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Proton-transfer supramolecular salts based on proton sponge 2,2′-dipyridylamine

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HIGHLIGHTS

- Three supramolecular salts with 3D framework structure have been prepared and characterized.
- Intramolecular N–H$^+$···N hydrogen bonding affords S(6) rings in the proton sponge dpaH$^+$.
- Robust intermolecular hydrogen bonding interactions generate various ring motifs, such as $R_2^2(8)$, $R_4^2(10)$, $R_4^4(12)$, $R_4^2(18)$ and $R_4^4(26)$.

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ABSTRACT

Reactions between proton sponge 2,2′-dipyridylamine and acidic synthons (2,4-dinitrobenzoic acid, 3,4-dinitrobenzoic acid and picronitric acid) afford three proton-transfer supramolecular ammonium salts, (2,4-dinitrobenzoate)···(2,2′-dipyridylammonium) (**1**), (3,4-dinitrobenzoate)···(2,2′-dipyridylammonium)···(H_2O) (**2**) and (picrate)···(2,2′-dipyridylammonium) (**3**), respectively. During solution crystallization, the proton transfers from the organic acid to the nitrogen atom in the pyridyl ring. It is found that monoprotonated dpaH$^+$ has an asymmetrical intramolecular hydrogen bond (IHB) N–H$^+$···N, which results in the intramolecular S(6) ring. All supramolecular architectures of **1**–**3** involve extensive classical hydrogen bonds and display a three-dimensional (3D) framework structure. Robust hydrogen bonding interactions generate various intermolecular ring motifs.

1. Introduction

Since the prototypal compound 1,8-bis(dimethylamino)naphthalene (DMAN) was reported by Alder et al. [1], the design of more basic proton sponges received increasing attention [2–8]. A large number of proton sponges have been systematically reviewed [9–13]. Proton sponges have been studied as models of proton substraction [14], as organic base catalysts in green chemistry [15], as effective H$^+$ scavengers in nanocluster formation [16], and play the important role in enzymatic catalysis [17], in biological systems [18], in asymmetric organic synthesis [19] as well as in the field of gene therapy [20]. A general feature of proton sponge is the presence of two closely basic nitrogen centers in the molecule, which have an orientation that allows the uptake of one proton to yield a stabilized N–H$^+$···N intramolecular hydrogen bond (IHB) [21].

With regard to proton sponges, particular interest has been mainly focused on neutral organic bases with chelating proton acceptor functionalities exhibiting enhanced basicity [5]. Compared to ordinary alkyl/aryl amines, amidines and guanidines, such proton chelators show a dramatic increase in basicity due to destabilization of the base as a consequence of strong repulsion of unshared electron pairs, formation of an IHB in the protonated form and relief from steric strain upon protonation [21].

Neutral 2,2′-dipyridylamine (dpa) has three potential nitrogen base functionalities. Despite the single bonds to the central nitrogen atom, it normally presents as a planar array, which impacts on its basicity. In comparison with the two pyridyl nitrogen atoms, the central secondary amino NH group is a little acidic and less favorable to be protonated. It is likely to be protonated only under very highly acidic conditions [22]. Therefore, dpa can be employed as a potential proton sponge on account of the presence of two closely positioned basic sites.

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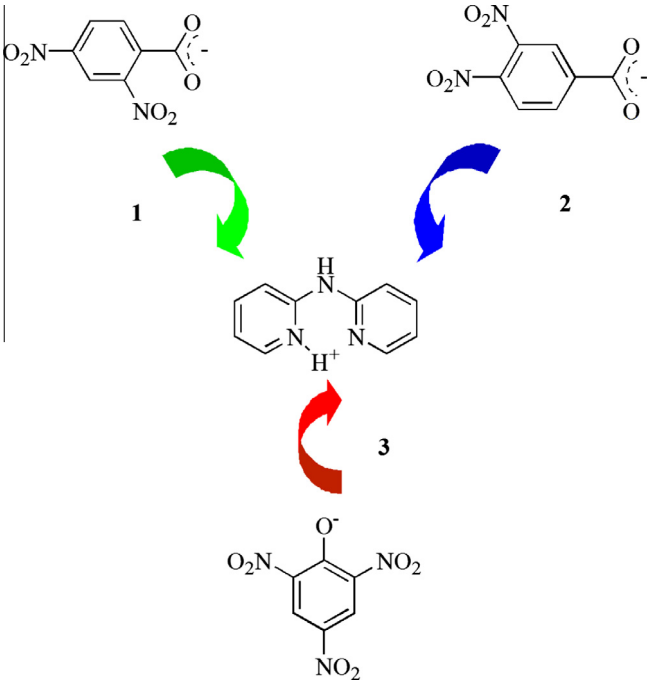
Moreover, basic pyridyl nitrogen atoms make dpa a promising synthon in the supramolecular synthesis of multicomponent molecular complexes. It is central to successful and rational synthesis of multicomponent supramolecular arrays that molecules with functional groups are often employed, showing a combination of complementary and specific interactions [23,24]. Supramolecular synthons with functional groups may be either Brønsted acids (proton donors, D–H) or Brønsted bases (proton acceptors, :A), which can interact by sharing the proton and form D–H···:A hydrogen bonding; and either Lewis bases (electron donors, :D) or Lewis acids (electron acceptors, A) endowed with groups can interact by sharing a couple of electrons in a similar way, resulting in D: → A electron donor–acceptor or charge-transfer interactions [25]. Carboxylic acids and N-containing molecules have been proved to be useful and powerful building blocks through hydrogen bonding interactions [25–31]. Hydrogen bonding has been the most common "tool" in crystal engineering due to its strength, directionality and predictability [32–40].

