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Study of picrate salts with amines

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HIGHLIGHTS

- Synthesis of four new salts of picric acid with amines.
- Comparison of solid state and gaseous phase structure for picrate salts.
- The mechanism of thermal decomposition was studied.
- ► Study of the explosive behavior.

G R A P H I C A L A B S T R A C T

The reaction of picric acid (2,4,6-trinitrophenol) with amines [urea, cyclohexane-1,2-diamine, *1H*-1,2,4-triazole-3,5-diamine, 6-phenyl-1,3.5-triazine-2,4-diamine] yielded the corresponding picrate salts **1–4**. Theoretical studies reveal that the hydrogen-bond interaction energy decreases on increasing the steric hindrance in amines. The solid state structure of compounds **1–4** was measured by X-ray techniques and compared to the gas phase optimized geometries (DFT/B3LYP). Thermal stability of these salts has been studied.



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ABSTRACT

The reaction of picric acid (2,4,6-trinitrophenol) with amines [urea, cyclohexane-1,2-diamine, *1H*-1,2,4-triazole-3,5-diamine, 6-phenyl-1,3.5-triazine-2,4-diamine] yielded the corresponding picrate salts **1–4**. Theoretical studies reveal that the hydrogen-bond interaction energy decreases on increasing the steric hindrance in amines. The solid state structure of compounds **1–4** was measured by X-ray techniques and compared to the gas phase optimized geometries (DFT/B3LYP). Thermal stability of these salts has been studied by means of thermogravimetric-differential scanning calorimetry (TG–DSC) while kinetic parameters have been evaluated using models fitting and isoconversional methods. Thermolytic pathways have also been suggested.

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1. Introduction

Picric acid (2,4,6-trinitrophenol) is used to produce very sensitive compounds since the nitro groups are the powerful oxidizing groups, which decompose and explode at elevated temperature [1-5]. The crystal structures of picrate salts with amines have been studied in the past [6-10] but the mechanism of thermal analysis, explosion delay measurement are not yet reported in literature. When the picric acid is combined with amines, the resultant salts undergoes self propagative decomposition reaction due to the presence of both oxidizing (picric acid) and reducing (amines)

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groups in the same molecule. A proton transfer mechanism has been postulated to play an important role in the thermal decomposition of almost all the ammonium salts as this was suggested as a primary step in the thermal decomposition [11–16]. Due to these attractive features, amines have been combined with picric acid to see the effect on explosive properties in comparison with picric acid. In the present article, the preparation, characterization and thermal study of picrate salts with amines are described. Thermoanalytical techniques provide the information about the overall kinetics of thermally induced reaction, which reveals the decomposition and mechanism of picrate salts via solid-state reactions.

2. Experimental

2.1. Materials

All manipulations were performed in air using commercial grade solvents. Picric acid, cyclohexane-1,2-diamine, *1H*-1,2,4-triazole-3,5-diamine and 6-phenyl-1,3,5-triazine-2,4-diamine were purchased from Aldrich Chemical Company, USA while urea was commercially available from SD Fine-Chem Limited, Mumbai.

2.2. Syntheses of organic salts

2.2.1. Synthesis of [uronium picrate] (1)

Picric acid (0.22 g, 1.0 mmol) and urea (0.06 g, 1.0 mmol) were mixed in a water-methanol mixture (v/v%, 1:4, 10 ml). The resulting solution was stirred for 6 h and filtered through celite. The filtrate was evaporated to dryness under vacuum and the yellow solid obtained was redissolved in methanol. The yellow crystals of salt **1** were obtained by slow evaporation (0.21 g, 71.5% yield). Anal. Calcd. (%) for C₇H₇N₅O₈ (289.18): C, 29.07; H, 2.43; N, 24.22; Found: C, 28.93; H, 2.34; N, 24.17. IR (KBr, cm⁻¹): 3412, 3103, 2882, 1856, 1709, 1635, 1534, 1432, 1345, 1148, 1082, 926, 826, 774, 729, 530. ¹H NMR (DMSO-*d*₆, ppm) δ: 8.75 (s, 2H, picrate), 6.49 (s, br, 4H, -NH₂). ¹³C NMR (DMSO-*d*₆, ppm) δ: 159.61, 140.95, 126.56, 125.17, 116.61.

