Hydrogen bonded supramolecular motifs in 2,4-diamino-6-methyl-1,3,5-triazinium adipate (1), 2,4-diamino-6-methyl-1,3,5-triazinium hydrogen phthalate (2), 2,4-diamino-6-methyl-1,3,5-triazinium 3-hydroxy picolinate monohydrate (3), 2,4-diamino-6-methyl-1,3,5-triazinium 5-chlorosalicylate (4) and 2,4-diamino-6-methyl-1,3,5-triazinium benzenesulfonate monohydrate (5).

6.1 Introduction

Adipic acid is used in manufacturing plasticizers and lubricants components. It is used in making polyester polyols for polyurethane systems. Food grade adipic acid is used as gelling aid, acidulant, leavening and buffering agent. The crystal structure of adipic acid,\textsuperscript{198} bis(2,6-diaminopyridinium)-adipate-adipic acid-water (2/1/1/2),\textsuperscript{199} piperazinium adipate\textsuperscript{200} have been reported in literature. The crystal structure of pyrimethamine hydrogen adipate\textsuperscript{141} and trimethoprim hydrogen adipate\textsuperscript{53} have been reported from our laboratory.

Phthalic acid is used mainly in the form of the anhydride to produce other chemicals such as dyes, perfumes and saccharin. The crystal structure of phthalic acid,\textsuperscript{201} phthalic acid-4,6-dimethylpyrimidin-2-amine (1/1),\textsuperscript{202} melaminium phthalate,\textsuperscript{203} 1,4-phenylenediammonium bis(hydrogen phthalate)\textsuperscript{204} and trimethoprim hydrogen phthalate\textsuperscript{53} have been reported in literature.

3-Hydroxypicolinic acid is a picolinic acid derivative and is a member of the pyridine family. Complexes of 3-hydroxypicolinic acid are of bioinorganic interest\textsuperscript{205} and also pose structural ambiguities since they display a number of possible coordination modes,\textsuperscript{206,207} The 3-hydroxypicolinate ion can also act as a monodentate or bridging ligand.\textsuperscript{206} The crystal structure of 3-hydroxypicolinic acid\textsuperscript{208} and potassium oxodiperoxo(3-hydroxypryidine-2-
carboxylato)vanadate(V)\textsuperscript{209} have been reported. Hydrogen bonding patterns involving aryl sulphonates and their metal complexes are of current interest.\textsuperscript{118,210-211} Such interactions can be utilized for designing supramolecular architectures.

In the present work, the 2,4-diamino-6-methyl-1,3,5-triazinium adipate (DAMTADI), 2,4-diamino-6-methyl-1,3,5-triazinium hydrogen phthalate (DAMTHPH), 2,4-diamino-6-methyl-1,3,5-triazinium 3-hydroxypicolinate monohydrate (DAMT3-HPA), 2,4-diamino-6-methyl-1,3,5-triazinium 5-chlorosalicylate (DAMT5-CISA) and 2,4-diamino-6-methyl-1,3,5-triazinium benzenesulfonate monohydrate (DAMTBS) have been prepared and hydrogen bonding patterns have been studied.

6.2. Experimental section

6.2.1. Preparation

Compounds 1, 2, & 4, were prepared by mixing a hot methanolic solution of 2,4-diamino-6-methyl-1,3,5-triazine (Aldrich) with a hot methanolic solution of the corresponding acids [adipic acid/phthalic acid/5-chlorosalicylic acid (LOBA Chemie)] in a 1:1 molar ratio, and warming for half an hour over a water bath. The mixture was cooled slowly and kept at room temperature. After a few days colourless crystals were obtained.

Compounds 3 & 5, were prepared by mixing a hot methanolic solutions of 2,4-diamino-6-methyl-1,3,5-triazine (Aldrich) and hot aqueous solution of the corresponding acids [3-hydroxypicolinic acid/ benzenesulfonic acid (LOBA Chemie)] were warmed for half an hour over a water bath. The mixture was cooled slowly and kept at room temperature; after a few days colourless crystals were obtained.

6.2.2. X-ray data collection

For compounds 1 & 2, the X-ray data were collected on a Bruker--Nonius 95mm CCD camera on k-goniostat diffractometer\textsuperscript{68-70} provided with a graphite monochromated MoKα radiation. The data [θ range= 3.3° to 27.5° (compound 1); 3.0° to 27.5° (compound 2)] were corrected for polarization and Lorentz
effects. The absorption correction was performed by multi-scan method using SADABS. For compounds 3-5, the X-ray data were collected on a Bruker Smart APEX-II CCD diffractometer provided with a monochromated MoKα radiation. The data [θ range= 2.8° to 28.4° (compound 3); 1.5° to 30.9° (compound 4); 2.3° to 34.0° (compound 5)] were corrected for polarization and Lorentz effects. The absorption correction was performed by multi-scan method using SADABS.

