ORIGINAL RESEARCH

N-H...O, C-H... O hydrogen-bonded supramolecular frameworks in 4-fluoroanilinium and dicyclohexylaminium picrate salts

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Abstract



The asymmetric unit of compound (I), 4-fluoroanilinium picrate, $C_6H_7NF^+$. $C_6H_2N_3O_7^-$ contain one 4-fluoroanilinium cation and one picrate anion whereas in compound (II), dicyclohexylaminium picrate, $C_{12}H_{22}N^+$. $C_6H_2N_3O_7^-$ the asymmetric unit contains two sets of dicyclohexylaminium cation and picrate anion due to conformational difference between the molecules. In (I), all three nitro groups of the picrate anion are positionally disordered over two sites refined to major and minor components. The molecular ions of (I), interlinked through N–H O and C–H O hydrogen bonds forming two-dimensional supramolecular sheet along (-1 0 1) plane. Whereas in (II), the symmetry-independent molecules labeled as A and B molecule form independent one-dimensional supramolecular tape extending along (1 1 0) and (1 0 0) direction. The supramolecular tapes are interlinked through C–H O interaction to form three-dimensional network in the crystalline solid in (II).

Keywords Supramolecular · Hydrogen bond · Picrate · Framework · FT-IR · Motif

Introduction

Crystal engineering of organic solids, especially with respect to understanding the nature of various intermolecular interactions, have profoundly influenced the concept of supramolecular chemistry [1, 2]. The nature of intermolecular interactions influences crystal engineering including hydrogen bond, weak interaction, halogen bond, $\pi \dots \pi$ interaction, and short contacts between molecular or ionic compounds [3]. The specificity, directionality, and predictability of intermolecular interaction/hydrogen bond can be utilized to assemble supramolecular structures with controlled dimensionality which tend to exhibit interesting electrical, magnetic, and optical properties of our interest [4, 5]. Among all non-covalent interactions, hydrogen bond plays an important role in chemistry, biology, and materials science. Identifying hydrogen-bonded motifs and supramolecular synthons are very important to crystal

☑ Jagan Rajamoni phyjagan@gmail.com engineering as hydrogen bonded motifs between building blocks that can be used to propagate networks or supramolecular structures [6, 7]. Formation of salts and co-crystals favors the understanding of supramolecular synthon which enables us to enhance the desired properties. Picric acid forms crystalline co-crystals and salts with various organic molecules by virtue of its acidic nature and forms salts through specific electrostatic and hydrogen bonding interactions. Picric acid (2,4,6 trinitrophenol) is an organic acid which is used in dyeing industry and explosive. Picric acid is used in human therapy as treating burns, antiseptic, and astringent agent [8]. The presence of electron-withdrawing groups makes it as a π -acceptor for a neutral carrier donor molecule. A variety of picrate salts have been previously reported by us and others such as piperidinium picrate, 3methylanilinium picrate, 1-prolinium picrate, and 2-amino 4.6 dimethoxypyrimidinium picrate [9-12]. It is observed that picrate salts form interesting hydrogen-bonded supramolecular motifs and one-, two-, and three-dimensional networks with respect to the nature of the substitution present in cations. Reported literature shows that bulk crystals of picrate salts are best candidates which exhibit good nonlinear optical properties [13, 14]. In the present work, we have studied the crystal structure and hydrogen-bonded supramolecular networks in 4-fluoroanilinium picrate and dicyclohexylamminium picrate salts as follows.

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Experimental

Synthesis and crystallization

Compound (I) was prepared by taking an equimolar mixture of 4-fluoroaniline (1.11 g, 0.01 mol) and picric acid (2.29 g, 0.01 mol) in ethanol solution. The mixture was continuously stirred for 2 h to attain a homogenous solution. The saturated yellow-colored solution was filtered to a clean beaker and kept for crystallization without any atmospheric disturbance. Good diffraction quality yellow-colored crystals were obtained after 2 weeks.

