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Synthesis, structure characterization, Hirshfeld surface analysis, and computational studies of 3-nitro-1,2,4-triazol-5-one (NTO): Acridine

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Abstract

To modify the physical features and extend applications of the 3-nitro-1,2,4-triazol-5-one (NTO), we synthesized NTO with acridine (ACR) at a molar ratio of 1:1, a neutralization reaction. Through altering the chemical composition, it was possible to alter physical properties such as thermal stability, free space (voids), packing coefficient, crystal density, difference in pKa of co-formers, morphology, solubility, impact sensitivity, and calculated detonation parameters. It appears that physical attributes could be entirely altered. Single-crystal and powder X-ray diffraction methods, infrared spectroscopy, mass spectrometry, nuclear magnetic resonance spectroscopy (^{1}H-NMR and ^{13}C-NMR), and thermal analysis were utilized to comprehensively characterize and confirm the formation of the structure of NTO: ACR. The substantial hydrogen bond interactions and planar layered structures observed between the cations and anions generated a complex 3D network, providing insight into the structure-property interrelationship. One intriguing feature discovered is the layered structure present in NTO:ACR, which may be responsible for the low impact sensitivity. According to the experimental results, NTO: ACR showed good thermal stability (Td = 229 °C) and outstanding impact sensitivity (IS = 100 J). Detonation velocity and pressure, were calculated using the EXPLO5 software program and found to be 7006 m·s^{-1}, 20.02 G Pa, respectively.

Keywords: Energetic salts, 3-nitro-1,2,4-triazol-5-one, Acridine, Non-covalent interactions, NTO

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1. Introduction

Energetic materials (EMs) include explosives, propellants, and pyrotechnics, are described as those that produce a substantial quantity of heat and/or gaseous products being stimulated by heat, impact, shock, spark, and so on. EMs's widely employed in military and civilian applications including weapons, mining, quarrying, demolition, emergency signalling, breathing device, vehicle safety, space exploration, and entertainment **[1-3]**. Significant efforts are being made to create high-performance EMs that have not merely outstanding in their combustion and detonation properties, high densities, and positive oxygen balances, but also have good thermal stability, sensitivity to external forces, low-cost synthesis, safe handling, and good environmental compatibility. **[4-7]**. Despite an almost 1200-year existence, they have gradually progressed in terms of detonation power as a basic feature. For instance, during the previous century, the detonation velocity of TNT (2,4,6-trinitrotoluene), HMX (1,3,5,7-tetranitro-1,3,5,7-tetrazocane) and CL-20 (hexanitrohexaazaisowurtzitane) has increased by just 30% **[8-13].** The challenge of balancing high detonation performance with low sensitivity is difficult since the energy and sensitivity of explosives frequently conflict **[14-17].** Instead of focusing solely on high energy, we can attempt to maximize the utilization of current compounds or develop new ones with remarkable, all-encompassing qualities.

3-nitro-1,2,4-triazol-5-one (NTO) is a heterocyclic carbonyl insensitive munition that was discovered in 1905, but its explosive characteristics were not studied until the 1980s **[18]**. It has a higher margin of safety against unanticipated stimulus reactions and outstanding physical qualities **[19-22].** It exhibits energetic performance features comparable to those of currently used secondary explosives and has the potential to be used as an explosive and propellant ingredient **[23].** This compound has been demonstrated to be less hazardous to human health than conventional explosives **[24-25].** Nevertheless, this nitrogen heterocyclic energetic molecule has numerous limitations that limit its future applications, especially negative enthalpy of formation and slightly acidic nature (pKa 3.67) **[26-27].** Furthermore, because of NTO's extremely solubility in water, it is likely to be found in substantial concentrations in effluent, depending on the formulation. In rats, NTO has a high LD_{50} relative to other EMs of around 5000 $mg.kg^{-1}$, and investigations of water toxicity studies have yielded comparable results, with toxicity levels so low that NTO might be categorized as non-toxic **[28-30]**. Nevertheless, at amounts greater than 100 mg. L^{-1}, NTO contamination of the water supply causes noticeable coloration, which can lead to environmental harm by perception as it displays a bright yellow tinge to water even if no ecotoxicological impact is shown **[31].**

To address these problems, researchers took two basic strategies: the initial one corresponds to the acidity of NTO-derivative salts, and the second relates to the development of NTO co-crystals. The first is the well-known technique, in which numerous metal and amine salts, as well as other NTO compounds, have been and continue to be made. The second new strategy, co-crystallization, might pave the road for the use of NTO. Co-crystallization is a prominent approach to enhancing the solubility, bioavailability, and physical and chemical stability of pharmaceuticals without affecting their chemical structure **[32-35]**. As a unique technology, co-crystals are composed of two or more components that are found together by hydrogen bonds, π - π stacking, van der Waals forces, and halogen bonds **[36-38]**. Co-crystallization is used to enhance the physicochemical features and energetic performance of the composition for certain applications. **[39-42]**. Different NTO co-crystals and salts have lately been studied theoretically and experimentally **[19, 43-47]**. It is demonstrated that this technology allows for the modification of physicochemical parameters and the creation of improved co-crystals with

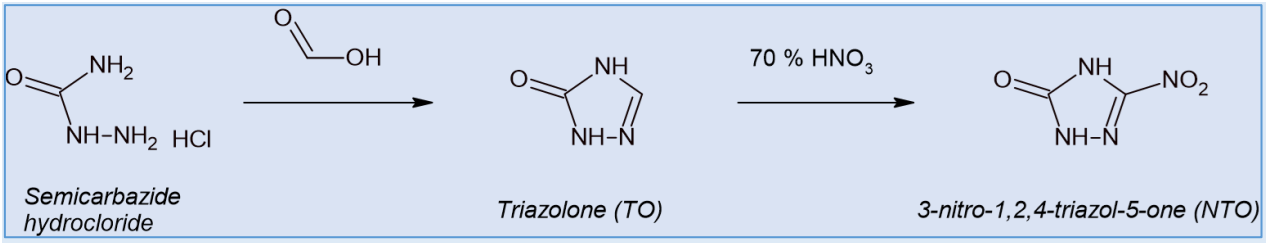
enhanced features at the molecular level. ACR, an important nitrogen-containing heterocyclic systems, acting as a weak base (pK_b = 5.4 in water) **[48]**, and its salt display modest detonation performance. It may mitigate the acidity of NTO to some extent by co-crystallizing with mildly basic ACR, without consuming less energy and giving NTO an enhanced integrated performance.

The research disclosed in this paper aims to investigate a concept that has an opportunity to step-change for the control of the properties of EMs, leading in safer and more effective performance. The lack of structure-property relationships presents a challenge for the design of new NTO-based co-crystals and salts. This research thereby intends to exploit the concepts of crystal engineering and co-crystallisation as applied to selected energetic materials in order to accomplish the following objectives: (i) develop an enhanced understanding of how structure influences key properties (ii) control the sensitivity of existing, and (iii) identify new EM with improved energetic properties.