Particularly attractive are the cases with polytopic potential hydrogen donors or acceptors in acids or bases. Generally, the strongest donor will form a bond with the strongest acceptor and the second strongest donor with the second acceptor [41]. The assembly of supramolecular compounds will follow this "rule", though many exceptions would exist because of steric or packing effects [42]. Proton transfer may occur when the hydrogen acceptor is a noticeably stronger base than the deprotonated donor [41,43,44]. The charge separation leads to the formation of supramolecular salts, which have the potential to alter and optimize physical properties such as crystalline form, solubility and stability [45–47]. The pK_a values of DH and AH^+ are commonly used to measure the relative proton affinities of the donor and the acceptor atoms [41].

Recently we have reported the proton-transfer supramolecular salts assembled from 3,5-dinitrobenzoic acid and (2, 3 and 4)-aminomethyl pyridine [48]. The nitrogen atom of the primary amino NH_2 group in aminomethyl pyridine has been protonated. Continuing our efforts in this line, we choose dpa and acidic organic components as supramolecular synthons and report the synthesis and crystal structure of three supramolecular salts, (2,4-dinitrobenzoate)···(2,2′-dipyridylammonium) (**1**), (3,4-dinitrobenzoate)···(2,2′-dipyridylammonium)···(H_2O) (**2**) and (picrate)···(2,2′-dipyridylammonium) (**3**), respectively (Scheme 1). The proton transfers from the acid to pyridyl nitrogen atom.



Scheme 1. Structures of the proton-transfer ammonium salts.

2. Experimental section

2.1. Preparation of the salts

The chemicals and solvents used in this work are of analytical grade and available commercially and were used without further purification.

2.1.1. (2,4-Dinitrobenzoate)···(2,2′-dipyridylammonium) (*1*)

A solution of 2,2′-dipyridylamine (0.05 mmol) in acetonitrile (3 mL) was added dropwise to a stirred solution of 2,4-dinitrobenzoic acid (0.05 mmol) in acetonitrile (3 mL). The colorless solution was stirred for a few minutes at ambient condition, and then refluxed for about half an hour. After the natural cooling, the resulting solution was left standing at room temperature for several days. Colorless rhombus crystals were isolated after slow evaporation in air.

2.1.2. (3,4-Dinitrobenzoate)···(2,2′-dipyridylammonium)···(H_2O) (*2*)

Complex **2** was obtained as colorless rod crystals by the similar procedure described for **1**, except with the addition of 3,4-dinitrobenzoic acid instead of 2,4-dinitrobenzoic acid.

2.1.3. (Picrate)···(2,2′-dipyridylammonium) (*3*)

A solution of 2,2′-dipyridylamine (0.05 mmol) in methanol (3 mL) was added dropwise to a stirred solution of picric acid (0.05 mmol) in methanol (3 mL). A yellow precipitate appeared immediately. The mixture was refluxed for about half an hour. After the powder was dissolved, the solution was filtered. Upon slow evaporation of the filtrate at room temperature for several days, well-shaped yellow slice crystals suitable for X-ray diffraction were obtained.

2.2. X-ray crystallography

Data collections were made by using graphite monochromated Mo Kα diffraction (λ = 0.71073 Å) at 293 K. The structures were solved by direct methods using the *SHELXS97* (Sheldrick, 1990) program and refined by a full-matrix least squares technique based on F^2 using the *SHELXL97* (Sheldrick, 1997) program. Primary atoms were refined by structure-invariant direct methods; secondary atoms were located from Difference Fourier maps and hydrogen site location was inferred from neighboring sites. Hydrogen atom positions for the three structures were generated geometrically. Further details of the structural analysis are summarized in Table 1 for compounds **1–3**. The relevant hydrogen bond parameters are listed in Table 2.

3. Results and discussion

3.1. Proton sponge 2,2′-dipyridylamine

According to the Cambridge Structural Data Base (CSD), different kinds of crystal structures related to 2,2′-dipyridylamine (dpa) are shown in Scheme 2. Two pyridyl nitrogen atoms in free dpa are on both sides of the central NH group and adopt a *trans* conformation, which may be caused by severe repulsion between two nitrogen lone electron pairs [49–51]. In the monoprotonated

Table 1
Crystallographic data for the complex of **1–3**.

