



Crystal structures and supramolecular studies of three organic picrate salts

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ABSTRACT

Three crystalline picrate salts with benzimidamidium (**I**), 2-isopropyl-6-methylpyrimidin-1,3-dium-4-olate (**II**) and *N*-(amino(pyrimidin-2-yl)methylene)hydroxyl ammonium (**III**) cations, respectively, were self-assembled and their three-dimensional structures were characterized by single-crystal X-ray diffraction. Salt **I** is crystallized in orthorhombic space group $P2_12_12_1$ with $a = 5.031(3) \text{ \AA}$, $b = 13.692(7) \text{ \AA}$, $c = 21.821(10) \text{ \AA}$, $V = 1503.1(13) \text{ \AA}^3$ and $Z = 4$. Salt **II** is crystallized in monoclinic space group $P2_1/c$ with $a = 7.9360(8) \text{ \AA}$, $b = 18.852(2) \text{ \AA}$, $c = 11.9140(11) \text{ \AA}$, $\beta = 100.067(2)^\circ$, $V = 1755.0(3) \text{ \AA}^3$ and $Z = 2$. Salt **III** is crystallized in non-centrosymmetric monoclinic space group $P2_1$ with $a = 12.0404(11) \text{ \AA}$, $b = 4.0308(4) \text{ \AA}$, $c = 15.0078(14) \text{ \AA}$, $\beta = 99.680(2)^\circ$, $V = 1503.1(13) \text{ \AA}^3$ and $Z = 2$. Proton transfers are observed in all picrate salts, featuring short intermolecular $N^+ \cdots H \cdots O$ hydrogen bonds [$d(N \cdots O) \sim 2.7 \text{ \AA}$]. Salt **I** displayed a three-dimensional structural network while salts **II** and **III** formed zero-dimensional tetramer and two-dimensional plane, respectively, under the interactions of intermolecular hydrogen bonds.

Keywords: Picrate salts, supramolecular, crystal structure, three-dimensional, stability.

INTRODUCTION

Similarly to trinitrotoluene (TNT), picric acid is served as a high-energy-density materials (HEDMs) in artillery projectile, ammunition and explosives [1]. The extensive use of picric acid was slowly replaced by RDX (Research Department Formula X) due to its higher performance, but with the increase of environmental concerns, replacement of commonly used toxic RDX is required [2]. Performance and sensitivity are often contradictory parameters. High detonation velocity and high detonation pressure are important for high performance HEDMs and in contrast high thermal and mechanical stabilities are also vital for safe handling of HEDMs [3]. One way to encounter the contradiction between sensitivity and performance is to form hydrogen bond with other nitrogen-rich compound [4]. Present study is focused on the protonation effect to the geometrical features, molecular conformation and intermolecular interactions in crystalline organic picrate salts, namely benzimidamidium picrate (**I**), 2-isopropyl-6-methylpyrimidin-1,3-dium-4-olate picrate (**II**) and *N*-(amino(pyrimidin-2-yl)methylene)hydroxylammonium picrate (**III**).

EXPERIMENTAL SECTION

The reagents and solvents for synthesis were obtained commercially from Sigma Aldrich and Merck Corporation and were used without any additional purification. Picric acid (1 mmol, 0.23 g) and 1 mmol of corresponding base (Figure 1) were dissolved in methanol (30 ml) and warmed on a hotplate with stirring for a few minutes. The

solutions were allowed to cool to room temperature and crystals were formed *via* slow evaporation after few days. X-ray analysis for all samples were performed using Bruker APEX II DUO CCD diffractometer, employing MoK α radiation ($\lambda = 0.71073 \text{ \AA}$) with φ and ω scans, at room temperature. Data reduction and absorption correction were performed using *SAINTE* and *SADABS* programs [5]. All structures were solved by direct methods and refined by full-matrix least-squares techniques on F^2 using *SHELXTL* software package [6].