6.2.3. Structure solution and refinement

In the compounds 1-3 & 5, the E-statistics revealed the centrosymmetric distribution. Among the reflections of the general type $hkl$ there are no systematic absences. This indicates that the lattice is primitive. In the $0k0$ type of reflections, $l$ odd are absent. This reveals 2 screw parallel to b-axis. The absence of $h0l$ type of reflections with $l$ odd, reveals $c$ glide perpendicular to b-axis. Hence the space group $P2_1/c$ was assigned.

In compound 4, the data set contained no systematic absences. The E-statistics analysis reveals the centrosymmetric distribution. Among the reflections of the general type $hkl$, there is no systematic absence. This indicates that the lattice is primitive. Hence the space group P-1 was assigned. It was later confirmed by successful structure solution and refinement.

All the structures were solved by direct method using SHELXS97 and refined by full matrix least squares on $F^2$ using the program SHELXL97. In all the above crystal structures (1-5), the non-hydrogen atoms were refined with anisotropic thermal parameters. In compounds 1, 2 & 4, the hydrogen atoms were positioned geometrically and refined as riding model. In compounds 3 & 5, the hydrogen atoms of the water molecules were located in a difference Fourier map and refined as riding. The other hydrogen atoms are placed in idealized locations and refined as riding model. The final $R$ value was 0.050 for 1756 reflections $I>2\sigma(I)$ in compound 1, 0.045 for 2614 reflections $I>2\sigma(I)$ in compound 2, 0.051 for 2090 reflections $I>2\sigma(I)$ in compound 3, 0.0493 for 5516 reflections $I>2\sigma(I)$ in compound 4 and 0.0569 for 3684 reflections $I>2\sigma(I)$ in compound 5. The geometric calculations were performed by PLATON97. The crystal data and refinement parameters are listed in Table 6.1 for compound 1,
Table 6.2 for compound 2, Table 6.3 for compound 3, Table 6.4 for compound 4 and Table 6.5 for compound 5. The atomic coordinates together with equivalent isotropic temperature factors for non-hydrogen atoms are listed in Table 6.6 for compound 1, Table 6.7 for compound 2 and Table 6.8 for compound 3, Table 6.9 for compound 4 and Table 6.10 for compound 5.

6.3. Results and Discussion

The ORTEP view of the title compounds 1-5 are shown in Figures 6.1a-6.1e. In compound 1, the asymmetric unit contains a molecule of 2,4-diamino-6-methyl-1,3,5-triazinium cation (Acetoguanamine) (DAMT) and half of the adipate anion. In compound 2, the asymmetric unit contains an 2,4-diamino-6-methyl-1,3,5-triazinium cations and a hydrogen phthalate anion. In compound 3, the asymmetric unit contains an 2,4-diamino-6-methyl-1,3,5-triazinium cation, a 3-hydroxy picolinate anion and a water molecule. In compound 4, the asymmetric unit contains an 2,4-diamino-6-methyl-1,3,5-triazinium cation and a 5-chlorosalicylate anion. In compound 5, the asymmetric unit contains an 2,4-diamino-6-methyl-1,3,5-triazinium cation, a benzenesulfonate anion and a water molecule.

In all the compounds, the triazine rings are protonated at atom N1. Protonation of the triazine base on the N1 site is reflected by an increase in bond angle at N1[C2-N1-C6= 118.56(12)° in compound 1, 119.47(10)° in compound 2, 119.83(14)° in compound 3, 119.35(14)° (cation A) and 119.46(17)° (cation B) in compound 4 and 119.443(14)° in compound 5] when compared with that at the unprotonated atom N3[C2-N3-C4= 116.24(12)° in compound 1, 116.13(10)° in compound 2, 116.65(13)° in compound 3, 116.33(13)° (cation A) and 115.95(14)° cation B) in compound 4 and 116.33(14)° in compound 5] and N5 atom [C4-N5-C6= 115.29(13)° in compound 1, 114.98(11)° in compound 2, 115.70(14)° in compound 3, 115.74(14)° (cation A) and 115.67(15)° (cation B) in compound 4 and 115.68(15)° in compound 5]. In compound 1, the adipate anion is almost planar and is in trans-trans-trans conformation. The actual values of the torsion angles are –177.77(12)°, -180° and –177.77(12)° for C8-C9-C10-C10’, C9-C10-C10’-C9’ and C10-C10’-C9’-C8’.
respectively. This conformation is similar to that of adipic acid. The bond distances and bond angles are listed in Table 6.11 for compound 1, Table 6.12 for compound 2 and Table 6.13 for compound 3, Table 6.14 for compound 4 and Table 6.15 for compound 5.