Parameter	**1**	**2**	**3**
Formula	$C_{17}H_{13}N_5O_6$	$C_{17}H_{15}N_5O_7$	$C_{16}H_{12}N_6O_7$
Formula weight	383.32	401.34	400.32
Crystal system	Triclinic	Triclinic	Triclinic
Space group	*P*−1	*P*−1	*P*−1
a (Å)	7.8583(7)	7.322(8)	7.892(11)
b (Å)	8.4537(8)	11.223(12)	9.252(13)
c (Å)	13.0553(12)	12.265(13)	12.336(17)
α (°)	96.678 (1)	92.998(14)	105.045(16)
β (°)	94.674 (1)	107.030(13)	101.672(16)
γ (°)	101.906 (1)	104.631(14)	96.214(16)
V (Å^3)	837.89(13)	923.7(17)	839(2)
D_x (Mg m^{-3})	1.519	1.443	1.584
μ (mm^{-1})	0.12	0.12	0.13
Z	2	2	2
T (K)	296	296	296
F (000)	396	416	412
θ range for data collection (°)	2.5–28.3	1.8–28.8	2.3–28.7
Index ranges	$-10 \leqslant h \leqslant 10$, $-8 \leqslant k \leqslant 11$, $-13 \leqslant l \leqslant 17$	$-9 \leqslant h \leqslant 9$, $-14 \leqslant k \leqslant 9$, $-13 \leqslant l \leqslant 16$	$-10 \leqslant h \leqslant 10$, $-11 \leqslant k \leqslant 12$, $-16 \leqslant l \leqslant 16$
Measured reflections	5328	5649	6933
Independent reflections	3871	4208	3827
Data/restraints/parameters	3871/0/261	4208/2/272	3827/0/262
R_{int}	0.017	0.115	0.078
Reflections with $I > 2\sigma(I)$	2290	1018	1744
R_1 [$I > 2\sigma(I)$]	0.041	0.067	0.147
wR_2 (all data)	0.100	0.211	0.244
S	0.88	0.75	1.28

Table 2
Hydrogen Bond Distances and Parameters for the complex of **1–3** (Å, °).

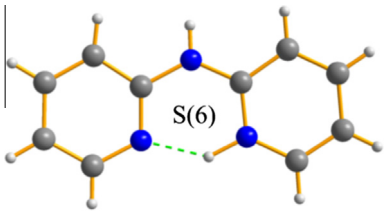
D–H···A	D–H	H···A	D···A	D–H···A
Compound ***1***				
N1–H1A···O1	0.86	1.84	2.6961(17)	171
N2–H2···O5^{i}	1.06(2)	2.55(2)	3.0688(18)	109.4(14)
N2–H2···N3	1.06(2)	1.72(2)	2.6124(19)	138.8(19
C10–H10A···O6^{i}	0.93	2.51	3.326(2)	147
C5–H5A···O5^{i}	0.93	2.50	3.073(2)	120
C5–H5A···O3^{ii}	0.93	2.55	3.278(2)	135
C9–H9A···O6^{iii}	0.93	2.41	3.240(2)	148
C2–H2A···O2	0.93	2.54	3.386(2)	151
C7–H7A···O1	0.908(15)	2.551(15)	3.272(2)	136.8(12)
Compound ***2***				
N1–H1A···O7^{iv}	0.86	1.85	2.712(6)	176
N2–H2···O2^{v}	0.86	2.50	3.200(6)	139
N2–H2···N3	0.86	1.92	2.591(7)	134
O7–H17···O1^{v}	0.86(4)	1.92(4)	2.738(6)	159(6)
O7–H18···O2^{vi}	0.82(3)	1.93(4)	2.732(6)	167(5)
C4–H4A···O5^{vii}	0.93	2.51	3.302(7)	143
Compound ***3***				
N1–H1A···O1^{iii}	0.86	2.07	2.816(7)	145
N3–H3···N2	0.86	1.92	2.594(9)	134
C2–H2A···O3^{vi}	0.93	2.59	3.212(8)	125
C7–H7A···O4^{iii}	0.93	2.46	3.217(10)	139
C10–H10A···O2^{i}	0.93	2.43	3.151(9)	135

Symmetry codes: (i) *x*, *y* + 1, *z* + 1; (ii) −*x* + 1, −*y* + 1, −*z* + 2; (iii) −*x*, −*y* + 1, −*z* + 1; (iv) *x*, *y* − 1, *z*; (v) −*x* + 1, −*y* + 1, −*z* + 1; (vi) *x* − 1, *y*, *z*; (vii) *x* + 1, *y*, *z* + 1.