Table 1: Crystal data and parameters for structure refinement of I, II and III

Compound	I	II	III
CCDC no.	938989	938990	938991
Molecular formula	$(C_7H_9N_2)^+ \cdot (C_6H_2N_3O_7)^-$	$(C_8H_{13}N_2O)^+ \cdot (C_6H_2N_3O_7)^-$	$(C_5H_7N_4O)^+ \cdot (C_6H_2N_3O_7)^-$
Molecular weight	349.27	381.31	367.25
Crystal system	Orthorhombic	Monoclinic	Monoclinic
Space group	$P2_12_12_1$	$P2_1/c$	$P2_1$
a (Å)	5.031 (3)	7.9360 (8)	12.0404 (11)
b (Å)	13.692 (7)	18.852 (2)	4.0308 (4)
c (Å)	21.821 (10)	11.9140 (11)	15.0078 (14)
α (°)	90	90	90
β (°)	90	100.067 (2)	99.680 (2)
γ (°)	90	90	90
V (Å ³)	1503.1 (13)	1755.0 (3)	717.99 (12)
Z	4	4	2
D_{calc} (g cm ⁻³)	1.543	1.443	1.699
Crystal dimensions (mm)	$0.51 \times 0.11 \times 0.06$	$0.95 \times 0.19 \times 0.08$	$0.70 \times 0.10 \times 0.08$
μ (mm ⁻¹)	0.13	0.12	0.15
$T_{\text{min}}/T_{\text{max}}$	0.937/0.992	0.894/0.991	0.904/0.989
Reflections measured	6598	17212	8688
Ranges of indices (h, k, l)	$-5 \rightarrow 3; -16 \rightarrow 16; -25 \rightarrow 25$	$-11 \rightarrow 11; -26 \rightarrow 25; -16 \rightarrow 16$	$-16 \rightarrow 16; -5 \rightarrow 5; -21 \rightarrow 20$
θ limit (°)	1.8 - 25.0	2.6 - 30.0	1.4 - 30.0
Unique reflections	1560	5083	2363
Observed reflections [$I > 2\sigma(I)$]	1154	2635	2089
Parameters	226	252	251
Restraints	0	0	1
Goodness of fit on F^2	1.12	1.05	1.05
R_1, wR_2 [$I \geq 2\sigma(I)$]	0.066, 0.246	0.066, 0.234	0.034, 0.093