2. Experimental section

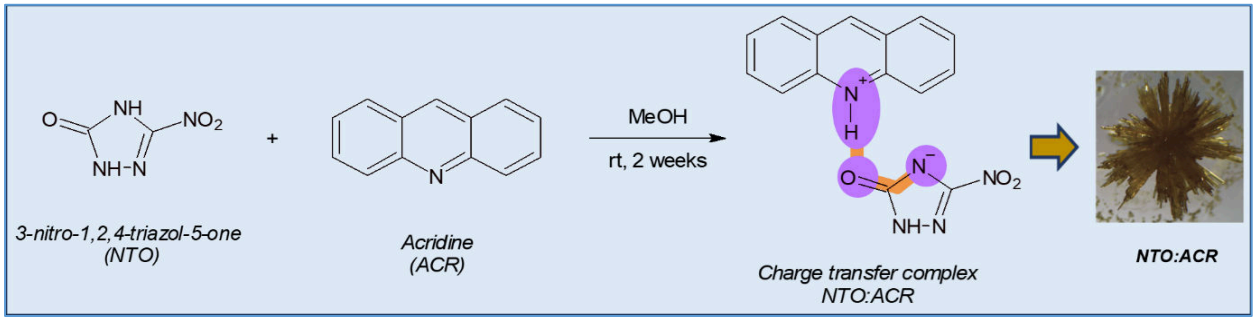
2.1. Chemicals and preparation of the sample

Sigma-Aldrich supplied sulfuric acid (H_2SO4, 95-97%), semicarbazide hydrochloride (CH_6ClN_3O), formic acid (CH_2O_2, 85%), nitric acid (HNO_3, 70%), and ACR ($C_{13}H_9N$, 97%). NTO was synthesized in two processes, beginning with the synthesis of TO (1,2,4-triazol-5-one). It was synthesized by the reaction of semicarbazide hydrochloride with formic acid and nitrated with 70% HNO_3 (**Scheme 1**) **[49]**. NTO was verified using nuclear magnetic resonance and infrared spectroscopy (**Figs**. **S1-S6**).



Scheme 1. NTO synthesis process.

Crystallization was accomplished by dissolving an equimolar ratio of NTO (46 mg) with ACR (90 mg) in methanol (about 5-10 mL) at 50 °C and for 30 minutes (**Scheme 2**).



Scheme 2. Crystal formation mechanism of the NTO: ACR

2.2. Characterisation techniques

2.2.a. Optical Microscopy. Optical micrographs of the NTO, ACR, and NTO: ACR were examined using an Olympus BX51 microscope.

2.2.b. Single Crystal X-ray Diffraction (SCXRD). The measurements were carried out with a Bruker APEX II CCD three-circle diffractometer with MoKα (λ = 0.71073) radiation. APEX2 was used to index the data (Bruker. APEX2. Ver. 2014.11-0, Bruker AXS Inc., Madison, WI 2014). SAINT was used for data integration and reduction (SAINT, version 8.34A, Bruker, Bruker AXS Inc., Madison, W. No. Title, 2013). SADABS' multi-scan approach was used to adjust absorption (SADABS, version2014/5, Bruker, Bruker AXS Inc., Madison, W. No Title. 2014). NTO: ACR structure was solved by SHELXT **[50]** in Olex2 Software Package **[51]**, then refined by full-matrix least-squares refinements on *F2* using the SHELXL **[52]**. Additional crystallographic data with CCDC reference number **2253569** for NTO: ACR has been deposited within the Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/deposit.

2.2.c. Powder X-ray Diffraction (PXRD). PXRD patterns were obtained using the Bruker D8Advance using Cu-Kα radiation (λ= 1.54439 Å) and an operating voltage and current of 40 kV and 40 mA, respectively. The temperatures ranged from 5 to 80 degrees.

2.2.d. Nuclear Magnetic Resonance Spectroscopy (NMR) spectral studies. ^{1}H-NMR characterisation of ACR, NTO and NTO: ACR were obtained using a Bruker Ascend 400 MHz spectrometer with a BBFO probe, and the spectra recorded at ambient temperature in dimethyl sulfoxide (DMSO-d_6) (Typical solution of 10 mg/mL). The solvent peaks were referenced to DMSO-d_6 (2.50 ppm). Peak multiplicities were described as follows: singlet (s), triplet (t), broad triplet (brt), doublet of triplet (dt) and multiplet (m).

2.2.e. Infrared (IR) Spectroscopy. The IR spectra were obtained with a Bruker Equinox55 with ATR equipment (wavenumber range :4000-400 cm^{-1}, resolution: 4 cm^{-1}).

2.2.f. Differential Scanning Calorimetry (DSC). Thermal characterization was performed on the materials using a Mettler Toledo LF1100 TGA/DSC 3+ equipped with a DSC sensor and operated by Stare System software v15.00 (build 8992). The tests were carried out in an inert atmosphere (N_2 flowing at 50 cm^3 min^{-1}) and at one heating rates: 10 °C min^{-1} over a range of 25–400 °C.

2.2.g. Mass spectrometry (MS). Mass spectra were attained by an X500 QTOF mass spectrometer system equipped with a direct inlet (DI) unit and an electron impact ionizer. And the data was analysed with Bruker Compass Data Analysis systems.

2.2.h. ***pH measurement***. Thermo Scientific's Orion 720Aplus and pH/mV/ISE Benchtop Meters were used to measure the pH values of NTO, ACR, and NTO:ACR. pH values were measured with combined glass pH electrode and found to be 3.48, 5.34 and 4.28, respectively **(Fig S7**).

Thermo Scientific™ Orion™ 720Aplus and pH/mV/ISE Benchtop Meters was used to measured pH solutions of NTO, ACR, and NTO: ACR.

2.3. Impact sensitivity measurement test

The impact sensitivity was measured using a BAM fall hammer (BFH-12) and used 30-trial Bruceton method **[54, 55].**

2.4. Explosive performance analysis

The EXPLO5 software program was used to calculate all explosive properties presented in this work, including detonation velocity, pressure, and oxygen balance **[56].**

2.5. Hirshfeld surface analysis

Hirshfeld surface and 2D fingerprint calculations were carried out on crystal structures imported from CIF files using Crystal Explorer software version 3.1 **[57].**

3. Theoretical Calculations

3.1. *Calculation of heat of formation (HOF)*

In this study, ab initio calculations were performed using the program package Gaussian 09 (Revision-D.01) **[58]** and visualized with GaussView 5.0.8 **[59]**. SCXRD data was used to initial input data. For those computations, the hybrid B3LYP density functional with the def2-TVZP basis set in the gas phase was applied. Enthalpy values in the gas and solid phases were calculated using the complete basis set method (CBS-4M; M refers to the method of using minimum population localization).

3.2. Non-covalent interactions (NCIs)

The NCI index is an excellent tool for studying non-covalent interactions. It has been frequently used to investigate hydrogen, halogen, and pi-pi stacking interactions **[60, 61]**. The basic density gradients were calculated using Multiwfn software (v.3.8) **[62]**. These gradients were then used for generating the demonstration graphs using the VMD (Visual Molecular Dynamics) program (v.1.9.3) **[63].**

4. Results and Discussion

4.1. The outcomes of the experiments

4.1.1. The microscope images of NTO, ACR, NTO:ACR

The microscope images of the NTO, ACR, and the NTO: ACR are presented in **Fig. 1**. The morphological distinctions between them are obvious. With the comparison of NTO and ACR, it came to light that the NTO: ACR was a yellow prism-like clear crystal with a well-defined morphology. The crystal shapes and colours are distinct from those of their co-formers (NTO in **Fig. 1a**, ACR in **Fig. 1b,** NTO: ACR in **Fig. 1c**).

a **b** **c**

Fig. 1. Microscope images of NTO (a), ACR (b), NTO: ACR (c)

4.1.2. Characterization of the NTO: ACR

SCXRD Analysis

A new energetic compound, NTO: ACR crystals, which are appropriate for SCXRD analysis measurements, was attained by the slow solvent evaporation method. NTO: ACR was acquired in high yields and stable in an open atmosphere under ambient conditions. The compound (NTO: ACR) SCXRD analysis was performed by choosing good-quality crystals of sufficient size (0.15×0.13×0.12 mm^3). **Table S1** summarizes the crystallographic data attained and the structural refinement consequences of NTO: ACR. The ORTEP drawing and crystal structure of NTO: ACR are indicated in **Figs. 2a–b**. NTO: ACR forms crystals in the triclinic crystal system and corresponds to the *P*-1 space group with four molecules. (**Fig. 2c**). Four of the two molecules per unit cell have face-to-face connection, and each side is stacked with another molecule to form an edge-to-edge configuration (**Fig. 2d**). In line with our design concept, the significant to building a layer-by-layer structure in EMs is strategically opt for H-bond donor-acceptor units. The acridinium cation is the hydrogen bond donor, while NTO is the acceptor. The deprotonation of NTO and protonation of ACR result in a hydrogen bond between the carbonyl of NTO and the N of the acridine ($N^+…H^-…O$).