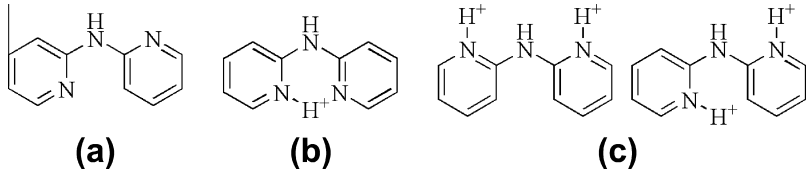
form dpaH$^+$, formation of a strong intramolecular hydrogen bond (IHB) is beneficial to the arrangement, where two pyridyl nitrogen atoms are arranged on the same side [22,52]. When it comes to diprotonated salt dpaH$_2^{2+}$, two positioned nitrogen atoms on both sides of the central NH group are generally in a *cis* position. However, *trans* conformations similar to that in free dpa are found in the isomorphous salts of $[MCl_4]^{2-}$ (Co and Cu) [53,54]. Relief from steric strain upon diprotonation and intermolecular hydrogen bond may play an key role. In contrast to two twisted rings in free

Table 3
Bond lengths (Å) and angles (°) in the proton sponges in compounds **1–3.**

Proton sponge	N···N	N–H	H···N	(N–H···N)
dpaH$^+$(**1**)	2.6124(19)	1.06(2)	1.72(2)	138.8(19)
dpaH$^+$(**2**)	2.591(7)	0.86	1.92	134
dpaH$^+$(**3**)	2.594(9)	0.86	1.92	134



Scheme 3. The graph set for intramolecular ring S(6) in protonated 2,2′-dipyridylammonium cation in salts **1–3** through the N–H$^+$···N hydrogen bond, which are shown by dashed lines in green. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)



Scheme 2. Structures in relation to dpa. (a) The free base of dpa; (b) monoprotonated ammonium salt dpaH$^+$; (c) diprotonated ammonium salt dpaH$_2^{2+}$.

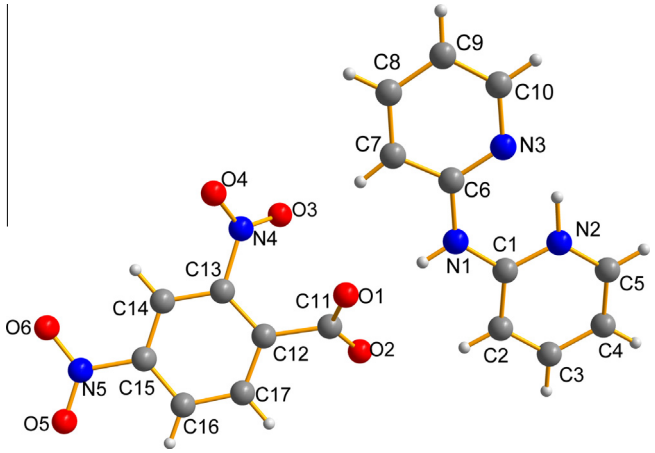


Fig. 1. View of the asymmetric unit for **1** with the labelled atoms.

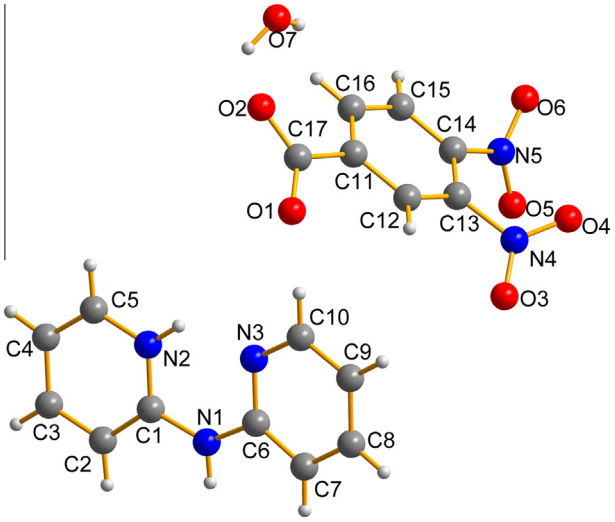


Fig. 3. View of the asymmetric unit for **2**, showing the crystallographic numbering scheme.

dpa and diprotonated $dpaH_2^{2+}$, the two pyridyl rings tend to lie parallel and quasi-coplanar in monoprotonated $dpaH^+$.