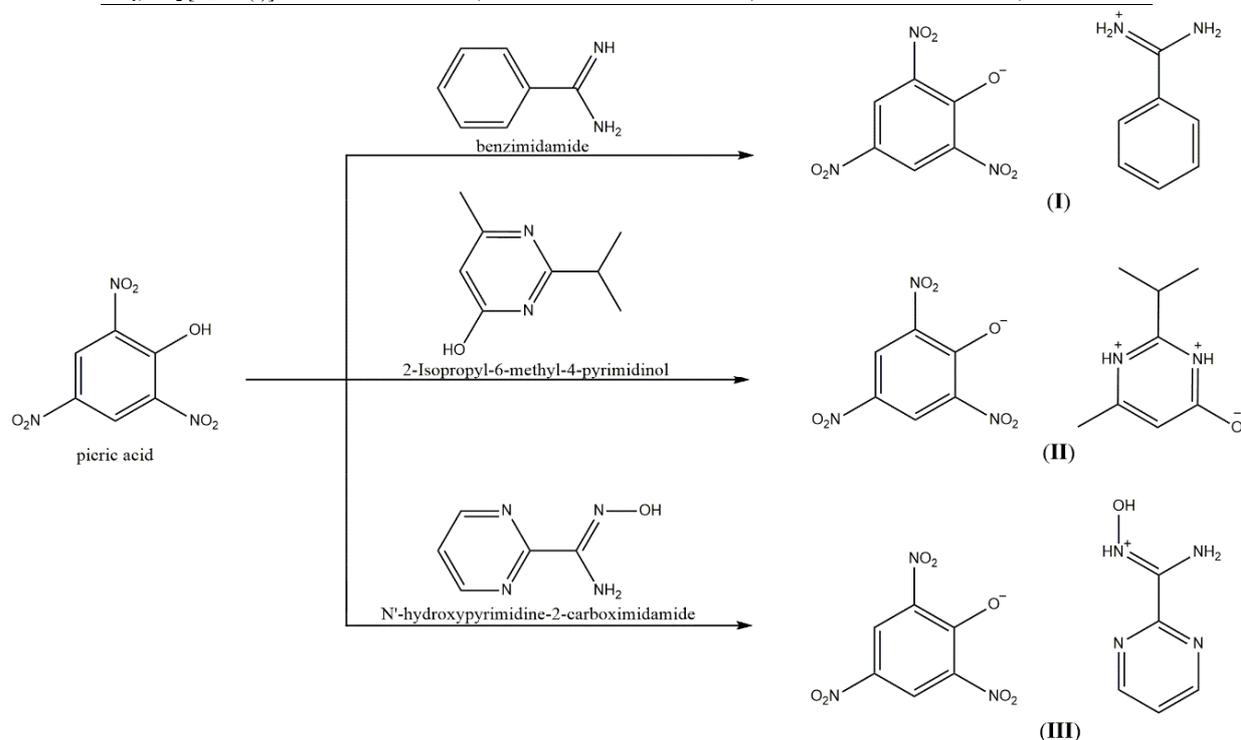


Figure 1: Reaction scheme for the synthesis of picrate salts

All non-hydrogen atoms were refined anisotropically and all C-bound H atoms were calculated geometrically with isotropic displacement parameters set to 1.2 (or 1.5 for methyl group) times the equivalent isotropic U value of the parent carbon atoms. The N-bound H atoms were calculated geometrically and refined with $U_{\text{iso}}(\text{H}) = 1.2 \times U_{\text{eq}}(\text{N})$ for salt I. The N-bound and O-bound H atoms for II and III were located from difference Fourier map and refined

freely. Crystallographic data for **I**, **II** and **III** are summarized in Table 1 and have been deposited with the Cambridge Crystallographic Data Centre as supplementary publications, namely CCDC 938989, 938990 and 938991, respectively. Copies of available material can be obtained free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK, (Fax: +44-(0)1223-336033 or e-mail: deposit@ccdc.cam.ac.uk).

X-ray crystal structure description of picrate salts **I**, **II** and **III**

Salt **I** is crystallized in orthorhombic crystal system with space group $P2_12_12_1$. The asymmetric unit of **I** consists of a benzimidamidium cation and a picrate anion as depicted in Figure 2.

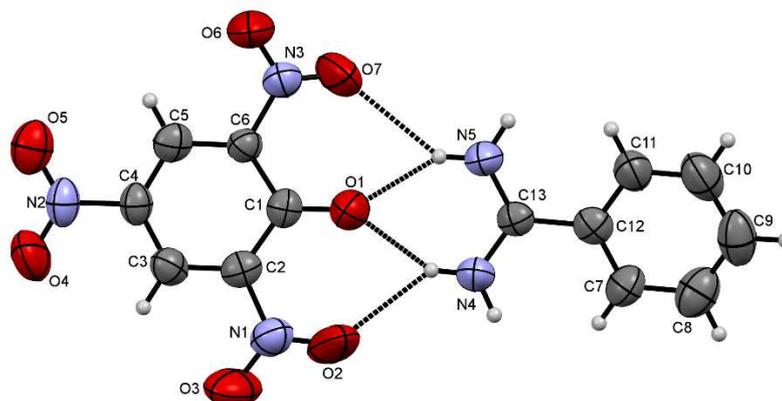


Figure 2. The molecular structure of **I** with displacement ellipsoids at 50% probability level and atomic numbering scheme

The OH group of picric acid is deprotonated and proton-transferred to the imine group of benzimidamide which indicated by changes in bond distance of C1–O1, C13–N4 and C13–N5. The bond lengths of C1–O1 in **I** is reduced from 1.32 Å to 1.26 Å as compared to neutral picric acid [7], while symmetrical C(NH₂)₂ group in **I** with similar C–N bond lengths (1.32 Å and 1.31 Å) are differs from asymmetrical (HN)C(NH₂) group (C–N = 1.29 Å and 1.35 Å) in reported benzimidamide crystal [8] (Table 2). The similar C13–N4 and C13–N5 bond lengths suggested a delocalized N–C–N fragment. The cation and anion are connected into a hydrogen-bonded dimer through bifurcated N–H...O (N4–H4A...O1, N4–H4A...O2, N5–H5B...O1 and N5–H5B...O7) hydrogen bonds, featuring a $R_1^2(6)R_2^1(6)R_1^2(6)$ supramolecular heterosynthon [9]. Under the influence of synthons, torsion angles of nitro groups at 2- and 6-positions (O2–N1–C2–C1 and O6–N3–C6–C5) in **I** are smaller as compared to **II** and **III** (Table 3). In the crystal of **I**, molecules are linked into a zig-zag chain along *c*-axis via N4–H4B...O4, N4–H4B...O5, N5–H5C...O6 and N5–H5C...O7 hydrogen bonds (Figure 3a). In overall, a 3D network is built by intermolecular N4–H4B...O4 hydrogen bonds (Figure 3b).