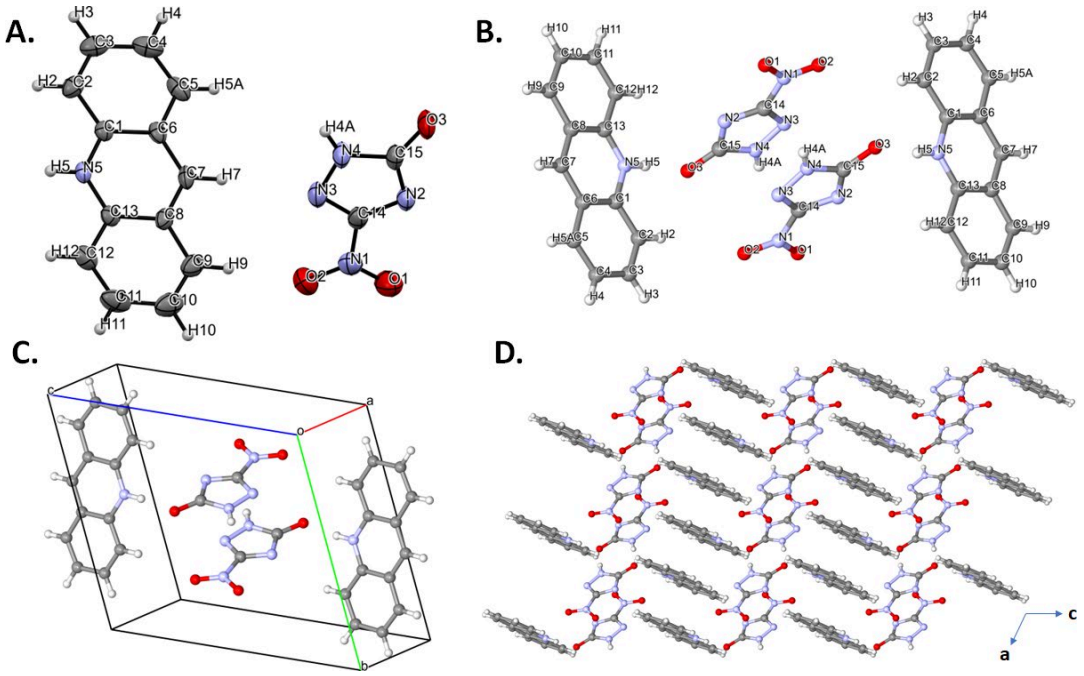


Fig. 2. ORTEP drawing of A) NTO: ACR, B) Crystal structure of NTO: ACR c) Structure of NTO: ACR in unit cell, d) Packing diagram in the unit cell of NTO: ACR.

The introduction of one hydrogen to the ACR, it altered the planer structure of the NTO precursor (**Fig.2D**). The heterodimers are held together to create a molecular layer. Given the rising quantity of eutectic molecules identified through this technology, co-crystallization to get compounds with unique characteristics has been intensively investigated. NTO act as anions and ACR (N-base) as cation (**Fig.3**). The presence of a (mildly) basic nitrogen of ACR helps forming the interactions seen, in particular the hydrogen bonding network. This is not surprising since the pK_a of NTO is ~3.7 and the pK_a for ACR is ~5.4 **[48]**. It has two ionizable hydrogen sites, which are crucial for salt formation; also, it is soluble in water, making it excellent for evaporative crystallisation. Furthermore, it is nitrogen-rich and contains functional groups that are favorable for interactions such as hydrogen bonding. For acid–base complexes whose ΔpKa values lie between -1 and 4, a linear relationship between the possibility of salt formation and their ΔpKa value has been established. This relationship has enabled us to quantify prior formulations of the pKa rule, and it can be a useful tool for scientists involved in co-crystal design and salt selection strategies **[64].** There are two moderate hydrogen bonds at the NTO: ACR (N_4-H_{4A}…O_3 and N_5-H_5…O_3), which is already transferred onto the nitrogen atom (ACR) (**Fig.4b and Table 1**). Other interaction in **Fig.4a** are not hydrogen bonds; they should be regarded as necessary interactions that occur in the absence of stacking **[65]**. The formation of hydrogen bonds is a thermodynamically advantageous and exothermic reaction. Inter-molecular bonds of hydrogen decrease molecular volume and vapor pressure while increasing molar mass, viscosity, thermal conductivity, dissolving power, phase transition temperatures, dielectric constant, dipole moment, and surface tension **[66].**

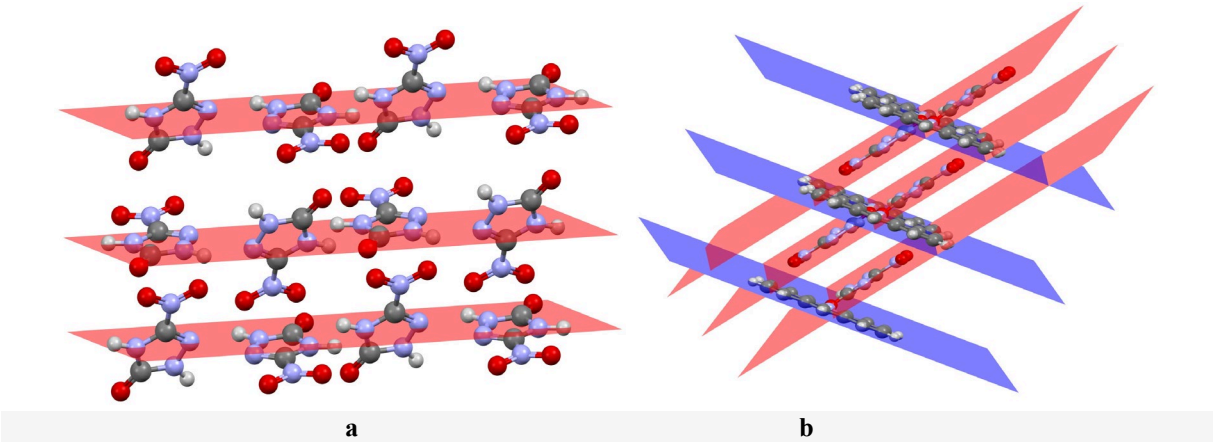


Fig. 3. Calculated planes indicating NTO- stacking a), Calculated planes indicating zig-zag relationship of NTO-packing in NTO: ACR b)

Given the nature of electrostatic interactions, these interactions are extremely weak. The π… π stacking interaction occurs between two parallel ACR cations (center to center distance of 3.66 Å, Fig. 4a). IR spectrum data, ^{1}H- and ^{13}C-NMR spectra, and mass spectrometry were used to further characterize and support the SCXRD analysis of NTO: ACR structure.

Table 1. Hydrogen bond geometries for NTO: ACR [Å, °].