2.2.2. Synthesis of [1/2cyclohexane-1,2-diaminium picrate] (2)

Picric acid (0.22 g, 1.0 mmol) and cyclohexane 1,2-diamine (0.11 g, 0.5 mmol) were mixed in a water-methanol mixture (v/ v%, 1:4, 10 ml). The resulting solution was refluxed for 2 h and filtered through celite. The filtrate was evaporated to dryness under vacuum and the yellow solid obtained was redissolved in methanol. The yellow diamond shaped crystals of salt **2** were obtained by slow evaporation (0.39 g, 69.7% yields). Anal. Calcd. (%) for C₁₈H₂₀N₈O₁₄ (572.42): C, 37.77; H, 3.52; N, 19.57; Found: C, 37.53; H, 3.41; N, 19.47. IR (KBr, cm⁻¹): 3429, 2926, 1633, 1547, 1489, 1428, 1342, 1265, 1084, 910, 780, 702, 628. ¹H NMR (DMSO-*d*₆, ppm) δ: 8.76 (s, 2H, picrate), 2.89–3.23 (m, 2H, CH), 1.65–2.21 (m, 4H, CH₂), 1.31–1.81 (m, 4H, CH₂), 7.9 (s, br, 6H, NH₃). ¹³C NMR (DMSO-*d*₆, ppm) δ: 159.59, 140.94, 126.53, 125.15, 57.15, 51.22, 34.99, 30.38, 24.98, 21.33.

2.2.3. Synthesis of [3,5-diamino-1,2,4-triazolium picrate] (3)

Salt **3** was prepared by the same procedure as outlined above for **2** with *1H*-1,2,4-triazole-3,5-diamine (0.09 g, 1.0 mmol) in 77.8% (0.25 g) yield. Anal. Calcd. (%) for $C_8H_8N_8O_7$ (328.22): C, 29.37; H, 2.15; N, 34.25. Found: C, 29.23; H, 2.05; N, 34.11. IR (KBr, cm⁻¹): 3460, 3418, 3354, 3168, 1839, 1689, 1627, 1548, 1430, 1329, 1272, 1163, 1076, 999, 912, 788, 711, 656. ¹H NMR (DMSO-*d*₆, ppm) δ : 8.77 (s, 2H, picrate), 12.55 (s, br, 2H, NH), 6.43 (s, br, 4H, -NH₂). ¹³C NMR (DMSO-*d*₆, ppm) δ : 159.58, 156.02, 152.15, 140.92, 126.54, 125.21. 2.2.4. Synthesis of [6-phenyl-2,4 diamino-1,3,5-triazinium picrate] (4)

Salt **4** was prepared by the same procedure as outlined above for **2** with 6-phenyl-1,3,5-triazine-2,4-diamine (0.18 g, 1.0 mmol) in 67.0% (0.27 g) yield. Anal. Calcd. (%) for $C_{15}H_{12}N_8O_7$ (416.33): C, 43.28; H, 2.90; N, 26.91. Found: C, 43.19; H, 2.83; N, 26.49. IR (KBr, cm⁻¹): 3378, 3105, 2874, 1856, 1673, 1535, 1429, 1336, 1154, 1082, 976, 855, 778, 704, 534. ¹H NMR (DMSO-*d*₆, ppm) δ : 8.79 (s, 2H, picrate), 12.58 (s, br, 1H, NH), 7.49-8.31 (m, 5H, Ph), 6.81 (s, br, 4H, -NH₂). ¹³C NMR (DMSO-*d*₆, ppm) δ : 170.62, 167.88, 159.60, 140.93, 137.52, 131.50, 128.60, 128.12, 126.57, 125.16.

2.3. Instrumentation

Crystallized salts were carefully dried under vacuum for several hours prior to elemental analysis on Elementar Vario EL III analyzer. IR spectra were recorded on a Thermo Nikolet Nexus FT-IR spectrometer on KBr pellets. ¹H and ¹³C NMR spectra were recorded on Bruker-D-Avance 500 MHz spectrometer with Fourier transform technique using tetramethylsilane as internal standard.

2.3.1. X-ray crystallography

The X-ray data collection were performed on a Bruker Kappa Apex four circle-CCD diffractometer using graphite monochromated Mo K α radiation (λ = 0.71070 Å) at 100 K. In the reduction of data Lorentz and polarization corrections, empirical absorption corrections were applied [17,18]. Crystal structures were solved by direct methods. Structure solution, refinement and data output were carried out with the SHELXTL program [18,19]. Non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in geometrically calculated positions by using a riding model. Images and hydrogen bonding interactions were created in the crystal lattice with DIAMOND and MERCURY software [20,21].