Table 2: Selected bond lengths and angles of present compounds and related structures (in parentheses)

Bond length (Å) and angle (°)	
I	C1–O1 1.26 (1.32)
	C13–N4 1.32 (1.29)
	C13–N5 1.32 (1.35)
	N4–C13–N5 117 (124)
II	C1–O1 1.25 (1.32)
	C10–O8 1.23 (1.29)
	C7–N4–C8 124 (117)
	C7–N5–C10 123 (116)
III	C1–O1 1.27 (1.32)
	C11–N7 1.31 (1.36)
	N6–O8 1.38 (1.42)
	C11–N6–O8 119 (109)

Table 3: Torsion angles (°) of nitro groups from attached benzene ring

	O2–N1–C2–C1	O4–N2–C4–C3	O6–N3–C6–C5
I	1.7	-7.95	19.68
II	-25.7	7.52	43.59
III	-11.52	9.61	48.51
Picric acid [7]	9.26, -3.84	-0.17, -3.84	18.70, -18.80

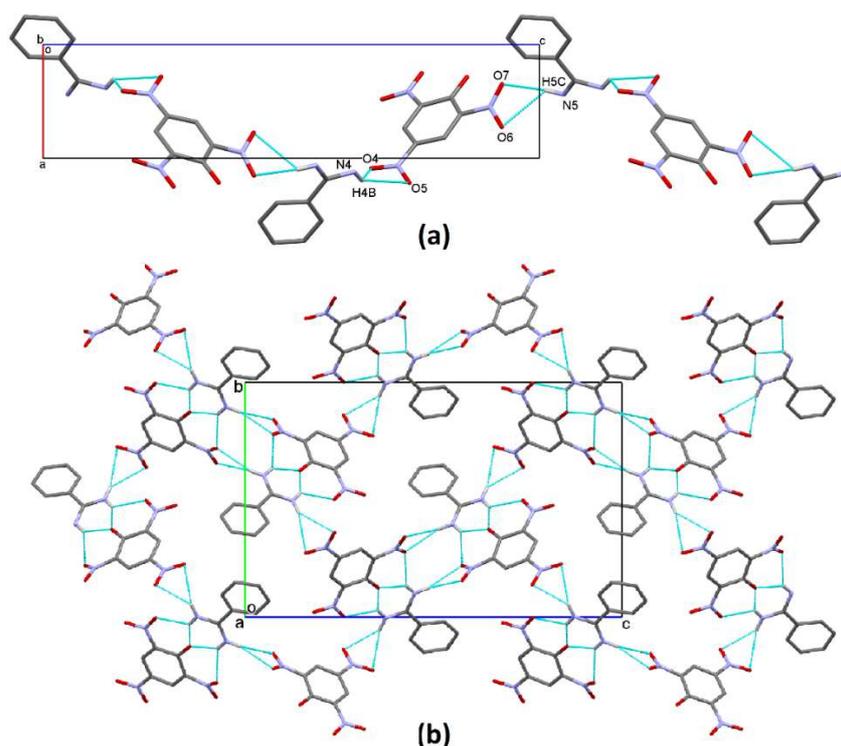


Figure 3: (a) Partial packing of I viewed along *b*-axis, forming a zig-zag chain. (b) Packing diagram of I viewed along *a*-axis