D (Donor)	H	A (Acceptor)	[ARU][a]	D-H [Å]	H…A [Å]	D…A [Å]	D-H…A [°]
N (4)	H (4A)	O (3)	**[1]**	0.86	1.9	2.759 (4)	174
N (5)	H (5)	O (3)	**[2]**	0.86	1.75	2.606 (3)	174

[a] Translation of ARU-code to CIF and equivalent position code: **[1]** = -x, 1-y, 3-z, **[2]** = x, y, -1+z, 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 **[47].**

N-H…O interactions are seen in the IR spectrum, but some signals are shifted. The N…H bands of the NTO at 3200 cm^{-1} shifts around 3300 cm^{-1}. This could also be the ACR N-H salt formation, or even an indication of the N-H...O=C hydrogen bond. Owing to formation of hydrogen bonds, stretching vibration of some signals shift about 100 cm^{-1} to the low energy levels **[67].**

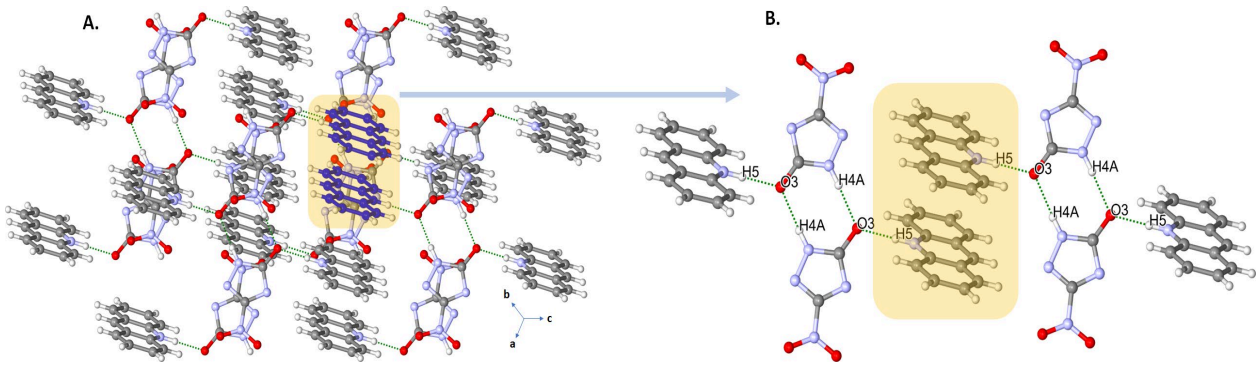


Fig. 4. The π… π stacking interaction and hydrogen-bonded pattern and in NTO:ACR.

PXRD Analysis

The PXRD examination confirmed the formation of NTO: ACR, and the PXRD patterns of NTO, ACR, and NTO: ACR are presented in **Fig. 5**. The PXRD pattern of the salt (NTO: ACR) is clearly distinct from its co-formers, identifying the NTO: ACR as a novel compound rather than product of crystal transformation.

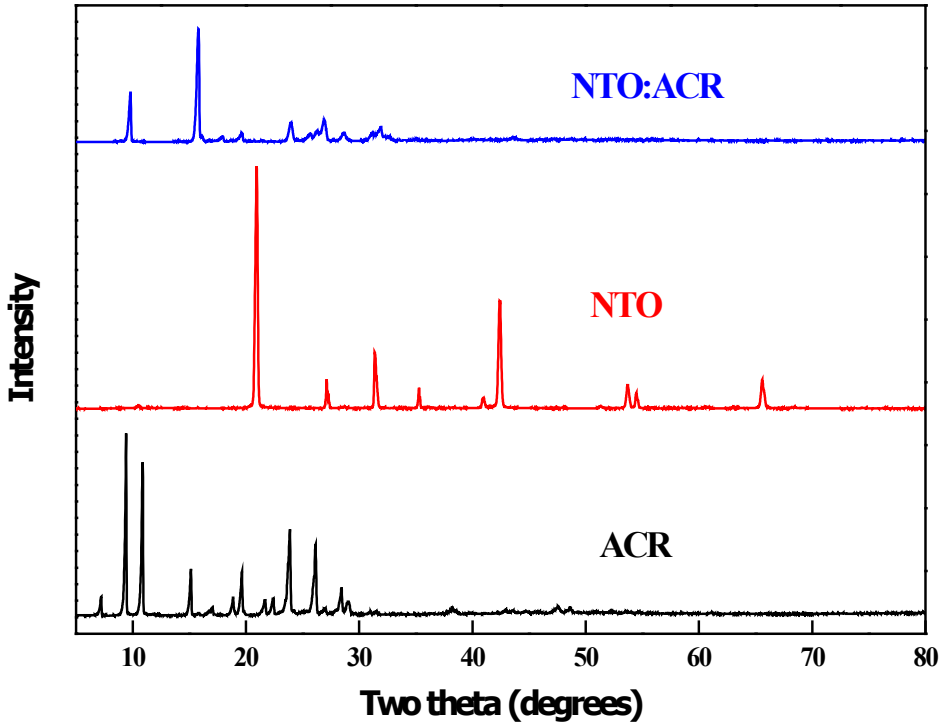


Fig. 5. PXRD patterns for ACR, NTO, and NTO: ACR.

4.1.3. NMR spectral studies

To confirm the type of interaction of ACR with NTO molecules, ^{1}H-NMR spectra of the single components and NTO:ACR were recorded in DMSO-d_6 solution. The ^{1}H-NMR spectrum of ACR (**Fig. 7**), shows all absorptions between 9.11 ppm and 7.60 ppm; a singlet at 9.11 ppm is attributed to H-7 proton, a multiplet centred at 8.17 ppm assigned to the overlapping signals of H-2, H-2', H-5 and H-5' and two sets of doublets of triplets assigned to H-3 and H3', H-4 and H-4' (**Fig.6**) at 7.86 ppm and 7.65 ppm respectively. The ^{1}H-NMR spectrum of NTO shows a singlet at 12.83 ppm attributed to the NH protons.

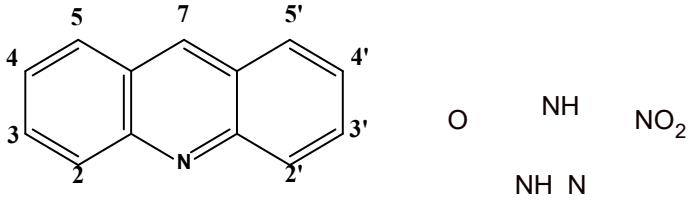


Fig. 6. Chemical structure of ACR (left) with assigned numbered carbon atoms and NTO (right)

^{1}H-NMR spectrum of the NTO: ACR (DMSO-d_6) shows the deshielding of all ACR protons (**Fig.7**, red line). In details, the singlet attributed to H-7 is deshielded by 0.03 ppm from 9.12 ppm to 9.15 ppm, and the multiplet assigned to H-2, H-2', H-5, and H-5' coalesces into a broad triplet and is deshielded by 0.02 ppm from 8.20–8.15 ppm to 8.22–8.15 ppm. The two multiplets assigned to H-3, H3', and H-4, H-4', are deshielded by 0.01 ppm to 7.90–7.85 ppm and by 0.02 ppm to 6.67–7.62 ppm, respectively. The small deshielding shifts observed by ^{1}H NMR supports the formation of the weak acridinium-NTO salt (NTO: ACR) (**Scheme 2**), which is also confirmed by SCXRD analysis.