Similarly, compound (II) was prepared by taking an equimolar mixture of dicyclohexylamine (1.81 g, 0.01 mol) and picric acid (2.29 g, 0.01 mol) in ethanol solution. The mixture was continuously stirred for an hour until it attains the state of homogenous solution. The resultant saturated solution was filtered in a clean beaker and kept aside for crystallization by the method of slow evaporation. Good diffraction quality yellow-colored crystals were obtained after 10 days. The chemical diagram of compounds (I) and (II) is shown in Scheme 1.

FT-IR studies

The presence of functional groups in the molecular crystal is found from FT-IT analysis. FT-IR spectrum of **(I)** and **(II)** was recorded in the region 4000–400 cm⁻¹ at room temperature using Perkin Elmer Spectrum₁ FT-IR Spectrometer by KBr pellet method.

4-fluoroanilinium picrate

The NO₂ asymmetric stretching vibrations appear in the region 1557–1570 cm⁻¹. The two bands that appear in the region 1330–1370 cm⁻¹ in the spectra of the above salts could be attributed to NO₂ symmetric stretching vibrations. The shift in the frequencies of NO₂ asymmetric and symmetric

Scheme 1 Schematic diagram of compounds (I) and (II)

vibrations on the higher side suggests the formation of picrate salt. From the spectral studies, it is reported that the NH₂ (amine) group gives rise to six characteristic vibrationsasymmetric and symmetric stretching, scissoring, rocking, wagging, and twisting modes. The asymmetric and symmetric stretching modes generally absorbs in the region 3550- 3250 cm^{-1} , the former mode being at a higher magnitude than the latter. The scissoring and twisting modes appear at 1619 cm⁻¹ and 1054 cm⁻¹, respectively, is due to the salt formation between 4-fluoroaniline and picric acid; phenolic hydrogen of picric acid is transferred to the aniline forming NH_3^+ ion, and hence, the bond is formed between the anion and cation. As a result of this, the vibrations of NH_3^+ ion are shifted to lower wave numbers. As shown in Fig. 1, the medium intensity band centered at 3149 cm^{-1} in the spectrum of (I) could be due to NH_3^+ asymmetric stretching vibration. The symmetric NH_3^+ vibration appears at 2860 cm⁻¹ in the spectrum of (I). The corresponding asymmetric vibrations appear at around 1483 cm⁻¹ and 1506 cm⁻¹. The vibrational spectrum of 4-fluoroaniline has been investigated and the C - F stretching vibration appears at 1227 cm⁻¹ with medium intensity.

dicyclohexylamminium picrate

The asymmetric and symmetric stretching vibrations of the NO₂ group have strong absorptions in regions 1570–1485 cm⁻¹ and 1370–1320 cm⁻¹, respectively. As expected, the strong band observed at 1341 cm⁻¹ in the FT-IR spectrum (Fig. 2) could be attributed to NO₂ symmetric vibrations. The asymmetric stretching vibrations of the NO₂ group appear at 1530 cm⁻¹. In phenols, a broad absorption band appears in the region 2500–3500 cm⁻¹ which is primarily due to the OH stretching vibration. The broad medium intensity band centered at 3417 cm⁻¹ in the spectrum of (II) could be attributed to phenolic OH stretching vibration. In the spectrum of (II) (shown in Fig. 2), the NH₂⁺ vibration is present. The weak intensity bands that appear at 3183 cm⁻¹ and 3142 cm⁻¹ could







be attributed to $\rm NH_2^+$ asymmetric stretching vibrations. The corresponding symmetric vibration appears at 2808 cm⁻¹. The bands that appear in the region 1610–1557 cm⁻¹ are due to $\rm NH_2^+$ deformation vibration and this overlaps with the NO₂ vibrations. The out-of-plane deformation of $\rm NH_2^+$ appears at 795 cm⁻¹ and 935 cm⁻¹. The methylene (CH₂) stretching vibrations appear at around 2939 cm⁻¹. The deformations of methylene groups give rise to absorption at 1483 cm⁻¹. The presence of $\rm NH_2^+$ vibrations confirms the transfer of protons from the picric acid to the counter cation.