Salt **II** is crystallized in monoclinic $P2_1/c$ space group. The asymmetric unit of **II** consists of a 2-isopropyl-6-methylpyrimidin-1,3-dium-4-olate cation and a picrate anion as shown in Figure 4. The hydroxyl groups in both molecules are deprotonated and the protons are transferred to the nitrogen atoms in pyrimidine ring. The ionic C1–O1 (1.25 Å) and C10–O8 (1.23 Å) bond lengths in **I** are shorter than reported neutral picric acid (1.32 Å) and 2-((4-hydroxy-6-methylpyrimidin-2-yl)trisulfanyl)-6-methylpyrimidin-4(3*H*)-one (1.29 Å) [10], respectively. The C–N–C bond angles in protonated pyrimidine ring (C7–N4–C8 and C7–N5–C10 ~ 123°, Table 2) of **II** are larger than non-protonated pyrimidine ring (~116°) [10]. The molecules of **II** are linked into supramolecular heterodimers through N4–H1N4···O1 and C11–H11A···O2 hydrogen bonds, forming a $R_2^2(10)$ ring motif (Figure 4). In the crystal of **II**, heterodimers are linked into a centrosymmetric tetramer *via* N5–H1N5···O8 hydrogen bonds, forming a $R_2^2(8)$ ring motif. Crystal **II** is further stabilized by weak $\pi\cdots\pi$ interaction, involving the centroid of phenyl ring of picrate anion (Figure 5).

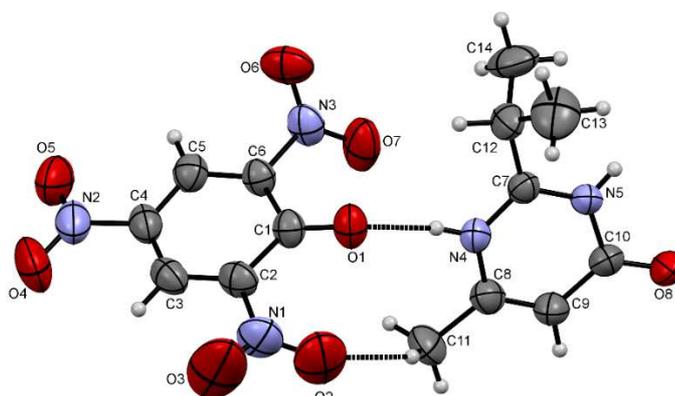


Figure 4: The molecular structure of compound **II** with displacement ellipsoids at 50% probability level and atomic numbering scheme

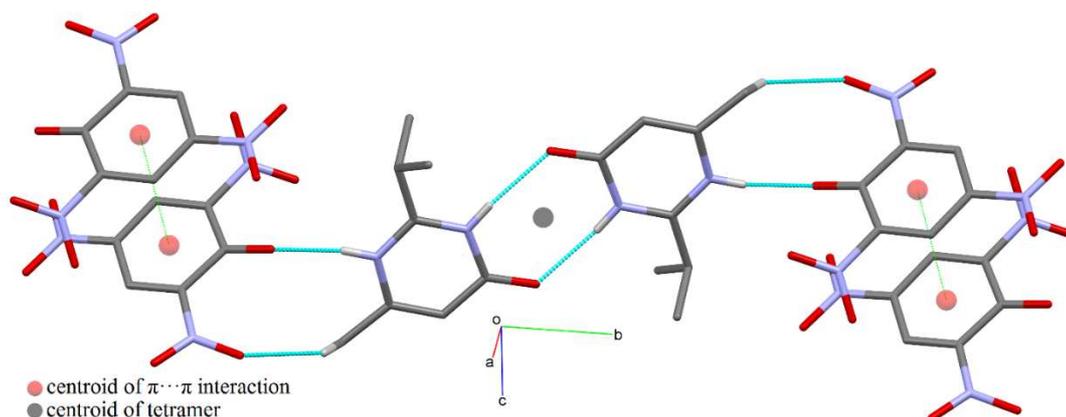


Figure 5: Partial packing diagram of **II** shows centrosymmetric tetramer and $\pi\cdots\pi$ interaction