2.3.2. Computational study

Geometry optimization of the different compounds in this work was carried out using Density Functional Methods with a 6-31G(d,p) basis set using Gaussian 03 suite of program [22,23]. The input for the simulation was the *Z* matrix generalized by Gaussview that was also used for visualizing the molecules with optimized geometries. Lastly, we performed a frequency calculation using the same method.

2.3.3. Thermal analysis

2.3.3.1. *TG–DSC*. Thermogravimetry and differential scanning calorimetry (TG–DSC) was carried out at a rate of 10 °C/min (sample mass = 5.5 mg) under a nitrogen atmosphere at a flow rate of 200 ml/min on a Perkin–Elmer's (Pyris Diamond) thermogravimetry analyzer.

2.3.3.2. Isothermal TG. The isothermal TG studies (wt. 0.03 g, 100–200 mesh) of salts **1–4** were performed at appropriate temperatures (230–270 °C) in static air using indigenously fabricated TG apparatus [24] fitted with a temperature cum controller.

2.3.3.3. Explosion delay measurements. The explosion delay (D_E) data were recorded using the tube furnace technique [25] (mass 0.02 g, 100–200 mesh) in the temperature range 380–420 °C (±1 °C). Each run was repeated five times and the mean D_E values were calculated. The D_E data were found to fit in the following equation [26–28].

$$D_E = A e^{E_a^*/RT}$$

where E_a^* is the activation energy for thermal explosion, *A* is the pre-exponential factor and *T* is the absolute temperature. E_a^* was

determined from the slope of a plot of $\ln (D_E)$ vs. 1/T (Fig. 13). The percent oxygen balance (OB) was calculated by a general equation suggested by Martin and Yallop [29].

2.3.4. Kinetics analysis of isothermal TG data

The kinetic analysis of a solid state decomposition is usually based on the following single step kinetic equation [30].

$$d\alpha/dt = k(T)f(\alpha) \tag{1}$$

where *t* is the time, *T* is the temperature, α is the extent of conversion ($0 < \alpha < 1$), k(T) is the rate constant and $f(\alpha)$ is the reaction model [31], which describes the dependence of the reaction rate

on the extent of reactions. The value of α is experimentally derived from the global mass loss in TG experiments. The reaction model may take various forms; the temperature dependence of k(T) can be satisfactorily described by the Arrhenius equation, whose substitution into Eq. (1) yields

$$d\alpha/dt = A \exp(-E/RT) \cdot f(\alpha)$$
⁽²⁾

where A is pre exponential factor, E is activation energy and R is the gas constant.

2.3.4.1. Model fitting method. Rearrangement and integration of Eq. (1) for isothermal conditions gives



Scheme 1. General method for preparation of salts 1-4.

Table 1

Crystal data and structure refinement parameters of salts 1-4.

Salts	(1)	(2)	(3)	(4)
Formula	C ₇ H ₇ N ₅ O ₈	C ₁₈ H ₂₀ N ₈ O ₁₄	$C_8H_8N_8O_7$	C ₁₅ H ₁₂ N ₈ O ₇
Formula weight	289.18	572.42	328.22	416.33
Crystal system	Monoclinic	Monoclinic	Monoclinic	Triclinic
Space group	P21/c	C2/c	C2/c	<i>P</i> – 1
a (Å)	3.886(11)	22.105(8)	22.834(14)	7.604(16)
b (Å)	25.824(8)	8.165(3)	4.808(3)	7.940(19)
c (Å)	11.167(3)	14.524(5)	22.557(14)	14.596(4)
α (°)	90	90	90	88.56(9)
β(°)	93.71(11)	117.74(16)	94.17(3)	81.72(9)
γ(°)	90	90	90	77.43(9)
V (Å ³)	1118.4(6)	2319.8(14)	2470(3)	851.3(3)
Ζ	4	4	8	2
Temperature	296(2)	296(2)	296(2)	296(2)
D_{Calc} (g/cm ³)	1.717	1.639	1.765	1.624
μ (Mo K _{α}) (cm ⁻¹)	0.158	0.143	0.156	0.133
F(000)	592	1184	1344	428
Crystal size	0.32 ↓ 0.26 ↓ 0.21	0.31 ↓ 0.27 ↓ 0.21	0.24 ↓ 0.21 ↓ 0.17	0.29 ↓ 0.19 ↓ 0.13
Theta for data collection (°)	1.58-28.29	2.88-28.43	1.79-29.56	1.41-27.21
No. of measured reflections	2754	2699	3353	3678
No. of observed reflections	1934	1650	2137	1609
Data/restraints/parameters	2754/0/182	2699/0/182	3353/0/224	3678/0/275
Goodness-of-fit	1.222	1.563	0.917	1.084
Final R indices $[I > 2(I) R_1^a]$	0.046	0.078	0.044	0.090
wR ₂ ^b	0.146	0.223	0.125	0.168