Single crystal X-ray data collection and refinement

Intensity data collection for both the compounds (I) and (II) were performed using Enraf-Nonius CAD-4 diffractometer with CuK α radiation employed by ω -2 θ scan mode at room temperature. Single crystals of (I) and (II) having size $0.35 \times 0.25 \times 0.20$ mm was used for single crystal X-ray diffraction experiments, after careful selection using a polarizing microscope. Accurate unit cell parameters and orientation matrix for both crystals





Fig. 3 Displacement ellipsoid plot of compound (I) drawn at 40% probability level. Only the major component of the disordered picrate anion is shown for clarity

were obtained by a least-square fit of 25 reflections. The intensity data for (I) and (II) were collected in the θ —range from 4.35° to 67.86° and 2.312° to 67.726°, respectively. During data collection, two standard reflections were monitored for every 100 measurements (reflections), and it showed no significant intensity variations. The intensities were corrected for Lorentz and polarization factor corrections using the XCAD4 computer program [15] followed by the absorption correction carried out using ψ scan data [16].

Crystal structures of compounds (I) and (II) was solved by direct methods procedure using the SHELXS-2018 [17] program and refined by Full-matrix least squares procedure on F^2 using SHELXL-2018 [17] program (Table 1). All the non-hydrogen atoms were subjected to anisotropic refinement whereas the hydrogen

Fig. 4 Displacement ellipsoid plot of compound (**II**) drawn at 40% probability level. Only the major component of the disordered picrate anion is shown for clarity atoms were refined isotropically. In compound (I), all three nitro (NO₂) groups of the picrate anions are positionally disordered over two sites with refined occupancies of 0.804(10) and 0.196(10), respectively. The N-O bond distances of major and minor components of all the three NO₂ groups are fixed to a distance of 1.24(1) Å using suitable restraint (DFIX). Atomic displacement parameters of adjacent atoms were made similar using suitable similarity restraints (SIMU) with an effective standard uncertainty (s.u.) of 0.02 Å for the major and minor components, respectively. Similarly, in compound (II), one of the nitro groups (ortho position) of the picrate anion-A is positionally disordered over two sites with refined occupancies of 0.784(6) and 0.216(6), respectively. Similar to (I), the N-O bond distance of the disordered NO₂ group is restrained to a distance of 1.24(1) Å followed by the atomic displacement parameters of adjacent atoms made similar using suitable similarity restraints (SIMU) with an effective s.u. of 0.02 Å. All the hydrogen atoms for (I) and (II) were identified from the different electron density map and refined accordingly. Hydrogen atoms associated with the carbon atoms were optimized and allowed to ride on the parent atoms with a C-H distance of 0.97 Å for CH₂ and 0.93 Å for aromatic CH and 0.98 Å for methine CH with $U_{iso}(H) =$ $1.2U_{eq}(C)$. Whereas, the hydrogen atoms bound to N atoms of both compounds were refined freely with their N-H distances restrained to a value of 0.90(1) Å. The molecular graphic images of the molecules were drawn using the ORTEP [18] and Mercury 3.9 [19] program. Both structures (I) and (II) (Figs. 3 and 4) were deposited in Cambridge Structural Database, and their reference IDs are CCDC 1938032 and CCDC 1938033.