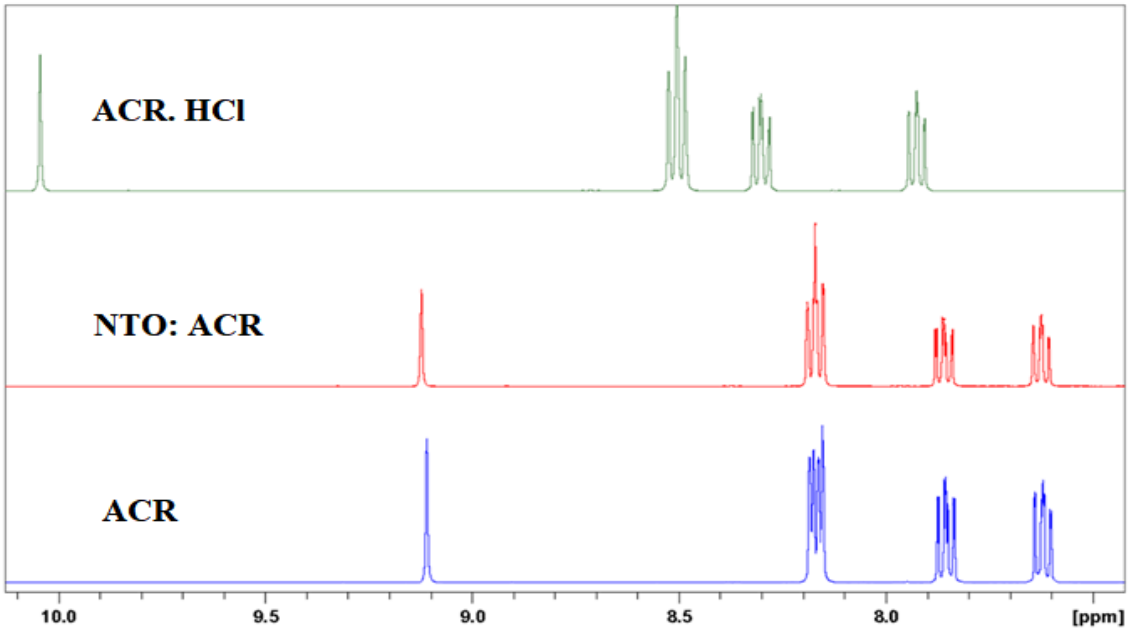


Fig. 7. ^{1}H-NMR spectra of the ACR, NTO:ACR and ACR.HCl.

Acridinium chloride: ^{1}H-NMR (DMSO d6 + DCl, δ) 7.93 (2H, m), 8.30 (2H, m), 8.51 (4H, brq, J=5.45 Hz), 10.04 (1H, s).
NTO: ACR: ^{1}H-NMR (DMSO d_6, δ): 7.62 (1H, m), 7.86 (1H, m), 8.17 (1H, s), 9.12 (1H, s), 12.82 (1H, s).

ACR: ^{1}H-NMR (DMSO d_6, δ):7.64 (2H, m), 7.86 (2H, m), 8.17 (4H, m), 9.11 (1H, s).

4.1.3. Mass spectra (MS) analysis

The base peaks correspond to the ACR and NTO compounds. It can be displayed in **Fig. S8** at m/z 180.08 $[ACR+H]^{+}$, $[C_{13}H_{10}N_1]^{+}$ and at m/z 129.00 $[NTO-H]^{-}$,$[C_2H_1N_4O_3]^{-}$. MS analysis only supports the presence of the two entities (NTO and ACR).

4.1.4. DSC analysis

In order to estimate the thermal stabilities of NTO: ACR, DSC testing was performed. The DSC traces in **Fig.8** show that NTO: ACR salt show only one exothermic peak with onset temperature 226 °C and peak maximum 229 °C. The decomposition temperature has a lower value than that of pure NTO (279 °C). The curves show that the thermal behaviour of NTO: ACR differs from that of their co-formers, and the variations in thermal stability of these substances imply the formation of a new compound. The formation of new compound could

lead to in inter molecular hydrogen bonding. Inter-molecular hydrogen bonds have been found to increase thermal conductivity, resulting in greater hot spot energy transmission, dissipation and greater insensitivity **[2, 68, 69,70]**.

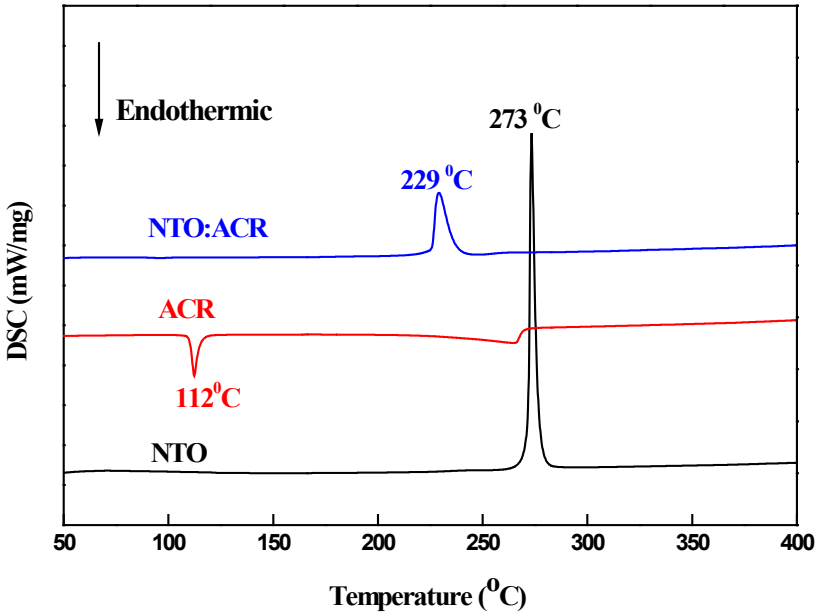


Fig. 8. Differential scanning calorimetry plots for NTO, ACR, and NTO: ACR [°C]

4.1.5. Infrared (IR) Spectroscopy analysis

The IR spectra of NTO, ACR, and NTO: ACR are indicated in **Figs. S6, S9, S10**. The assignments for the most characteristic vibrational bands are listed in **Table 2.** It can be determined from the **Table 2** that a group of low intensity bands assigned to N–H stretching vibration of NTO decreased from the region of 3203 cm^{-1} to 3047 cm^{-1}. While the C=O stretching of NTO shifted from the region of 1699 cm^{-1} to 1650 cm^{-1}, and the C-N stretching vibration decreased from 1188 cm^{-1} to 1047 cm^{-1}. At the same time, some peak shift occurs for both ACR and NTO bonds. The hydrogen bond increases the X–H bond length, causing the corresponding stretching vibrations band in the IR spectrum to move towards lower frequencies **[67].**

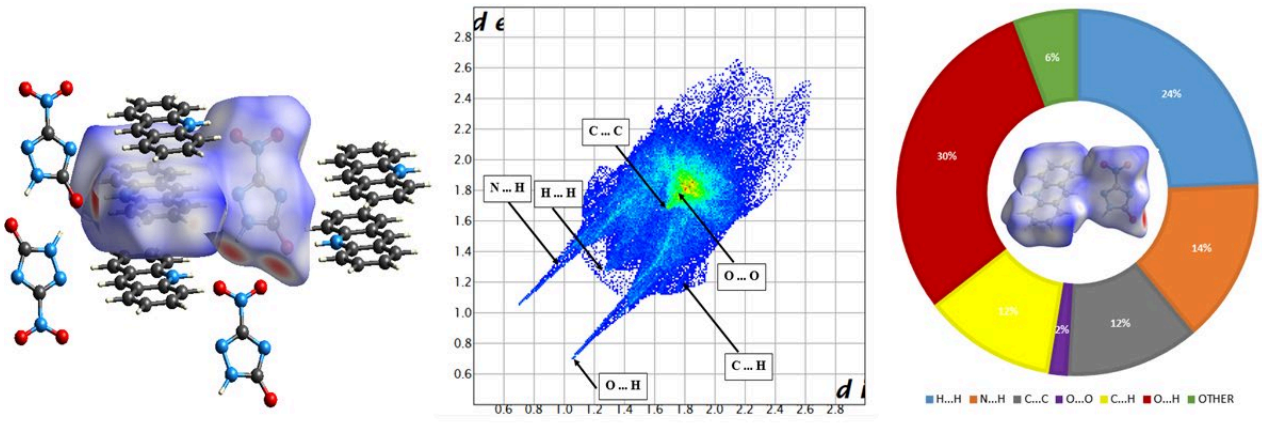
Table 2. The main bands of the IR spectra of NTO, ACR, and NTO: ACR [cm^{-1}]