^a $R1 = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|.$

^b wR2 = { $\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma w(F_o^2)^2$ }^{1/2}.

$$g_j(\alpha) = k_j(T)t \tag{3}$$

where $g(\alpha) = {}_{0}\int^{\alpha} [f(\alpha)]^{-1} d\alpha$ is the integrated form of the reaction model. The subscript *j* has been introduced to emphasize that substituting a particular reaction model in Eq. (3) results in evaluating the corresponding rate constant, which is determined from the slope of a plot of $g_{j}(\alpha)$ vs. *t*. For each reaction model selected, the rate constants are evaluated at several temperatures T_{i} and Arrhenius parameters are determined using the Arrhenius Eq. (4) in its logarithmic form

$$\ln k_j(T_i) = \ln A_j - E_j / RT_i \tag{4}$$

Arrhenius parameters were evaluated for isothermal experimental data by the model fitting method.

2.3.4.2. Isoconversional method. This method allows the activation energy to be calculated without making any assumptions about the reaction model. Additionally, the method evaluates the effective activation energy as a function of the extent of conversion which allows one to explore multistep kinetics. The basic assumption of the isoconversional method [31] is that the reaction model as defined in Eq. (1) is not dependent on temperature or heating rate. Under isothermal conditions, on combining Eqs. (3) and (4) we obtain:

Table 2	
Non-covalent interactions for 1-4	[distances (Å) angles (°)].

$$-\ln t_{\alpha,i} = \ln \left[A_{\alpha}/g(\alpha)\right] - E_{\alpha}/RT_i$$
(5)

where E_{α} is evaluated from the slope of the plot of $-\ln t_{\alpha,i}$ against T_i^-1 . Thus, E_{α} at various α_i for salts **1–4** have been evaluated.

3. Results and discussion

The reaction of picric acid with the following amines [urea, cyclohexane-1,2-diamine, 1H-1,2,4-triazole-3,5-diamine, 6-phenyl-1,3,5-triazine-2,4-diamine] in methanol-water mixtures resulted in the formation of ionic salts (1-4) according to Scheme 1. The formation of salts 1-4 was confirmed by elemental analysis, IR, NMR and crystallographic studies. The asymmetric and the symmetric stretching vibrations of -NO2 group show bands at 1536 cm^{-1} and 1334 cm^{-1} , respectively [32,33]. The shift of the $v_{as}(NO_2)$ vibration to lower frequency (1581–1530 cm⁻¹) in the spectrum of the salts (1-4) compared with the free picric acid (1607 cm^{-1}) suggested the large electron density on the picric acid. The NH stretching vibration is normally observed at 3500-3400 cm⁻¹ which is shifted to lower wave number due to the attraction of the -NH protons by the picrate anion leading to an increase in –NH bond length in salts (1–4) [34]. The shifting towards lower frequency in both cases, is due to the hydrogen bonded noncovalent interactions between donor (-NH protons) and acceptor (picrate anion) [35]. The hydrogen bonding characteristic of salts