Result and discussion

Structural features

4-fluoroanilinium picrate

The asymmetric unit comprises one 4-fluoroanilinium cation and a picrate anion. In the picrate anion, all the three nitro groups are disordered over two positions with refined site occupancies of 0.804(10) and 0.196(10), respectively. Interestingly, from the refinement, it is observed that all the nitro groups take same major and minor occupancies. The bond lengths and angles of the picrate anion show the characteristic values, with C1-C2, 1.440(2) Å, C1-C6, 1.439(2) Å, which are longer and deviate from the regular aromatic values, also the C1-O1 value is 1.258(2) Å, which is intermediate between the single and double bonds. These effects are due to the dissociation of a hydroxyl proton at O1, leading to a conversion of neutral to an anionic state of the molecule. Similar effect is observed on other reported salts like 2,2'bipyridinium picrate [20] and 4-dimethylaminopyridinium picrate [21]. The N-O bond distances associated with the nitro group of picrate anion varies from 1.225(4) Å to 1.240(4) Å whereas the C-N distances vary from 1.455(2) Å to 1.460(2) Å which are very much similar to other picrate salts reported in the literature [22]. In the picrate anion, the nitro group at para position is planar with phenyl moiety whereas nitro groups at 2,6 ortho positions deviate significantly from the phenyl plane due to steric effect. The dihedral angle between the ortho NO₂ groups and the benzene plane is observed to be 38.62(4)° and 21.09(1) ° for major and minor conformations and 60.55(4)° and 37.40(4)° for major and minor conformers of 2nd and 6th position respectively. The para nitro group (O4-N2-O5) makes a lesser tilt with the benzene plane compared with the ortho positioned nitro groups with a measured dihedral angle of 11.32(2)° and 18.02(2)° for major 2nd and minor conformations, respectively. The 4-fluoroanilinium molecular ions show the characteristic geometrical parameters except for the C-N bond length involving the protonated nitrogen atom, C7-N4 is 1.467(2) Å which is longer than the neutral value. The picrate and 4-fluoroanilinium ions lie parallel to (2 0-1) and (0 1-1) crystallographic planes, respectively.

dicyclohexylaminium picrate

In dicyclohexylamminum picrate salt (II), the asymmetric unit comprises two sets of anions and cations represented as A and B set of molecules. One of the *ortho* nitro groups (2nd position) of the picrate ion A has positional disorder, and hence, it was resolved into two components. The occupancies for major and minor components are 0.784(6) and 0.216(6), respectively. The bond lengths of the picrate anion show the characteristic values, with C1-O1 bond length [1.236(2) Å (A), 1.246(2) Å (B)] showing a deviation between single and double bond characters and C1-C2 distances [1.449(3) Å (A), 1.446(3) Å (B)] and C1-C6 distances [1.445(3) Å (A), 1.442(3) Å (B)] are longer and deviating from the average standard aromatic C-C value [1.375(3) Å (A), 1.376(3) Å (B)], as observed in other picrate salts. This lengthening of C1-C2 and C1-C6 bonds is ascribed to the dissociation hydrogen from the phenolic OH group to the nitrogen atom of the dicyclohexylamine molecule leading to the conversion of neutral picric acid to an anionic picrate salt. The N-O bond distance of the nitro group in the anion A varies from 1.195(3) Å to 1.228(2) Å and for anion B it ranges from 1.216(2) Å to 1.234(2) Å whereas the C-N distance varies from 1.443(2) Å to 1.464(3) Å for the anion A and the same varies from 1.437(2) Å to 1.460(2) Å for the anion B. This disordered ortho nitro group deviates significantly from the benzene ring moiety of the picrate ion by 33.56(2)° [O2-N2-O3] and 33.06(2)° [O2'-N1-O3'] for the major and minor components while the other ortho nitro group (6th position) is almost coplanar with benzene ring moiety of the picrate ion A [O6-N3-O7, 2.99(2)°]. The para nitro group [O4-N2-O5] of the picrate ion A has an intermediate deviation of 13.98(3)° from the benzene ring moiety. Similarly, one of the ortho nitro groups of the picrate ion B deviates significantly with a dihedral angle of 43.45(3)° [O2-N1-O3] and 9.62(3)° [O6-N3-O7] from the benzene ring moiety, and the para nitro group (4th position) has the tilting angle 11.85(2)°. The tilting behavior of the para nitro groups (O4-N2-O5) and the 6th positioned ortho nitro groups (O6-N3-O7) is different from the other structures, where the para nitro groups lie in the benzene plane and the ortho nitro groups deviate well from this plane (about 30-60°). This is attributed to the intermolecular interactions between the molecular ions through well-defined hydrogen bonds and short contacts. The bond lengths of the protonated nitrogen atom N4 of the cation are found to be 1.501(2) Å [N4-C7] and 1.509(2) Å [N4-C13] for molecule A and that of molecule B are 1.501(2) Å and 1.504(2) Å which is longer than the unprotonated C-N bond distances in dicyclohexylamine [23]. The mean plane calculation for the benzene planes of the picrate ions shows that the atom C2A of anion A deviates maximum [-0.023(2)], and C1B of anion B has the maximum deviation of 0.032(2). The dihedral angle between the anions $[4.2(1)^{\circ}]$ shows that they are essentially parallel to each other.