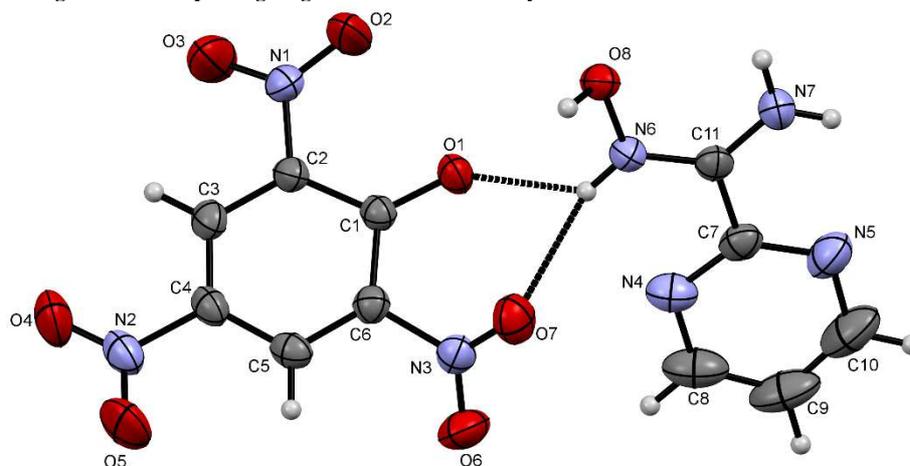


Figure 6: The molecular structure of compound **III** with displacement ellipsoids at 50% probability level and atomic numbering scheme

Salt **III** is crystallized in non-centrosymmetric monoclinic space group $P2_1$. The asymmetric unit of **III** consists of a *N*-(amino(pyrimidin-2-yl)methylene)hydroxylammonium cation and a picrate anion as shown in Figure 6. Proton transfer is observed from hydroxyl group in picric acid to the imine group in *N*-hydroxypyrimidine-2-carboximidamide. As compared to reported *N*-hydroxypyrimidine-2-carboximidamide crystal [11], bond angle of hydroxyamide moiety (C11–N6–O8) in **II** is stretched by 10° (Table 2). The protonation also caused bond lengths of C1–O1, C11–N7 and N6–O8 shortened to 1.27 Å, 1.31 Å, and 1.38 Å, respectively (Table 2). The N6–C11 double-bond length in **III** and neutral form [11] are similar (1.298 and 1.295, respectively) indicated the C11–N7 bond with similar length is a double-bond. Thus, we suggested a symmetrical delocalized N–C–N fragment is formed upon proton transfer similar to **I**. In the crystal of **III**, cation and anion are linked through bifurcated N6–H1N6 \cdots (O1,O7) hydrogen bond into a supramolecular heterodimer with $R_1^2(6)$ ring motif. These heterodimers are linked into helical chains along *b*-axis via N7–H1N7 \cdots O8 and O8–H1O8 \cdots O1 hydrogen bonds (Figure 7a). The helical chains are further connected by C8–H8A \cdots O5 hydrogen bond into 2D planes parallel to *bc*-plane (Figure 7b).