S.n	D−H···A	d(D-H)	d(D-H) d(H-A)		$\langle (DHA) \rangle$	
1	(1)					
	011-H11···01	0.821	1.740(2)	2.547	167.0	
	011-H11···07	0.821	2.340(9)	2.762	112.6	
	N6-H6A····O1	0.861	2.135(6)	2.817	135.7	
	N6-H6A···O2	0.861	2.651(4)	3.453	155.4	
	N6-H6B···O6	0.860	2.701(2)	3.384	137.2	
	N6-H6B····07	0.860	2.373(10)	3.218	167.5	
	N7–H7A···O2	0.860	2.246(8)	3.076	161.9	
	N7-H7A···O3	0.860	2.968(2)	3.753	152.7	
	N7−H7B· · · O4	0.860	2.625(5)	3.106	116.5	
	N7-H7B····O6	0.860	2.224(3)	3.024	154.5	
	C3-H3···O3	0.930	2.587(7)	3.478	160.6	
	C5-H505	0.930	2.999(15)	3.884	159.4	
2	(2)					
	N4−H4A…01	0.889	2.092(18)	2.755	141.6	
	N4−H4A…07	0.889	2.385(6)	2.928	119.5	
	N4-H4B····07	0.890	2.293(16)	3.126	155.9	
	N4-H4C····O1	0.890	1.928(8)	2.755	153.9	
	N4-H4C····O2	0.890	2.428(10)	2.940	116.9	
	C2−H2B···O6	0.969	2.431(22)	3.347	157.3	
3	(3)					
	N1-H1···O1	0.877	1.932(27)	2.674	141.4	
	N2-H2···O4	0.894	2.357(29)	3.229	165.0	
	N4-H4A05	0.867	2.689(35)	3.037	105.4	
	N4−H4B…05	0.867	2.688(49)	3.034	105.5	
	N5-H5A···O3	0.861	2.203(26)	3.034	161.0	
	N5-H5B01	0.860	2.234(28)	2.914	136.0	
	N4-H4BN3	0.867	2.115(31)	2.967	167.5	
	C7-H706	0.929	2.699(6)	3.042	102.7	
4	(4)					
	N6-H6···O1	0.810	1.920(37)	2.685	157.3	
	N6-H6···07	0.810	2.567(63)	3.159	131.0	
	N7–H7A···O2	0.859	2.389(15)	3.144	146.9	
	N7-H7A···O3	0.850	2.377(9)	3.172	154.0	
	N7−H7B…01	0.860	1.964(8)	2.710	144.4	
	N7−H7B…O2	0.860	2.227(12)	2.902	135.2	
	N8-H8B07	0.860	2.113(11)	2.925	157.0	
	N8-H8A····N5	0.861	2.248(13)	3.062	157.8	
	C12-H1204	0.930	2.593(8)	3.223	125.5	
	C13-H1304	0.930	2.728(11)	3.297	120.3	
	C14-H1405	0.930	2.537(11)	3.376	150.2	
	C15-H1503	0.930	3.012(16)	3.906	161.8	

1–4 in the solution was studied by ¹H NMR spectroscopy. The prominent downfield chemical shift in the NMR spectra observed in each case with respect to the free ligand [(DMSO- d_6 , 500 MHz) Picric acid, 8.72 (s, 2H); urea, 5.61 (s, br, 4 H, $-NH_2$); cyclohexane-1,2-diamine, 7.2 (s, br, 6H, $-NH_3$), 2.80–3.10 (m, 2H, CH), 1.55–2.10 (m, 4H, CH₂), 1.01–1.55 (m, 4H, CH₂); *1H*-1,2,4-triazole-3,5-diamine, 5.2 (s, br, 4H, $-NH_2$), 12.52 (s, br, 1H, NH); 6-phenyl-1,3,5-triazine-2,4-diamine, 6.76 (s, br, 4H, $-NH_2$), 7.44–8.26 (m, 5H, Ph] suggested the existence of hydrogen bonding in the solution. The crystallographic and the selected hydrogen bonding data are given in Tables 1 and 2, respectively.

3.1. Structure description

3.1.1. Crystal structure of [uronium picrate] (1)

Salt **1** crystallizes in monoclinic with the space group $P_{2_1/C}$ (*Z* = 4). The unit cell contains one uronium cation and one picrate anion. The molecular structure is depicted in Fig. 1, where it shows that the acidic hydrogen of the hydroxyl group on picric acid protonates the oxygen atom (O11) of urea and making the cation. The molecular packing analysis shows that the N–O (acceptor) and C–H

(donor) of picrates are self dimerized with $R_2^2(10)$ motif involving C–H···O [C3–H3···O3, 2.587(7) Å; C5–H5···O5, 2.999(15) Å] interactions and weak O···O [O5···O6, 2.889(8) Å; O3···O4, 3.198(16) Å] intermolecular interactions, which are responsible for one dimensional spiral molecular arrangement as shown in Fig. S1a. The protonated oxygen (O11) of urea shows the strong hydrogen bonding with the phenolic oxygen atom (O1) of picrate via O–H···O [O11–H11···O1, 1.740(2) Å] interaction. Both organic moieties make three dimensional zig-zag arrangement along the 'c' axis through N–H···O and O–H···O [O11–H11···O7, 2.340(9) Å] non-covalent interactions (Fig. 2, S1b, Table 2).