Supramolecular features

Both picrate salts (I) and (II) exhibit interesting self-assembled supramolecular features in the crystal structure

and is discussed in this section. As picrate anions contain good hydrogen bond acceptor oxygen atom from NO₂ and Ogroup, the molecular self-assembly is mainly due to N-H O and C-H O hydrogen bonds. The details of the hydrogen bond geometry are given in Tables 2 and 3 for (I) and (II), respectively.

4-fluoroanilinium picrate

In the hydrogen-bond formation of compound (I), the protondissociated oxygen atom O1 at (x,y,z) acts as a bifurcated acceptor for hydrogen atoms at H4A at (x,y,z) and H4C at (1-x, 1-y, 2-z) forming N4-H4A O1 and N4-H4C O1ⁱⁱ hydrogen bonds. Inversion related anions and cations form $R_4^{(2)}(8)$ supramolecular motif [24] through N4–H4A O1 and N4–H4C $O1^{ii}$. The nitrogen atom at (x, y, z) form bifurcated hydrogen bonds, N4-H4A O1, N4-H4A O7 and N4-H4C 01ⁱⁱ, N4–H4C 02 through H4A and H4C with acceptor oxygen atoms O1, O7 and O1, O2 to construct a $R_1^2(6)$ motif. In general, inversion related 4-fluoroanilinium cations and picrate anions are linked together by fused $R_4^2(8)$ and $R_1^2(6)$ motifs which constructs the basic molecule. Adjacent molecular motifs are interlinked through N4-H4B O6 hydrogen bond, which generated to a one-dimensional infinite

Table 1 Crystal structure refinement details of compounds Image: Compound structure	Parameters	Compound (I)	Compound (II)
(I) and (II)	Empirical formula	C ₁₂ H ₉ F N ₄ O ₇	C ₁₈ H ₂₆ N ₄ O ₇
	Formula weight	340.23	410.43
	Temperature (K)	296(2)	296(2)
	Wavelength (Å)	1.54184	1.54184
	Crystal system, space group	Triclinic, P -1	Triclinic, P -1
	Unit cell dimensions		
	a(Å)	8.2800(14)	8.7430(6)
	b(Å)	8.4330(14)	11.4872(10)
	c(Å)	10.3200(19)	21.349(3)
	$\alpha(^{\circ})$	97.070(12)	98.744(9)
	β(°)	95.880(14)	98.822(8)
	γ(°)	99.760(14)	101.499(7)
	Volume (Å ³)	699.1(2)	2039.0(3)
	Z, Calculated density (Mg/m ³)	2, 1.616	4, 1.337
	Absorption coefficient (mm ⁻¹)	1.259	0.874
	F(000)	348	872
	Crystal size (mm)	$0.350 \times 0.300 \times 0.250$	$0.350\times0.300\times0.250$
	Theta range for data collection (°)	4.352 to 67.865	2.132 to 67.926
	Limiting indices	0 < =h < =9,	0 < =h < =10,
		-10 < =k < =9,	-13 < =k < =13,
		-12 < =1 < =12	-25 < =1 < =25
	Reflections collected/unique	2718/2531	7720/7191
		(R(int) = 0.0350)	(R(int) = 0.0143)
	Completeness to theta $= 67.684$	100.00%	96.90%
	Absorption correction	Psi-scan	Psi-scan
	Max. and min. transmission	0.924 and 0.867	0.900 and 0.850
	Refinement method	Full-matrix least-squares on F ²	Full-matrix least-squares on F ²
	Data/restraints/parameters	2531/63/285	7191/26/555
	Goodness-of-fit on F ²	1.078	1.026
	Final R indices (I > 2sigma(I))	R1 = 0.0480	R1 = 0.0404
		wR2 = 0.1321	wR2 = 0.1089
	R indices (all data)	R1 = 0.0524	R1 = 0.0653
		wR2 = 0.1370	wR2 = 0.1232
	Extinction coefficient	0.022(2)	0.0057(3)
	Largest diff. peak and hole $(e.Å^{-3})$	0.365 and -0.205	0.19 and -0.17