Reactions between 2,2′-dipyridylamine and acidic synthons (2,4-dinitrobenzoic acid, 3,4-dinitrobenzoic acid and picronitric acid) have produced salts **1**–**3**. The presence of an electron-donating secondary amino NH group in the centre raises the charge on the pyridyl nitrogen atom and hence boosts its ability to remove a proton from the acid. The pyridyl-N is sufficiently basic to be protonated, resulting in monoprotonated salts in every case. It is worthwhile to notice that the 2,2′-dipyridylammonium salt has an asymmetrical and nonlinear intramolecular N–$H^+\cdots$N hydrogen bond, known as "proton sponges". Some of the principal geometrical parameters of monoprotonated optimized structures **1**–**3** are given in Table 3. The N–H^+ distance is much shorter than the $H^+\cdots$N distance, which suggests that the proton is located asymmetrically between pyridyl nitrogen atoms. Compared with that found in $DMANH^+$, the N–$H^+\cdots$N hydrogen bonding angles are smaller in the range of 130–140°. Nonbonded distances r(N···N) vary from 2.59 to 2.62 Å, which are slightly higher than the average value of 2.58 Å in $DMANH^+$ structures [8,10]. Intramolecular N–$H^+\cdots$N hydrogen bonding interactions afford similar rings S(6) in the proton sponge $dpaH^+$ of supramolecular ammonium salts **1**–**3** (Scheme 3), the nomenclature of which is according to Etter

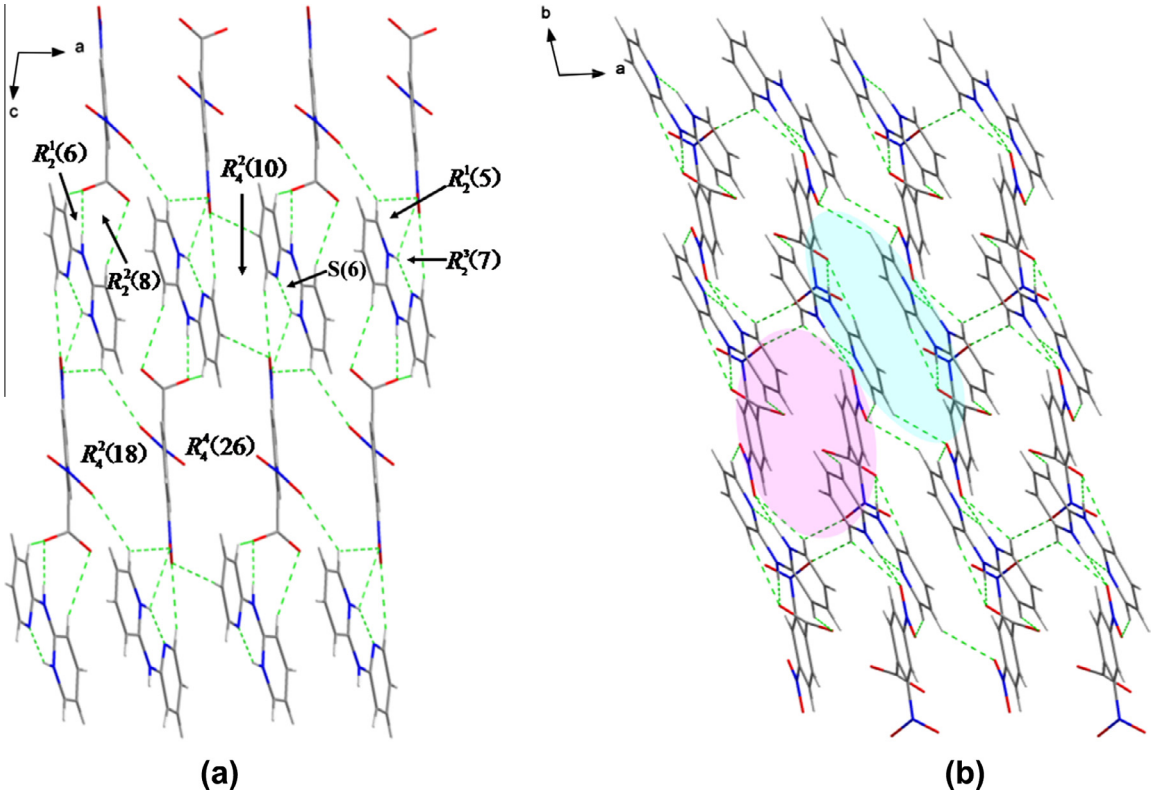


Fig. 2. (a) View of the 3D layer crystal structure in **1** parallel to the *ac*-plane, in which hydrogen bonds are shown by dashed lines in green. Various ring motifs are labelled respectively. (b) The 3D network by effective packing parallel to the *ab*-plane, where two types of grids are colored as pale pink and light green. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