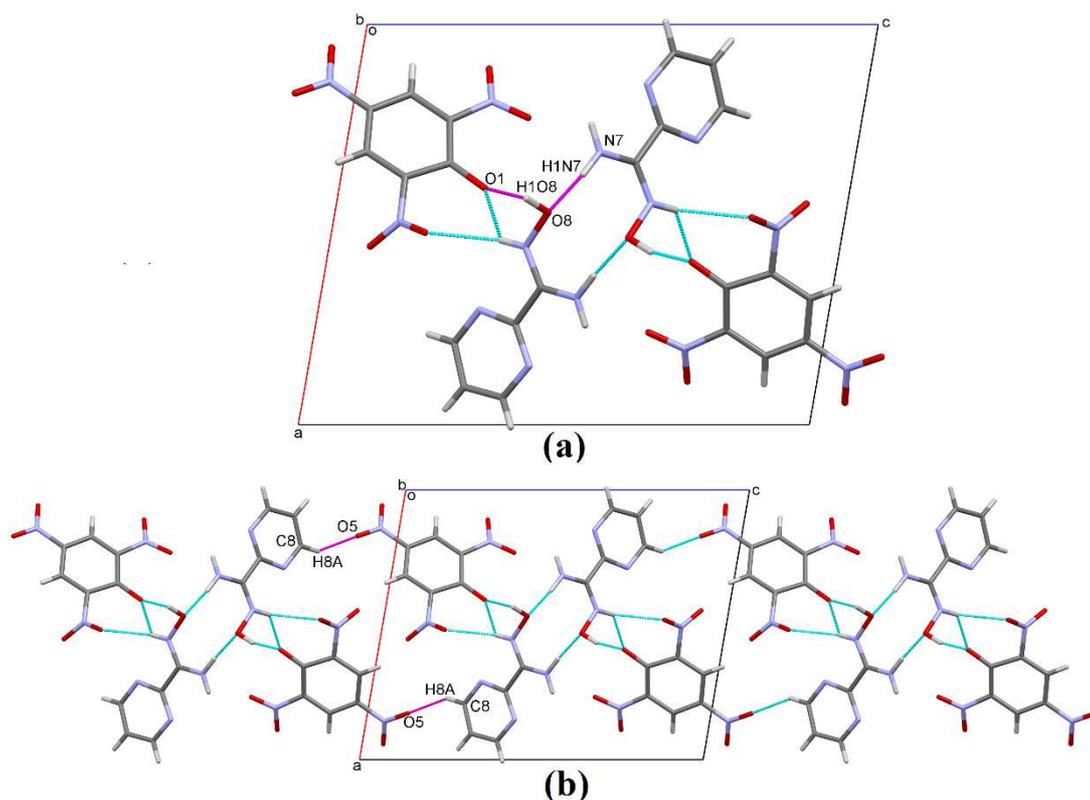


Figure 7: Partial packing of III viewed along *b*-axis shows (a) a helical chain along *b*-axis and (b) a 2D plane parallel to *bc*-plane

Table 4: Hydrogen bond geometries for picrate salts I, II and III

<i>D</i> —H... <i>A</i>	<i>D</i> —H (Å)	H... <i>A</i> (Å)	<i>D</i> ... <i>A</i> (Å)	∠ <i>D</i> —H... <i>A</i> (°)	Symmetry code
I					
N4—H4A...O1	0.86	1.97	2.728 (10)	147	1+x, y, z
N4—H4A...O2	0.86	2.37	3.049 (14)	136	1+x, y, z
N4—H4B...O4	0.86	2.46	3.158 (9)	139	2-x, 1/2+y, 3/2-z
N4—H4B...O5	0.86	2.39	3.098 (9)	139	2-x, 1/2+y, 3/2-z
N5—H5B...O1	0.86	2.00	2.757 (9)	145	1+x, y, z
N5—H5B...O7	0.86	2.49	3.220 (12)	143	1+x, y, z
N5—H5C...O6	0.86	2.57	3.177 (10)	129	1/2+x, 3/2-y, 2-z
N5—H5C...O7	0.86	2.35	3.186 (11)	165	1/2+x, 3/2-y, 2-z
II					
C11—H11A...O2	0.96	2.54	3.418 (4)	151	<i>x</i> , <i>y</i> , <i>z</i>
N4—H1N4...O1	0.82 (4)	1.87 (4)	2.676 (3)	167 (2)	<i>x</i> , <i>y</i> , <i>z</i>
N5—H1N5...O8	0.80 (3)	2.00 (3)	2.791 (2)	171 (3)	- <i>x</i> , 1- <i>y</i> , - <i>z</i>
III					
N6—H1N6...O1	0.88 (3)	2.11 (3)	2.797 (2)	134 (2)	<i>x</i> , <i>y</i> , <i>z</i>
N6—H1N6...O7	0.88 (3)	2.28 (3)	2.983 (2)	137 (3)	<i>x</i> , <i>y</i> , <i>z</i>
N7—H1N7...O8	0.92 (4)	2.05 (4)	2.951 (3)	166 (3)	1- <i>x</i> , -1/2+ <i>y</i> , 1- <i>z</i>
O8—H1O8...O1	0.92 (3)	1.63 (3)	2.533 (2)	165 (3)	<i>x</i> , -1+ <i>y</i> , <i>z</i>
C8—H8A...O5	0.93	2.43	3.259 (4)	149	1- <i>x</i> , 1/2+ <i>y</i> , - <i>z</i>

CONCLUSION

Supramolecular networks of three picrate crystals (**I**, **II** and **III**) are investigated by single-crystal X-ray diffraction analysis. The bond lengths and angles of moieties which involved in proton transfer are differ from their corresponding neutral co-former or related molecule. In all salts, the picrate anions are hydrogen-bonded to the protonated imine group or pyrimidine ring to form supramolecular heterosynthons *via* $N^+H\cdots O$ interactions.

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