6.3.1. Hydrogen bonding

In compounds 1-4, the carboxylate group interacts with the protonated 2,4-diamino-6-methyl-1,3,5-triazinium cation and 2-amino group via a pair of N-H…O hydrogen bonds to form a fork-like interaction with graph-set notation \( R_2^2(8) \)\(^{21,22} \) (Motif VIII). This motif VIII is one of the 24 most frequently observed bimolecular cyclic hydrogen-bonded motifs in organic crystal structures.\(^{110} \) This has also been observed in the crystal structures of trimethoprim acetate,\(^{213} \) trimethoprim sorbate dihydrate,\(^{187} \) trimethoprim p-toluene sulfonate\(^{214} \) and pyrimethamine hydrogen glutarate.\(^{129} \) In compound 5, the benzene sulfonate anion and water molecule interact with the protonated triazine moiety of 2,4-diamino-6-methyl-1,3,5-triazinium cation through N-H…O and O-H…O hydrogen bonds with graph-set motif \( R_3^2(10) \).

In compounds 1 & 3, the triazine moieties of 2,4-diamino-6-methyl-1,3,5-triazinium cations are centrosymmetrically paired via a pair of N-H…N hydrogen bonds (Motif XI) involving the 4-amino group and the N5 atom forming an eight-membered hydrogen-bonded \( R_2^2(8) \) motif.

In compound 1, the 2-amino group of the triazinium cation interacts with one of the carboxylate oxygen atom O2, through N-H…O hydrogen bond. The methyl group (C7) interacts with unprotonated N3 atom via C-H…N hydrogen bonds. Both N-H…O and C-H…N hydrogen bonds lead to \( R_3^2(10) \) ring (Figure 6.2). These types of interactions extend along the c-axis to form a supramolecular ribbon. The reaction of triazine with adipic acid, has been reported recently\(^{215} \) to yield a molecular complex, without protonation (cocrystal) of triazine moiety in contrast to the salt formation, in the present structure. However, the hydrogen bonding patterns and the other packing features are similar. This novel feature of reactivity of triazine with adipic acid, yielding a cocrystal as well as a salt, is interesting and worth noting.
In compounds 2, the inversion related $R_{2}^{2}(8)$ ring motif I (triazinium-carboxylate motif) are bridged on either sides via N-H···O and O-H···O(intramolecular) hydrogen bonds to form $R_{6}^{4}(12)$. [The graph set notation of the ring system - $R_{2}^{2}(8)$ $R_{6}^{4}(12)$ $R_{2}^{2}(8)$] (Figure 6.3). Similar type of interactions has also been observed in trimethoprim hydrogen phthalate.\textsuperscript{53} One of the hydrogen atoms of the 2-amino group form a bifurcated hydrogen bond with the carboxyl oxygen atoms O3 & O4 of hydrogen phthalate anions represented by graph-set $R_{1}^{2}$ (4). The carboxyl and carboxylate group of the hydrogen phthalate anion forms an intramolecular O-H···O hydrogen bond (graph-set notation S(7)]. $\pi$-$\pi$ stacking interactions between the aromatic rings are observed. The DAMT cations stack with the benzene ring of the hydrogen phthalate anion, with a perpendicular separation of 3.366(5) Å, centroid-to-centroid distance of 3.593(8) Å and a slip angle of 20.21°. These are typical aromatic stacking values.\textsuperscript{75}

In compound 3, the $R_{2}^{2}(8)$ motifs are centrosymmetrically paired via N-H···O hydrogen bonds to produce the DDAA (D=donor in hydrogen bonds, A=acceptor in hydrogen bonds) array of quadruple hydrogen bonds. This can be represented by the graph-set notation $R_{2}^{2}(8)$, $R_{4}^{2}(8)$ and $R_{2}^{2}(8)$ (Motif XIII) (Figure 6.4). This type of motif has been reported in the crystal structure of trimethoprim formate,\textsuperscript{111} trimethoprim hydrogen glutarate,\textsuperscript{112} trimethoprim m-chlorobenzoate,\textsuperscript{113} and pyrimethaminium 3,5-dinitrobenzoate.\textsuperscript{114} One of the hydrogen atoms of the 2-amino group forms a bifurcated hydrogen bond with the carboxyl oxygen atom O1 and picolinate N6 atom of 3-hydroxypicolinate anions represented by graph-set $R_{1}^{2}(4)$. Typical intramolecular hydrogen bond exists between the hydroxyl –OH group and the carboxylate group of the 3-hydroxypicolinate anion to form a six-membered hydrogen-bonded ring [S(6)]. These type of interactions are extended along the a-axis to form a supramolecular ribbon. The supramolecular ribbons are interlinked by O-H···O hydrogen bonds involving carboxylate oxygen atom (O2). hydroxyl –OH group of the 3-hydroxypicolinate anion and water molecules which plays a bridging role, as shown in Figure 6.5. Further, the 3-hydroxypicolinate anions are also bridged by alternating water molecules via O-H···O hydrogen bonds leading to one-dimensional supramolecular chain along the c-axis show in Figure 6.6. $\pi$-$\pi$ interaction is observed between two 2,4-diamino-6-methyl-1,3,5-triazinium
cations related by an inversion center. The centroid-to-centroid and interplanar distances are 3.5906(12) Å and 3.2875(6) Å, respectively, the slip angle being 23.71°.