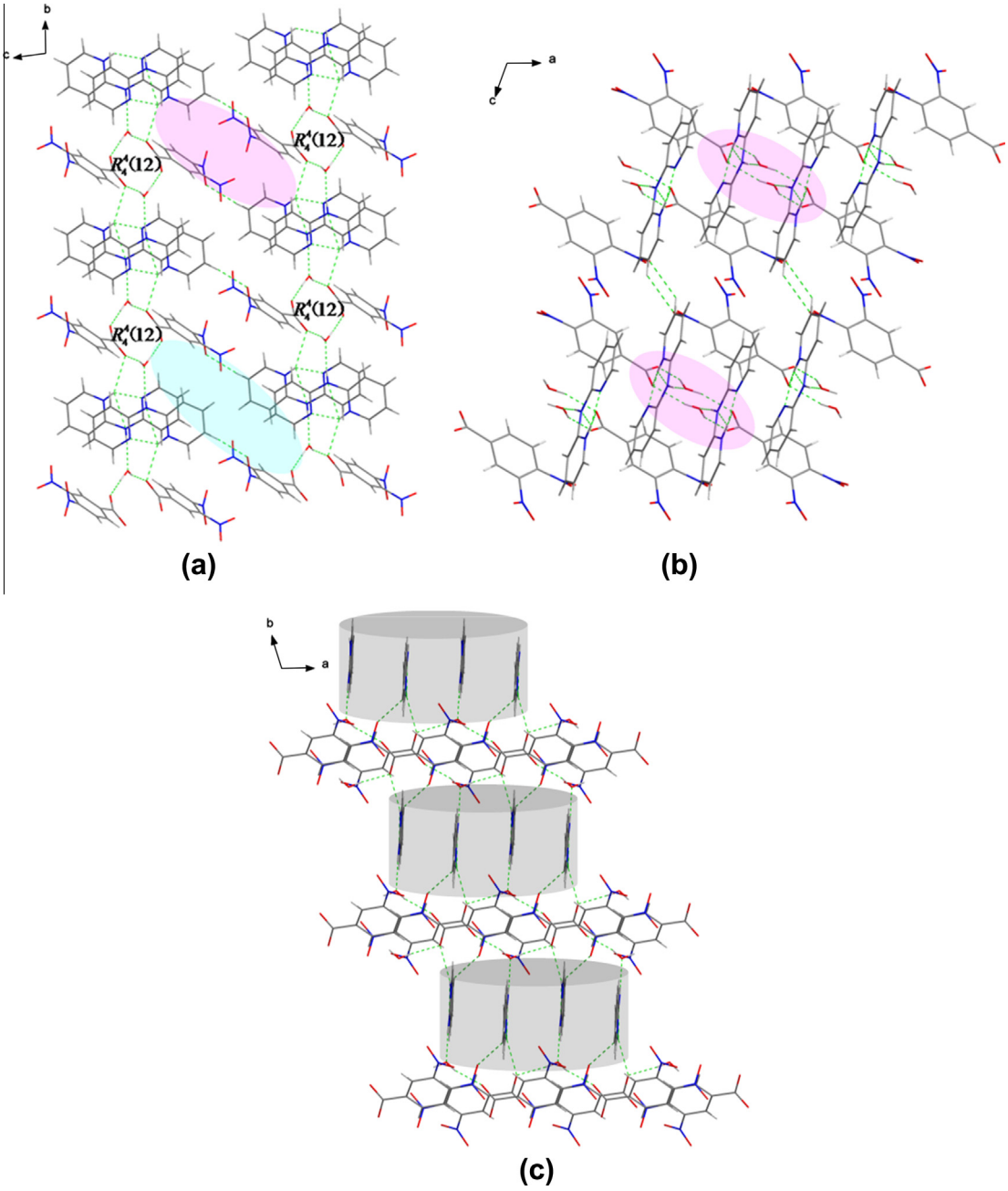


Fig. 4. (a) View of the 3D crystal structure in **2** parallel to the *bc*-plane, in which hydrogen bonds are shown by dashed lines in green. The $R_4^4(12)$ rings are labelled between carboxyl groups and water molecules through N1–H1A···O7 and N2–H2···O2 hydrogen bonding interactions. Besides, grids between two components form and are shown in the pink background. (b) The 3D packing diagram of the salt **2**, parallel to the *ac*-plane. The cations are involved with the $R_4^4(12)$ ring between carboxyl groups and water molecules *via* hydrogen bonding, colored as pale pink. (c) The 3D supramolecular framework extending on the *ab*-plane. The unique structure stacking by cations is in the pale gray pillar. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

et al. [32,55,56]. The following analysis on the crystal structure does not include the intramolecular hydrogen bond since it is not correlated with that of intermolecular interactions.

3.2. Structural descriptions

3.2.1. X-ray structure of (2,4-dinitrobenzoate)···(2,2′-dipyridylammonium) (**1**)

The carboxylic acid features the important hydrogen bonding functional group COOH. It is interesting to exploit the robust and directional recognition of carboxylic acids with N-containing moieties. 2,4-Dinitrobenzoic acid as a acidic synthon reacts with 2,2′-dipyridylamine in 1:1 ratio in acetonitrile, affording the colorless rhombus salt **1** and crystallizing in the triclinic space group $P\bar{1}$. The asymmetric unit consists of one cation of 2,2′-dipyridylammonium and one anion of 2,4-dinitrobenzoate with the labelled atoms, as shown in Fig. 1.