Table 2 Hydrogen bond geometries of compound (I)

D–HA	d(D–H)	d(H A)	d(D…A)	<(DHA)	
C12–H12…O4 ⁱ	0.93	2.64	3.299(9)	128.6	
С12-Н12…О7	0.93	2.56	3.314(3)	138.3	
N4–H4A…O1	0.878(10)	1.963(11)	2.8272(19)	167.5(19)	
N4–H4C…O1 ⁱⁱ	0.890(10)	1.932(12)	2.798(2)	164(2)	
N4–H4B…O6 ⁱⁱⁱ	0.881(10)	2.172(13)	3.037(6)	167(2)	

Symmetry codes: (i) -x,-y,-z + 1; (ii) -x + 1,-y + 1,-z + 2; (iii) -x + 1,-y,-z + 2

supramolecular tape along the crystallographic (0 1 0) direction as shown in Fig. 5. It is observed that the (0 1 0) tape is made of $R_4^{-2}(8)$, $R_1^{-2}(6)$, and $R_4^{-4}(12)$ motifs with the centroid of $R_4^{-2}(8)$ and $R_4^{-4}(12)$ rings occupy the center of inversion at (1/2, ½, 1) and (1/2, 0, 1,) respectively. Adjacent supramolecular tapes are further connected through a weak C–H O interaction (C12–H12 O4), which generates to a two-dimensional supramolecular sheet extending parallel to (-1 0 1) plane (Fig. 6).

dicyclohexylaminium picrate

In the crystal structure of compound (II), the anions and cations of A and B symmetry independent molecules form independent hydrogen-bonded motif which in turn develop in to a supramolecular framework through C–H O interaction. In A-molecule, the inversion-related anions and cations are linked through strong N–H O hydrogen bonds N4–H4A2 O1A, N4–H4A2 O7A and N4–H4A1 O6A to form two types of ring motifs $R_1^{2}(6)$ and $R_4^{4}(12)$ (Fig. 7a). Here $R_1^{2}(6)$ is formed as a result

 Table 3
 Hydrogen bond geometries of compound (I)

D–Н А	d(D–H)	d(H A)	d(D A)	<(DHA)
N4A–H4A1…O6A ⁱ	0.902(9)	2.429(15)	3.164(2)	138.8(16)
N4A-H4A2…O1A	0.896(9)	1.913(12)	2.759(2)	156.9(17)
N4A–H4A2…O7A	0.896(9)	2.499(16)	3.146(2)	129.5(15)
C13A–H13A…O5A ⁱⁱ	0.98	2.59	3.539(2)	161.8
C14A–H14B…O5B ⁱⁱⁱ	0.97	2.47	3.263(3)	138.3
C18A–H18A…O1A	0.97	2.54	3.297(3)	135
N4B–H4B1…O7B ⁱⁱⁱ	0.904(9)	2.095(10)	2.9986(19)	177.7(17)
N4B-H4B2…O1B	0.897(9)	1.862(11)	2.7038(18)	155.5(16)
N4B-H4B2···O7B	0.897(9)	2.410(15)	3.047(2)	128.2(14)
C18B-H18C…O1B	0.97	2.51	3.249(2)	132.8
C18B–H18C…O2B	0.97	2.64	3.577(2)	161.4