In compound 4, in cations (A & B), the $R_2^2(8)$ motifs are centrosymmetrically paired via N-H-O hydrogen bonds to produce the DDAA (D=donor in hydrogen bonds, A=accepter in hydrogen bonds) array of quadruple hydrogen bonds. This can be represented by the graph-set notation $R_2^2(8)$, $R_4^2(8)$ and $R_2^2(8)$ (Motif XIV). The inversely related cations (A&B) are paired via N-H-N hydrogen bonds [$R_2^2(8)$] involving 4-amino group and N3 atom (Motif XII). Consequently, the cations A & B are base paired via N4A-H-N5B and N4B-H-N5A hydrogen bonds [$R_2^2(8)$] (Motif XI). The salicylate anions (A & B) form the folded intramolecular O-H-O hydrogen bonds [graph-set S(6)] involving the phenolic –OH and carboxylate oxygen atoms (O2A and O2B). Furthermore, these arrays are connected via C-H-O hydrogen bonds, resulting in a two-dimensional supramolecular sheet (Figure 6.7).

In compound 5, an unusual ring motif of $R_3^3(10)$ is formed by N-H-O and O-H-O hydrogen bonds involving the sulfonate oxygen atoms, a water molecule, protonated nitrogen and 2-amino nitrogen of the 2,4-diamino-6-methyl-1,3,5-triazine moiety. This is in contrast with the usual $R_2^2(8)$ motif formed by the sulfonate-pyrimidine interaction where the sulfonate group is found to mimic the carboxyl group.214 The 2,4-diamino-6-methyl-1,3,5-triazinium cations are centrosymmetrically paired through N-H-N hydrogen bonds (Homosynthon) involving the 2-amino group and the N3 atom of the unprotonated pyrimidine to form the ring motif $R_2^2(8)$ (Motif XIII). In addition to the base pairing, one of the sulfonate oxygen atoms (O2) bridges the 2-amino and the 4-amino groups on both sides of the pairing. The combination of such base-pairing patterns and further bridging of the bases involved in the pairing by hydrogen bonds, lead to the formation of linear array of four hydrogen bonds to form a complementary DADA array of quadruple hydrogen-bonds (Motif XV). This can be represented by the graph-set notation $R_2^2(8)$, $R_2^2(8)$ and $R_3^2(8)$ (Figure 6.8). The water molecule plays a pivotal role in supramolecular organization within the chain-water molecule donating two hydrogen atoms (one hydrogen to one of the sulfonate oxygen atom O1 and another hydrogen to one of the sulfonate oxygen
atom O3), leading to hydrogen bonded supramolecular chains. This can be designated by graph-set notation C\(2^2\) (Figure 6.9). \(\pi-\pi\) stacking interactions between the aromatic rings are observed. The 2,4-diamino-6-methyl-1,3,5-triazinium cations stack with the benzene ring of the benzenesulfonate anion, with a perpendicular separation of 3.5664(6) Å, centroid-to-centroid distance of 3.5347(10) Å and a slip angle of 6.75°. The hydrogen bonding geometries are listed in Table 6.16 for compound 1, Table 6.17 for compound 2, Table 6.18 for compound 3, Table 6.19 for compound 4 and Table 6.20 for compound 5.

### 6.4. Supplementary Materials

The atomic coordinates and the isotopic displacement parameters for all hydrogen atoms, anisotropic displacement parameters for all the non-hydrogen atoms, bond distance and bond angles involving the hydrogen atom and torsion angle DAMTADI, DAMTHPH, DAMT3-HPA, DAMT5-CISA and DAMTBS are given in Tables A. 1.6.1, 1.6.2, 1.6.3, 1.6.4 and 1.6.5 (Appendix 1), A. 2.6.1, 2.6.2, 2.6.3, 2.6.4 and 2.6.5 (Appendix 2), A. 3.6.1, 3.6.2, 3.6.3, 3.6.4 and 3.6.5 (Appendix 3) and A. 4.6.1, 4.6.2, 4.6.3, 4.6.4 and 4.6.5 (Appendix 4) respectively. The least squares plane calculations (Appendix. 5. txt & Tables A. 5.6.1, 5.6.2, 5.6.3, 5.6.4 and 5.6.5) and Fo-Fc Tables DAMTADI, DAMTHPH, DAMT3-HPA, DAMT5-CISA and DAMTBS are given in the CD attached at the end of the thesis.