Extensive hydrogen bonding interactions have drawn our keen interest between anionic and cationic moieties. The secondary amino group (NH) forms the N–H···O^- hydrogen bond with deprotonated carboxylate group (COO^-) and the H···O^- distance is 1.84 Å. Another N–H^+···O hydrogen bond is produced between the positively charged pyridyl-NH^+ and nitro group (NO_2) as a acceptor in the para position with H^+···O distance of 2.55 Å. Compared with the above ionic N–H···O^- hydrogen bond, this hydrogen bond is more weaker. Besides the ionic N–H···O hydrogen

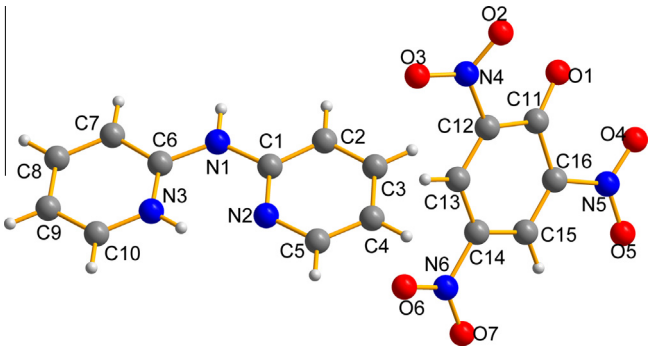


Fig. 5. View of the asymmetric unit for **3**, showing the crystallographic numbering scheme.

bonds, weak C–H···O hydrogen bonds are common in the structure, values of which are all above 2.40 Å (Table 3).

The directional hydrogen bonding determines the position and orientation of synthons and plays a crucial role on the formation of 3D structure. Viewed along the *b*-axis (Fig. 2a), every one 2,4-dinitrobenzoate anion layer is followed by one 2,2′-dipyridylammonium cation layer. The adjacent ions in the same layer are antiparallel to each other, no matter in the cation layer or in the anion one. The robust hydrogen bonding interactions generate various ring motifs in complex **1**, for instance, $R_2^1(6)$, $R_2^2(8)$, $R_2^1(5)$ and $R_2^3(7)$ between the neighboring two molecules while $R_4^2(10)$, $R_4^2(18)$ and $R_4^4(26)$ among the adjoining four ones. Stacked along the *c* axis as shown in Fig. 2b, two kinds of grids form in the close packing *via* hydrogen bonding, colored as pale pink and light green, respectively. The grids in the light green shadow are much "slim" than those in the pale pink ones. Such interesting grids alternate to be like ladders, producing a 3D supramolecular network.

*3.2.2. X-ray structure of (3,4-dinitrobenzoate)···(2,2′-dipyridylammonium)···(H_2O) (**2**)*

The similar synthesis procedure described for **1** is suitable for salt **2** as well, except with the use of 3,4-dinitrobenzoic acid instead of 2,4-dinitrobenzoic acid. The colorless rod crystal **2** has captured a water molecule from the solvent or ambient atmosphere, which crystallizes in the triclinic space group $P\bar{1}$. The asymmetric unit is occupied by one anionic 3,4-dinitrobenzoate, one cationic 2,2′-dipyridylammonium and one water molecule, where the proton of the carboxylic acid has transferred to the N atom of pyridyl group (Fig. 3).

Compared to the ring motifs in salt **1**, the ring motifs in **2** are not so abundant and multiple. Even though only one type of the $R_4^4(12)$ ring exists as shown in Fig. 4a, the molecular architecture is very fascinating. Generally, carboxylic acids aggregate in the solid state as dimer, catemer and bridged motifs [57–59]. Herein, two carboxyl groups and two inserted water molecules are both bifurcate and construct the $R_4^4(12)$ rings *via* O–H···O hydrogen bonds, which extremely differ from those rings offered by both acidic and basic components together in **1**. Moreover, N–H···O and C–H···O hydrogen bonds are associated to form the crystal packing, which possesses two types of similar grids, colored as pale pink and light green, respectively. Running along the *a* axis, the 2,2′-dipyridylammonium cation layer is slightly disordered and alternates with the 3,4-dinitrobenzoate anion layer.

Extending on the *ac* plane, 2,2′-dipyridylammonium cations seem to be comparatively ordered arrangement (Fig. 4b). As illustrated in the pale pink background, the cations insert themselves into the $R_4^4(12)$ ring between carboxyl groups and water molecules through N1–H1A···O7 and N2–H2···O2 hydrogen bonding interactions. When viewed along the *c* axis, the orderly assembly of ammonium cations results in a striking architecture just like a pillar, colored as pale gray (Fig. 4c). These unique pillars supported the layers packing by 3,4-dinitrobenzoate anions.

