoniot curve of the system by its first derivative. For EXPLO5 calculations, the following set of BKW EOS parameters was used: $\alpha=0.5$, $\beta=0.38$, $\kappa=9.32$, $\theta=4120$ [42]. The main detonation products were assumed to be CO, CO₂, N₂, H₂O, and H₂. (Fig.8S (a), (b)). Calculated gas phase and solid phase enthalpies, oxygen balance, density, detonation velocity and detonation pressure values are listed in Table 10 and Fig. S19- S24. Furthermore, compared to the gas phase, detonation velocity and pressure of PIC, PIC:ACR, TNT, and TNT:ACR were computed using solid phase ΔH°_f (s,M) utilizing EXPLO5 software. As stated in the literature, nearly identical results have been obtained [76].

Table 10. Comparison of explosive properties using gas phase and solid phase enthalpies of formation

Component	Ω	ρ	IS	Solid phase			Gas phase		
				$-\Delta H^{\circ}f$ (s,M)	D	P	$-\Delta H^{\circ}f$ (g,M)	D	P
PIC	-45	1.7	7.4 ^a	226 ^b	7.2	21	216 ^c	7.4 ^c	23 ^c
PIC:ACR	-144	1.6	70 ^d	134	5.8	11	34	6.0	12
TNT	-73	1.65	15 ^a	83 ^b	6.7	18	80 ^c	6.8 ^c	19 ^c
TNT:ACR	-161	1.5	89 ^d	198	5.3	8.5	123	5.8	11

Ω [%], oxygen balance; D, detonation velocity [km. s⁻¹]; P, detonation pressure [GPa] were calculated by using EXPLO5 V6.03

ρ , density [g.cm⁻³] was calculated by using SCXRD data

IS^a, impact sensitivity [J] of PIC and TNT were obtained from literature [30] and IS^d was measured by using BAM method

$\Delta H^{\circ}f$ (s,M)^b solid-phase heat of formation [kJ.mol⁻¹] of PIC and TNT were obtained from literature [90] and D, P were calculated by using EXPLO5 V6.03

$\Delta H^{\circ}f$ (sub,M)^c gas-phase heat of formation [kJ.mol⁻¹] and D, P of PIC and TNT were obtained from literature [91]

Conclusion

The attempted crystallization between two EMs (TNT, PIC) and one coformer (ACR) produced a new solid (new organic compound and salt), which were further confirmed through SCXRD characterization. The structures of TNT:ACR and PIC:ACR were detailed characterized through IR spectroscopy, ¹H-NMR and ¹³C-NMR, Elemental analysis, MS, and DSC. The development of new organic compound and salt documents that covalent interactions, noncovalent interactions, such as hydrogen bond (HB), π stacking, van der Waals forces, and steric and electrostatic interactions, are an important factor that affects the structure of the formed organic compound and salt and serves as the main driving force for stabilizing their structures. The experimental and theoretical results were found to be mutually compatible. The new EMs, TNT:ACR and PIC:ACR features has found excellent impact sensitivity (IS = 89.1 J; IS = 70.8 J) and moderate detonation performance (Dv= 5.87 km.s⁻¹, P= 11.01 GPa; Dv= 6.03 km.s⁻¹, P= 12.08 GPa;) than TNT and PIC, which suggest its potential as an insensitive explosive. The DSC results revealed that newly formed PIC:ACR and TNT:ACR compounds exhibit excellent thermal stabilities with decomposition temperatures (m.p= 266.5 °C; Td (onset)= 319.3 °C and m.p= 127.6 °C; Td (onset)= 215 °C), demonstrating that salt formation and crystallization are two strategies to modulate the thermal stability and the coformers play a vital role in the performance of the target products. The novel compounds' modest detonation velocity and good thermal stability highlight not only their potential applicability as a high-performance secondary explosive, but also the efficacy of our innovative approach for designing and synthesizing high-performance insensitive energetic materials. We believe that the findings of this work will serve as a forerunner of future advancement in the field of rational EMs design.

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