Assignment	NTO	NTO:ACR	ACR
C-H stretching aromatic vibration			3053
N-H stretching vibration	3203	3047	
C=O stretching vibration	1699	1650	1316
NO_2 asymmetric stretching vibration	1541	1591	
C-C stretching aromatic vibration		1487	1556
NO_2 symmetric stretching vibration	1346	1340	
C-N stretching vibration	1188	1047	1313
C=N stretching aromatic amine		1629	1616

4.2. Outcomes of the theoretical calculations

4.2.1. Hirshfeld surface (HS) analysis

Hirshfeld surface (HS) studies were carried out in order to acquire a better knowledge of the packing motifs and inputs of the key intermolecular interactions that determine the molecular design of substances. **Fig.9a** depicts HS projected in two orientations on the d_{norm} property. The Crystal Explorer 3.1 software program was utilized to assess the strength and relevance of hydrogen bonds along with additional intermolecular interactions, including their effect on crystal form, 2D fingerprints (FP), and the relevant HS **[71].** It was conducted according with the standards outlined in the literature and the instances presented **[72]**, demonstrating the existence of the interactions identified by Mercury software **[53]** and illustrated in **Tables 1**. The colour scale is utilized to differentiate the HS's various intermolecular interaction areas. The HS analyses for NTO: ACR are shown in **Fig. 9a**, which show surfaces that have been mapped over d_{norm} (-0.7844 to 1.4763 Å). The consequences of the details are shown in **Fig. 9a** are plainly visible in these locations, with considerable circular depressions (deep red) visible on the surface, demonstrating N_4-H_{4A}…O_3 and N_5-H_5…O_3 intermolecular interactions. The red colour dots in the FP plots represent short contacts for the O...H, H...H, N...H, C...H, O...O, and C...C interactions (**Fig. 10**), emphasizing their importance in the molecular packing between NTO and ACR. The FP graphs in **Fig. 9b** show two separate "tails" for N-H...O, hydrogen bonds extending down to approximately d_i=0.75 Å, d_e=1.16 Å for NTO: ACR. The 30% O...H, 24% H...H, and 14% N...H interactions remain the most significant contributors to total HS and can be seen as the "ridge" of the FP. The arrangement of red-blue triangles in **Fig. 11b** is typical of π... π stacking (ACR...ACR), showing in the FP as a characteristic value approximately de = di=1.8 Å **[73]**. Moderate hydrogen bonds (N-H…O) were some of the most critical intermolecular interactions, as seen in **Figs.4a-b**; this is dependable with the HS calculations and crystal structure data.



a b c

Fig. 9. a) HS mapped with d_{norm} b) FP plots c) Populations of inter-molecular and interatomic contacts of NTO: ACR.

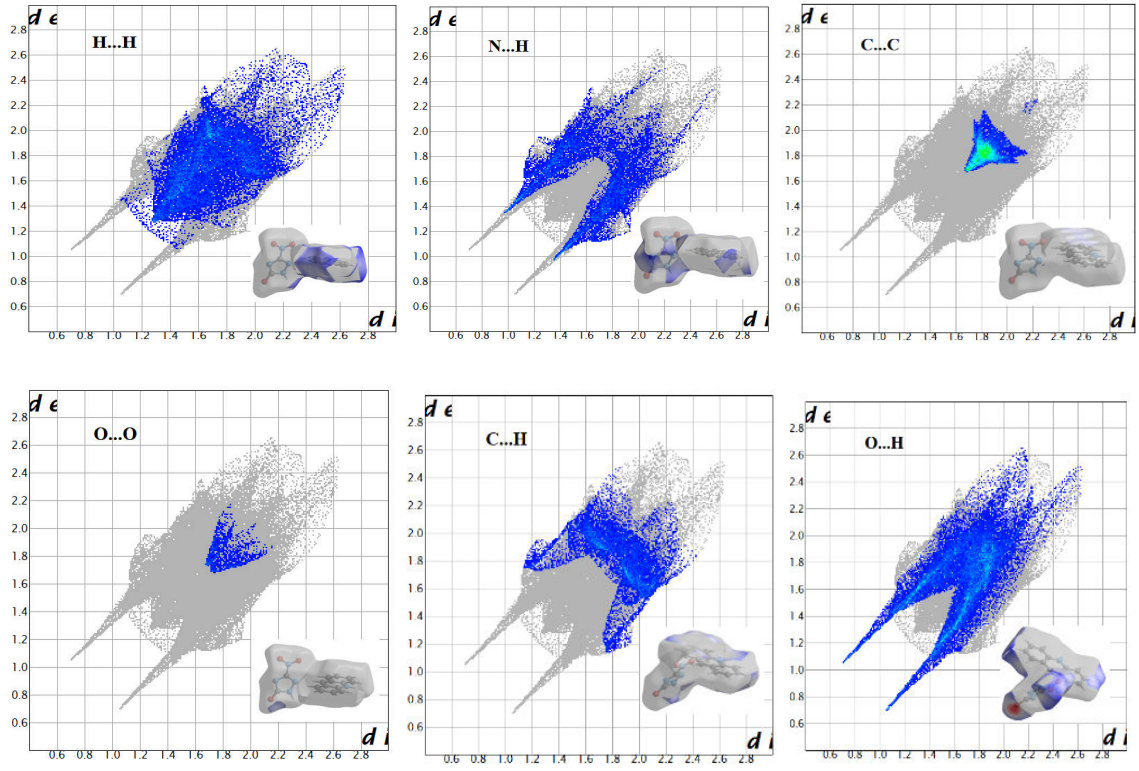
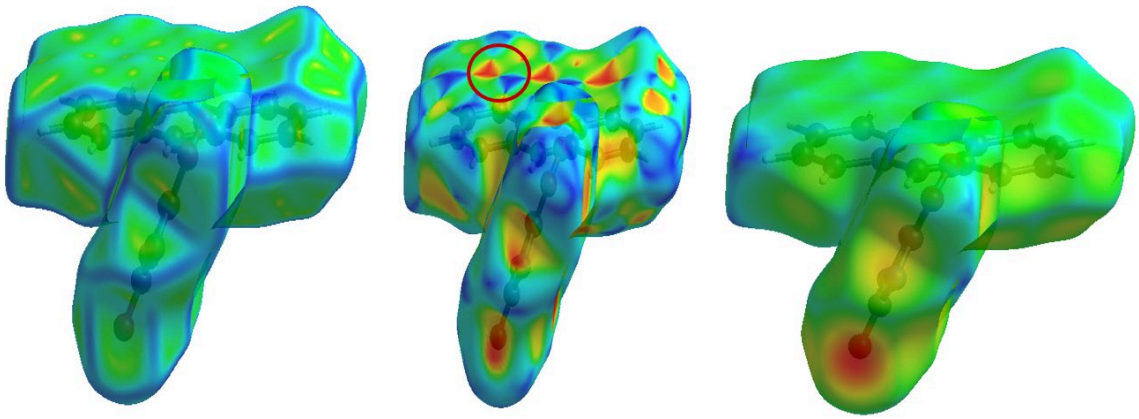


Fig. 10. FP plots for NTO:ACR, displaying contributions from various contacts.



a **b** **c**

Fig. 11. a) curvedness, b) shape index and c) d_e.