3.1.2. Crystal structure of [1/2cyclohexane-1,2-diaminium picrate] (2)

According to Fig. 3, the asymmetric unit of salt **2** contains one molecule of picrate and half molecule of ½ cyclohexane-1,2-diaminium which crystallizes in monoclinic system with *C*2/c space group. In 1,2-diaminocyclohexane, both amino nitrogens (N4) are protonated by the hydroxyl group of both picric acid molecules. Picrate anions are self assembled to form a hydrogen bonded homomeric synthons through $0\cdots 0$ [$02\cdots 06$, 3.109(10) Å; $05\cdots 07$, 3.160(12) Å; $04\cdots 06$, 3.139(5) Å]



Fig. 1. Molecular structure of salt 1.



Fig. 2. Three dimensional zig-zag molecular arrangements along the 'c' axis in 1.



Fig. 3. Molecular structure of salt 2.



Fig. 4. Perspective view of the supramolecular motif in 2.

and C8–H8… π [3.250(3)Å] intermolecular interactions. The four picrates non-covalently interact via O…O, generate a cavity of size 1.54 Å (Fig. S2a), resulting in the three dimensional spiral packing as shown in Fig. S2b. On the other side, ½ cyclohexane-1,2-diaminium acts as a base and does not assemble with the same molecule but shows non-covalent interactions with four molecules of picrate anions through N–H…O [N4–H4A…O1, 2.092(18)Å; N4–H4A…O7, 2.385(6)Å; N4–H4B…

O7, 2.293(16) Å, N4–H4C···O1, 1.928(8) Å; N4–H4C···O2, 2.428(30) Å]. The extended hydrogen bonding network is also formed which involves $R_2^2(8)$ graph-set association through C–H···O [C2–H2B···O6, 2.431(22) Å] intermolecular interactions (Fig. S3). The various non-covalent interactions present in the salt, help in the formation of pseudocavity through the self assembled interactions of acid and base where $\frac{1}{2}$ cyclohexane-1,2-diaminium act as a pseudoguest (Fig. 4).

3.1.3. Crystal structure of [3,5-diamino-1,2,4-triazolium picrate] (**3**) Salt **3** crystallizes in a monoclinic space group C2/c with one molecule of anionic deprotonated picric acid and one molecule of cationic protonated 1*H*-1,2,4-triazole-3,5-diamine in an asymmetric unit (Fig. 5). In this structure, two molecules of picrate anion are self dimerized with $R_2^2(10)$ motif involving C-H···O [C7-H7···O6, 2.699(6) Å] interaction and also a picrate anion is interconnected to the adjacent picrate via weak non-covalent interactions O···O [O2···O4, 3.117(43) Å; O3···O4, 2.948(17) Å], create a cavity of size

1.3 Å, resulting the ribbon shaped one dimensional packing along

'ac' plane. Meanwhile, two molecules of protonated 1H-1,2,4-tria-

zole-3,5-diamine are self dimerized with $R_2^2(8)$ motif involving

N-H···N [N4-H4···N3, 2.115(31) Å] interaction and also two tria-

zole molecules are stacked one above other via N–H··· π [N4–H4A·· π , 3.347(47) Å; N4–H4B·· π , 3.302(34) Å; N5–H5B·· π , 3.304(6) Å] interactions, forming two dimensional layer along 'c' axis (Fig. S4a and b). One molecule of cationic *1H*-1,2,4-triazole-3,5-diamine attracts three molecules of picrate anions and one N–H group of it shows the strong hydrogen bonding with the phenolic oxygen (O1) of picrate anion [N1–H1···O1, 1.932(27) Å]. Other non-covalent interactions N–H···O, are in the range of 2.202(26) – 2.689(39) Å (Fig. S4c). The resulting heterometric synthon due to these hydrogen bonds connects the acid and base into an infinite three dimensional packing as alternate channels of picrate anions and *1H*-1,2,4-triazole-3,5-diamine cations along the 'c' axis (Fig. 6).



Fig. 6. Three dimensional packing as alternate channels of picrates and 3,5-diamino-1,2,4-triazolium along the 'c' axis in 3.