Symmetry codes: (i) -x + 1, -y, -z; (ii) x + 1, y + 1, z; (iii) -x + 1, -y, -z + 1

of bifurcated hydrogen bonds with H4A2 at (x, y, z) and oxygen atoms O1A and O7A of same asymmetric unit. An expected N-H O hydrogen bond is absent between H A atoms H4A1 O7A whose D A distance is observed as 3.317(2) Å, which is longer than the standard value. The O- oxygen atom acts as bifurcated acceptor atom for two types of hydrogen bonds N4A-H4A O1A and C18A-H18A O1A. Adjacent A set of anion-cationic substructure is further linked through a $R_2^2(8)$ motif made of two C-H O interaction C17A-H17A O4A and C13A-H13A O5A which further develops to a onedimensional supramolecular tape extending infinitely along the (1 1 0) direction as shown in Fig. 8a. Similarly, in the case of B-molecules, inversion-related anions and cations are interlinked through N-H O hydrogen bonds N4B-H4B2 O1B, N4B-H4B2 O7B and N4B-H4B1 O7B to form $R_4^2(8)$ and $R_1^2(6)$ motif (Fig. 7b). C-H O interactions have a significant role in the construction of hydrogen-bonded motif. The inversionrelated dicyclohexylamminium cation and picrate anions are linked through C-H O interactions such as C18B-H18C O1B and C18B-H18C O2B, which in turn forms an additional $R_1^2(6)$ motif. Proton dissociated oxygen atom O2B acts as bifurcated acceptor atom for N-H O and C–H O hydrogen bonds which develop to a $R_2^{-1}(6)$ motif. Moreover, as depicted in Fig. 8b, adjacent B set of anions and cations are further interlinked through a weak C-H O interaction (C15–H15C O6B) and a C–H π contact (C16B–H16D π 1, where π 1 = C1B/C2B/C3B/C4B/C5B/ C6B with D A distance of 3.816(4) Å and D-H A angle of 129.01°) form a one-dimensional tape extending infinitely along the crystallographic (1 0 0) direction. In the crystal structure, the (1 1 0) and (1 0 0) one-dimensional supramolecular tapes are interlinked through two C-H O hydrogen bonds C10A-H10B O4B and C11A-H11A O3B to construct a three-dimensional supramolecular framework in the crystal structure.

Cambridge structural database analysis

A search of Cambridge Structural Database (CSD version 5.40) [25] has been done in order to understand the formation of hydrogen-bonded motifs as observed above in closely relevant structures of compounds (I) and (II). As observed in (I), in the crystal structure of 2hydroxyanilinium picrate (ref. code TEZMAO) [26], the inversion-related anions and cations are interlinked through N–H O hydrogen bonds forming similar motifs such as $R_1^2(6)$, $R_4^2(8)$, $R_1^2(6)$ fused together which extends to one-dimensional tape through $R_4^4(12)$ motif. Unit cell parameters of both the structures are similar to each other except for slight difference in angles. Also, in the crystal structure of anilinium picrate (ref. code