4.2.2. Theoretical calculation of heat of formation (HOF)

HOF is a significant measure for evaluating the explosive performance of EMs and can be determined using Eq. (1) **[74–76]**. where $\Delta H_f^\circ(g, M)$ symbolizes the enthalpy of formation of the investigated molecule (M) in gas phase; $H^\circ_{(molecule)}$ represents the calculated enthalpy value of the molecule M with the CBS-4M method (H^{298} in **Table 3**); $\Sigma H^\circ_{(atoms)}$ symbolizes of calculated enthalpies for the separate atoms (H, C, N, O) and $\Sigma\Delta H^\circ_{f(atoms)}$ stands for experimental values of the enthalpy of formation (ΔH_f°) for the corresponding atoms H, C, N, and O to be 217, 716, 472, and 249 kJ.mol^{-1}, respectively **[77]**.

$$\Delta H_f^\circ(\mathbf{g},\mathbf{M}) = H^\circ_{(molecule)} - \Sigma H^\circ_{(atoms)} + \Sigma \Delta H^\circ_{f(atoms)} \quad \mathbf{1}$$

Table 3. Gas-phase enthalpy of formation results

Entry	P.G.[1]	NIMAG[2]	-H[298] (a. u.)[3]	$\Delta H_f^\circ(g, M)$ (kJ.mol^{-1})[4]
NTO	C_1	0	519	38.00
NTO: ACR	C_1	0	1069	168.90

[1]Point group, [2]Number of imaginary frequencies.

[3]Enthalpy values obtained from the CBS-4M calculations,

[4]Enthalpy of formation (in gas phase).

Furthermore, it is widely accepted that, to precisely examine the detonation properties of EMs, the calculation of the solid-phase heat of formation $\Delta H_f^\circ(\mathrm{s},\mathrm{M})$ is necessary, and this is easily performed done by applying Hess's law (Eq. 2) **[78]**.

$$\Delta H_f^\circ(\mathrm{s},\mathrm{M}) = \Delta H_f^\circ(\mathrm{g},\mathrm{M}) - \Delta H_f^\circ(\mathrm{sub},\mathrm{M}) \quad \mathbf{2}$$

where $\Delta H_f^\circ(\mathrm{sub},\mathrm{M})$ indicates the heat of sublimation, which may be determined through the Rice and Politzer equation (Eq. 3) **[79].**

$$\Delta H_f^\circ(\mathrm{sub},\mathrm{M}) = aA^2 + b(\nu\sigma_{tot}^2)^{0.5} + c \quad \mathbf{3}$$

where A denotes the surface area of the 0.001 electron/Bohr^3 iso-surface of the electronic density, ν represents the degree of balance between positive and negative potentials on the isosurface, and finally σ_{tot}^2 is an index of evaluating the variability of the electrostatic potential on the molecular surface (**Table 4**). A, ν and σ_{tot}^2 values were calculated by using Multiwfn program (v.3.8 – submenu 12: quantitative analysis of molecular surface) **[80]**, other coefficients (a= 2.670x10^{-4} kcal.mol^{-1}, b=1.650 kcal.mol^{-1}, and c=2.966 kcal.mol^{-1}) were obtained from the literature **[81].**

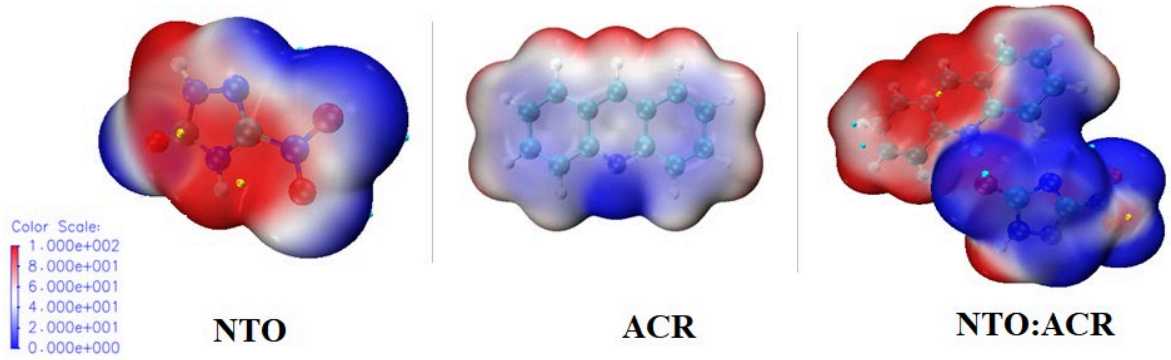
Table 4. Calculated ΔH°f (sub, M), ΔH°f (s, M), and ΔH°f (g, M) results of NTO and NTO: ACR

Entry	gas phase	solid phase	
	ΔH°f (g, M)	**-ΔH°f (s, M)**	**ΔH°f (sub, M)**
NTO	38	58	96
NTO:ACR	168	37	206

4.2.3. Electrostatic potential (ESP) maps

ESP is essentially significant physical property of compounds since it offers information on charge density distribution and chemical reactivity. In accordance with **Fig. 12**, positive ESP (red regions) is mainly dispersed across the main skeleton, while negative ESP (blue areas)

focuses on the molecules' borders, particularly around the nitrogen and oxygen atoms, due to their higher electronegativity. The entirety of the following alterations points to variances in NTO: ACR charge dispersion may result in changes in sensitivity.



NTO	ACR	NTO: ACR

Fig.12. ESP of NTO, ACR, and NTO: ACR

4.2.4. Non-covalent interaction (NCI) plots

In order to show the intermolecular interactions of the NTO: ACR in real space, a reduced density gradient (RDG) study utilizing electron density was performed. RDG can identify non-covalent interactions (NCIs), which can provide important information on the source of molecular change, crystal packing, and stability **[82, 83].** Erin et al. suggested the following relationship between the functions RDG and (r): **[84].**

$$RGD = \frac{1}{2\,(3\,\pi^2)^{1/3}} \frac{|\nabla\,\rho\,(r)|}{\rho\,(r)^{4/3}} \qquad \textbf{4}$$

$$(\Omega) = sign\,(\lambda_2(r))\,\rho(r) \qquad \textbf{5}$$

where $\rho\,(r)$ is the electron density, $sign\,(\lambda_2\,(r))$ is the sign of the second largest Hessian eigenvalue. The spikes are classified into three groups in RDG maps: the hydrogen bond area, the vdW interaction area, and the steric area. Initially, we investigate a case with ρ ranging from -0.04 to -0.03 a.u., whose occurs within the hydrogen bond area. (**Figs. 13a-b**). It is obvious that NTO: ACR salt is formed through intermolecular interactions including N_4-H_{4A}...O_3 and N_5-H_5...O_3. Following that, in the vdW interaction region with values ranging from -0.01 to 0.005 a.u., it is shown that NTO: ACR exhibits greater spikes, confirming significant vdW interactions (**Figs. 13a–b**). As shown in **Figs.13a-b**, the scatter points and electron density of NTO: ACR in the steric area (varying from 0.01 to 0.05 a.u) has sharper spikes and more points, confirming significant strong repulsion interactions. It is straightforward to deduce that moderate hydrogen bonds, vdW forces, and steric effects account for a significant portion of NTO:ACR intermolecular interactions.