3.1.4. Crystal structure of [6-phenyl-2,4-diamino-1,3,5-triazinium picrate] (**4**)

The crystal structure of salt **4** showed that the asymmetric unit contains one molecule of picrate anion and one molecule of 6-phenyl-2,4-diamino-1,3,5 triazine cation, crystallizes in triclinic with space group P - 1. The ionic species is formed by the transfer of the proton from the hydroxyl group of picric acid to the one nitrogen atom (N6) of 6-phenyl-2,4-diamino-1,3,5 triazine (Fig. 7). Crystal packing reveals that the four molecules of picrate anions are intermolecularly hydrogen bonded and make cavity of size 1.9 Å. Also two molecules of picrates are self dimerized with $R_2^2(10)$ motif through C–H···O [C5–H5A···O5, 2.722(15) Å] interactions, forms other cavity of size 1.1 Å (Fig. S5a). The non-covalent interactions among different picrate anions cause the formation



Fig. 7. Molecular structure of salt 4.



Fig. 8. Three dimensional packing as alternate channels of picrates and 6-phenyl-2,4-diamino-1,3,5 triazinium in 4.



Fig. 9. Optimized geometry of salts: (a) 1, (b) 2, (c) 3, and (d) 4.

(d)

Table 3
Hydrogen bond interaction energy (HBE) in Kcal/mol

S.n	Salts HBE (Kcal/mol)	
1	(1)	19.83
2	(2)	17.32
3	(3)	15.33
4	(4)	10.26

Table 4
TG-DSC phenomenological data of salts $1\mathchar`-4$ in an N_2 atmosphere

S.n	Salts	TG		DSC		
		T_i (°C)	$T_f(^{\circ}C)$	α	Peak temp. (°C)	Nature
1	(1)	244	381	96.6	341 °C	Exo
2	(2)	190	307	95.6	292 °C	Exo
3	(3)	247	349	98.4	331 °C	Exo
4	(4)	268	377	95.1	319 °C	Exo





Fig. 11. Isothermal TG in static air atmosphere for salts 1-4: (a) 1, (b) 2, (c) 3, and (d) 4.



Fig. 12. Dependence of activation energy (E_a) on the extent of conversion (α) for salts **1–4**.





of three dimensional zig-zag molecular arrangement along 'bc' plane as shown in Fig. S5b. The base 6-phenyl-2,4-diamino-1,3,5triazinium also interconnected with other same molecule through C-H···N [C11-H11···N8, 2.572(15) Å] and N-H···N [N8-H8···N5, 2.248(13) Å] intermolecular interactions, resulted in the formation of spiral molecular structure along the 'a' axis (Fig. S5c). These molecules are partially stacked one above the other via weak $\pi \cdots \pi$ [3.504(15)Å] interactions as shown in Fig. S5d. The protonated nitrogen (N6) of 6-phenyl-2,4-diamino-1,3,5-triazinium shows the strong hydrogen bonding with the phenolic oxygen (O1) of picrate, i.e., N6–H6···O1 [1.920(57) Å]. Both organic moieties are held together by various non-covalent interactions viz., C-H···O and N- $H \cdots O$ (Fig. S6, Table 2). These non-covalent interactions present between cation and anion resulted in the formation of entirely different three dimensional packing as alternate channels of picric acid and 6-phenyl-2,4-diamino-1,3,5 triazine (Fig. 8).

3.2. DFT energy calculation

The optimized structural parameters of all individual amine, acids and their salts were calculated at B3LYP/6-31G(d, p) basis sets and are summarized in Table S1. Each optimized geometries showed positive vibrational frequencies suggesting that optimized structure is the global minimum on the potential energy surface. Single point energy calculations were performed and zero point corrected total energies for various species were recorded. In addition to the characterization of these salts, the gas phase geometries, harmonic vibrational frequencies and binding energies of a series of amine were computed. The B3LYP predicted structure of salts is shown in Fig. 9 and geometrical parameters are given in Table S1.

The hydrogen bond interaction energies were determined according to the following equation.

$$\Delta E = E_{\text{Salt}} - (E_{\text{amine}} + E_{\text{acid}})$$



Scheme 2. Proton transfer mechanism leading to explosion in salts 1-4 PT = Proton Transfer, ORR = Oxidation-Reduction Reaction.

where E_{Salt} , E_{amine} and E_{acid} are the zero point corrected total energies of salt, amine and acid calculated at DFT(B3LYP)/6-31G(d, p) level of theory.

The trend observed for the hydrogen bond interaction energy is given in Table 3. In case of salts **1–4**, the steric hindrance plays an important role to describe the order of hydrogen bond interaction energy. It is important to point out that the salt **4** shows the lowest hydrogen bond interaction energy of all compounds as the substituted phenyl group on the triazine ring produce the greater steric hindrance. Along with this, the negligible difference in the energy of the optimized structure and the crystal structure of salts suggest that the orientation and interaction remain almost the same for the solid state as for the gas phase structure (Table S2). The optimized bond lengths and angles for the salts **1–4** are given in Table S1, and further supports that the molecules are arranged in same fashion in both solid and gaseous phases.