ZZZLBS02) [27] and 2-iodoanilinium picrate (ref. code ZEDPON01) [28] the inversion-related anions and cations are interlinked through N–H O hydrogen bonds forming the expected $R_1^2(6)$, $R_4^2(8)$, $R_1^2(6)$ fused motif. In this structure the $R_4^4(12)$ motif is absent, instead it forms a linear N–H O hydrogen bond between the adjacent inversion-related anion-cation pair. Interestingly, in both structures ZZZLBS02 and ZEDPON01, the inversionsrelated anionic-cationic pairs are twisted away each other compared with planar motifs in compound (I). The expected hydrogen-bonded supramolecular motif is not observed in closely related structure, 4-methylanilinium picrate (ref. code LIGYAD) [29]. Absence of inversionrelated motifs may be attributed to the large deviation of both nitro groups from the phenyl plane due to steric effect. Attempt was made for CSD search relevant to compound (II) with cyclohexyl amine and NH_2^+ substitution. But during the search, to our observation, in the crystal structure of cyclohexylaminium picrate salt (Ref. code GAWCOX) [30] and Gabapentinium picrate (Ref. code LORQIT) [31] due to the presence of NH_3^+ group, the inversion-related anions and cations are interlinked through N–H O hydrogen bonds showing $R_1^2(6)$, $R_4^2(8)$, $R_1^2(6)$ motifs fused together which extends to one-dimensional supramolecular tape through $R_4^4(12)$ motif. Similar type of supramolecular motifs is observed in the crystal structures of cyclohexane 1,2 diaminium bis (picrate) (ref. code HEWFAS) [32] and piperazinium di picrate (ref. code TONBEF) [33] salts except for the absence of connecting $R_4^4(12)$ motif. From the above



Fig. 6 Part of the crystal structure of (I) showing the formation of two-dimensional supramolecular sheet extending parallel to (-1 0 1) plane. Hydrogen atoms not involved in hydrogen bonds are omitted for clarity

Fig. 7 Part of structure **(II) a** shows the formation of inversion related A set of anions and cations linked through N–H O and C–H O hydrogen bonds thus constructing $R_1^{2}(6)$, $R_4^{4}(12)$, $R_2^{1}(6)$ motifs and **b** shows the formation of inversion related B set of anions and cations linked through N–H O and C–H O hydrogen bonds thus constructing $R_1^{2}(6)$, $R_4^{2}(8)$, $R_2^{1}(6)$, $R_2^{1}(7)$ motifs. Hydrogen atoms not involved in hydrogen bonds are omitted for clarity



discussion and comparison with reported structures show that in picrate salts, the formation of $R_1^2(6)$ motif is dominant over other hydrogen bond motifs. This is due to the presence of deprotonated oxygen atom (O⁻) and ortho NO₂ groups. Also, the formation of $R_4^{-2}(8)$ and $R_4^{-4}(12)$ motifs are expected in most of inversion-related molecules having $\rm NH_3^+$ and $\rm NH_2^+$ functional groups. Absence of these motifs in organic picrate salts may be attributed due to the deviation of ortho NO₂ groups from mean benzene plane as well as the presence of other functional



Fig. 8 Part of the crystal structure of (**II**) showing **a** the formation of onedimensional supramolecular tape constructed by A-set of anions and cations through N–H O and C–H O hydrogen bonds extending along (1 1 0) direction. **b** Showing the formation of one-dimensional supramolecular

tape constructed by B-set of anions and cations through N–H $\,$ O, C–H O hydrogen bonds and C–H $\,\pi$ interaction extending along (1 0 0) direction. Hydrogen atoms not involved in the hydrogen bonds are omitted for clarity

groups in counter molecule which has the tendency to form hydrogen bonds with ortho nitro groups.

Conclusion

The presence of functional groups such as NO₂, O⁻, NH₂⁺ and NH₃⁺ in 4-fluoranilinium and dicyclhexylaminium picrate form strong N–H O, C–H O hydrogen bonds leading to the formation of one-, two-, and three-dimensional supramolecular frameworks. Picrate salts form interesting $R_4^2(8)$ and $R_4^4(12)$ hydrogen-bonded supramolecular motifs in molecules having NH₂⁺ and NH₃⁺ groups. Absence of $R_4^2(8)$ and $R_4^4(12)$ motifs in certain picrate salts may be due to the deviation of ortho nitro group (NO2) from the mean benzene plane. Structural and hydrogen bond analysis of picrate salts shows that the choice of functional group in cation moiety will help to tune the supramolecular framework/motif of desired fashion.

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