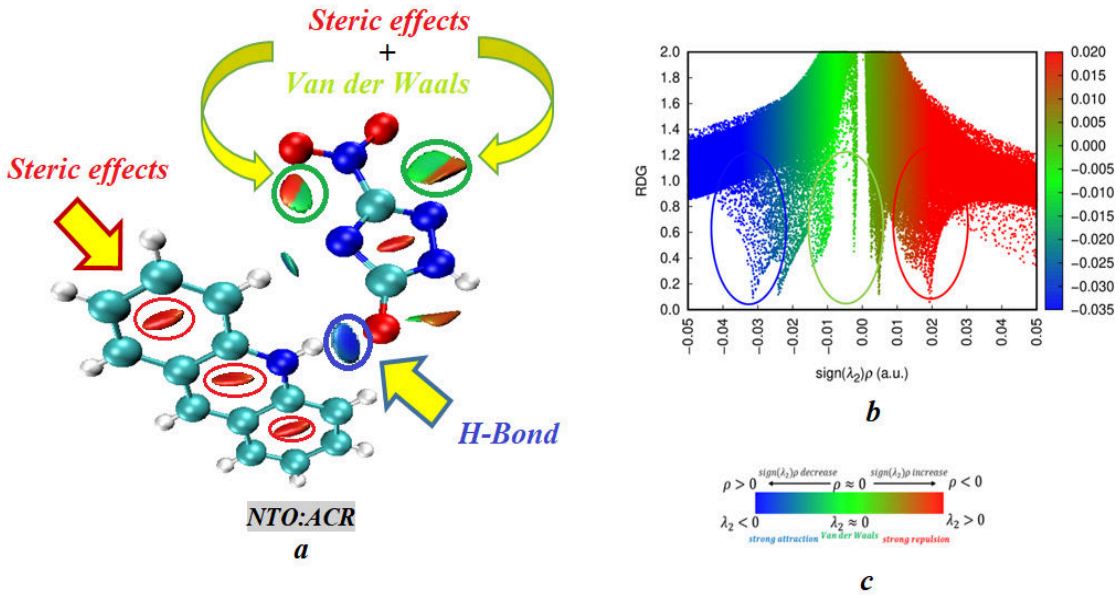


Fig. 13. RDG map and non-covalent interaction plots of low-gradient iso-surfaces for NTO: ACR.

4.3. Detonation Parameters for NTO: ACR

4.3.1. Impact sensitivity

Impact sensitivity was executed on NTO and NTO:ACR. NTO:ACR are insensitive, with no signs of initiation up to the testing limit of 100 J (**Table 5**). NTO:ACR is substantially less impact sensitive than NTO, and this is attributed to the layered structure of NTO:ACR. NTO:ACR has layered structures akin to TATB (triaminotrinitrobenzene), one of the most insensitive traditional EMs.

4.3.2. Free space in the crystal lattice and packing coefficient

By applying Mercury CSD Ver. 4.1, the free space, i.e., voids, and packing coefficient of NTO and NTO: ACR were calculated **[53]**. As a consequence of the formation of NTO: ACR, the packing coefficient altered. Despite NTO: ACR is not dense than NTO, the new compound's making drastically altered the packing coefficient and voids (**Table 5**) **Figs. S11-S12**. Furthermore, higher compactness indicates less free volume in the crystal, causing molecular breakdown and the occurrence of hotspots, resulting in greater insensitivity **[69, 85, 86].**

Table 5. Packing coefficient and free space of NTO, and NTO: ACR.

Entry	Packing Coefficient (%)	Free space (voids) (%)	Impact sensitivity (J)
NTO	74.13	5.9	100
NTO: ACR	69.04	12.7	100

4.3.3. Calculation of detonation velocity, pressure, and oxygen balance

The characteristics of detonation are crucial for acquiring a fundamental comprehension of EMs performance. The oxygen balance, detonation velocity and pressure were calculated using EXPLO5 V6.04. It uses the Becker-Kistiakowsky-Wilson's equation of state for gaseous detonation products and Cowan-Fickett's equation of state for solid carbon **[56].** The

detonation parameters were calculated at the C-J point. The primary detonation products were thought to consist of C, N_2, H_2O, CH_4, NH_3, CO_2, C_2H_6, H_2, CO, CH_2O_2, C_2H_4, HCN, CH_3OH (**Figs. S13-S15.**) Calculated heat of formation ($\Delta H°f$ (g, M), $\Delta H°f$ (s, M)), and detonation parameters are listed in **Table 6**.

Table 6. Calculated detonation properties of NTO, and NTO: ACR.

Entry	Ω [%][a]	IS [J][b]	Gas phase		Solid phase	
			D[m.s^{-1}][c]	P[GPa][c]	D [m.s^{-1}][c]	P[GPa][d]
NTO	-24.6	100	8747	33.01	7200	21.04
NTO: ACR	-168.1	100	7006	20.02	5480	8.75

[a]Oxygen balance, [c]Detonation velocity, and [d]Detonation pressure was calculated using EXPLO5 V6.04
[b]Impact sensitivity was measured by BAM hammer instrument

5. Conclusion

The co-crystallization method was utilized to form a novel energetic compound 3-nitro-1,2,4-triazol-5-one (NTO): acridine (ACR), which was then comprehensively characterized by IR spectroscopy, ^{1}H-NMR, ^{13}C-NMR spectroscopy, mass spectrometry, and DSC study. The structure attributes of NTO: ACR were investigated using SCXRD and PCXRD. Through changing the chemical composition, it was possible to alter physical properties such as thermal stability, free space (voids), packing coefficient, crystal density, difference in pKa of co-formers, morphology, solubility, impact sensitivity, and calculated detonation parameters were also gathered and compared. Appears it was possible to completely modify physical properties. The crystal structure and crystal packing features of NTO: ACR demonstrate that the anions and cations in this energetic compound have modest hydrogen-bond intermolecular interactions (N_4-H_{4A}…O_3 and N_5-H_5…O_3). Furthermore, Hirshfeld surface analysis and non-covalent interaction studies gave theoretical support to better investigate its structure-property relationship. The detonation velocity and pressure of NTO: ACR were calculated with the assistance of the EXPLO5 program and found to be 7006 ms^{-1} and 20.02 G Pa, respectively, slightly less than those of NTO. Although non-energetic components usually decrease the detonation velocity and pressure, they can significantly enhance the number of energetic co-crystals and salts, enabling a rich database for subsequent investigations in a data-driven or crystal engineering approach.

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Author contribution

All authors contributed to the study conception and design. Nilgün Şen: Conceptualisation, Investigation, Methodology, Data curation, Formal Analysis, Writing-Editing, Funding acquisition. Jean-François Pons: Investigation, Methodology, Data curation, Formal Analysis, Writing-review and editing. Yunus Zorlu: Data curation, Visualization. Eleftheria Dossi:

Investigation, Methodology, Data curation, Formal Analysis, Writing-review and editing. Federica Persico: Formal Analysis, Writing-review and editing. Tracey Temple: Formal Analysis, Writing-review and editing, Nazife Aslan: Investigation, Methodology, Data curation, Akachai Khumsri: Data curation, Formal Analysis, Validation, Software. All authors read and approved the final manuscript.

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Data availability
The corresponding CIF files are available in the Cambridge Structural Database (CSD); for 1,2,4-triazol-5-one (NTO): Acridine, the CCDC number is 2253569.

Code availability
Not applicable.

Declarations
Competing interests, the authors declare no competing interests.

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