3.3. Thermal analysis

The thermal stability of salts **1–4** is demonstrated by a thermogravimetry (TG) and differential scanning calorimetry (DSC). The thermoanalytical data of these salts are listed in Table 4 and the TGA–DSC curves are shown in Fig. 10. All salts are stable up to 200 °C and show single step decompositions. The salt **1** shows a weight loss of 96.6% between 244 and 381 °C, corresponding to the release of both picrate anion and uronium cation. This stage corresponds to single exotherm in the DSC curve at 341 °C. In salt **2** the decomposition starts at 190 °C and continue up to 307 °C with 95.6% mass loss due to the release of picrate anion and cyclohexane-1,2-diaminium. The exothermic peak is observed at 292 °C in the DSC curve. Salts **3** and **4** also follow a similar pathway for their decomposition (Table 4). Beyond 405 °C, explosion occurs with the formation of gaseous products. The exotherms are due to oxidation-reduction reactions and can be associated with explosive decomposition processes.

The kinetics of thermal decomposition of salts 1-4 were evaluated using fourteen mechanisms based kinetic models as given in Table S3. The set of reaction models [31] were used to analyze the isothermal TG data in the range of 230-270 °C for 1-4 (Fig. 11), to calculate the E_a values for thermal decomposition. The activation energy values are reported in Table S4. In the model fitting method, the kinetics is analyzed by choosing a "best fit" model based on the value of the correlation coefficient r close to 1. Among various values of *r* calculated for different models, the highest values of r for salt 1, 4 is model 11 (three dimensional diffusion), for salt 2, model 7 (Avrami-Erofeev) and for salt 3, model 14 (Ginstling–Brounshtein). The corresponding value of E_a are reported in Table S4 for salt 1-4 are 199.4(1), 152.1(2), 109.8(3) and 108.2(4) kJ mol⁻¹ respectively. The isoconversional method is known to permit estimation of activation energy independent of the model used. This method is being used to establish a relation between activation energy and extent of conversion (α) of the sample. According to Fig. 12, for a particular salt each activation energy has a separate value at different α . Although these salts are stable at room temperature but experience has shown that when subjected sudden to high temperature, they explode. Freeman and Gordon [28] have suggested the heat balance equation in order to evaluate the pre-explosion reactions as given in supporting Information.

Further to evaluate the sensitivity of these salts, their explosion delay measurement was carried out in temperature ranges 380–420 °C for salts **1–4** (Table S5). For salts **1–4**, E_a^* was determined from the slope of a plot of ln (D_E) vs. 1/*T* as shown in Fig. 13. The energy of activation for explosion is 92.8, 69.4, 47.3 and 43.4 kJ mol⁻¹ for salts **1–4**, respectively. It has also been observed experimentally that salt **4** has the least activation energy which

could be due to high aromaticity of the amine, i.e., it is less stable. The activation energy (calculated by isothermal TG) and explosion delay measurement has different values which may be due to the different temperature ranges. The oxygen balance values reported in Table S5, suggest that these salts belong to the low explosives class. The thermal decomposition process of energetic materials often involves a concert of bond breaking and bond forming steps under condensed or gas phase reaction. The weakening of a particular bond seems to enhance the tendency to have a predominant, identified path to decomposition. The overall process of decomposition takes place at higher temperature by transfer of proton (N–H bond cleavage) from amines to picrates and form the corresponding $O \cdots H$ bond in the condensed phase prior to explosion to form finally gaseous products leaving a black carbon residues [36] (Scheme 2).

4. Conclusions

In summary, we synthesized four new salts of picric acid with amines. The X-ray studies shows that the hydrogen bonding gives entirely different three dimensional packing views, i.e., salt **1** give zig-zag arrangement, salt **2** pseudocavity, while salts **3** and **4** involved in the formation of alternate channels of picrate and amines. Theoretical studies also suggested that in both solid and gaseous phase, structure is same and hydrogen bond interaction energy largely depends on the functional moieties. The thermolysis of these salts seems to involve proton transfer from the cation to picrate anion. At higher temperature, interaction between cation and anion leads to an explosion. From the explosion delay measurements, it is also clear that the salt **4** is less thermal stable than others as it has the highest tendency to explode.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.molstruc.2012. 12.020.

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