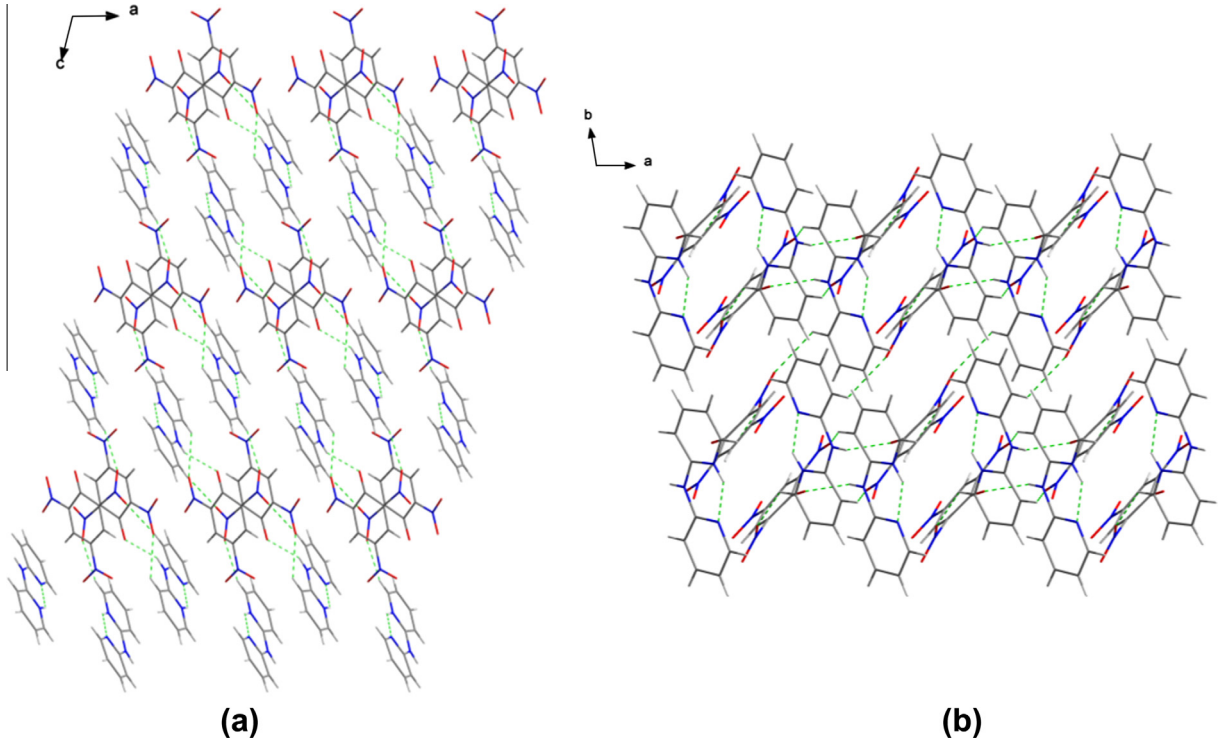


Fig. 6. (a) View of the 3D supramolecular networks in **3**, in which hydrogen bonds are shown by dashed lines in green. (b) The 3D wavelike structure in **3**. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

*3.2.3. X-ray structure of (picrate)···(2,2′-dipyridylammonium) (**3**)*

As an extension of our study of hydrogen bonding interactions concerning organic acids, we chose the picric acid (PAc) with the strong withdrawing groups. PAc is a good candidate of polytopic hydrogen acceptor. The pK_a(O–H) of 0.36 indicates its strong acidity and ensures proton transfer to amines to form a rather strong hydrogen bond between the protonated cation and the picrate anion. Meanwhile, the nitro groups are left free to interact with other potential hydrogen donors in the structure, even though they are not ideal H-bond acceptors due to their pK_a of nearly −12 [25,41,60].

Well-shaped salt **3** is obtained from 2,2′-dipyridylamine and picric acid in methanol, which crystallizes as triclinic yellow crystals in the centrosymmetric space group *P*−1. As shown in Fig. 5, one crystallographically independent 2,2′-dipyridylammonium cation and one picrate anion compose the asymmetric unit, with no solvent molecules included. In comparison with those in the compounds **1**–**2**, hydrogen bonds in **3** are not so rich in variety. Parallel to the *ac* plane, the picrate anion layer by random stacking treads on the heels of the 2,2′-dipyridylammonium cation layer, leading to the formation of the 3D supramolecular framework through N–H···O$^-$ and C–H···O hydrogen bonds (Fig. 6a). The strength of these hydrogen bonding interactions is relatively weaker, with H···O distance of over 2.00 Å. The adjacent cations in the same layer are antiparallel to each other.

Especially attractive is the wavelike architecture viewed along the *a*-axis, where everyone transverse anion layer is surrounded by two endwise cation layers (Fig. 6b). The neighboring anions in the same layer are antiparallel to each other while all the cations are homo-orientated in the same column. In addition, the directions of the molecular arrangement are opposite between the two close columns.

4. Conclusions

The 2,2′-dipyridylamine (dpa) has been employed as a proton sponge due to the presence of two closely positioned basic sites that can accept a proton between the two nitrogen atoms. Basic pyridyl nitrogen atoms make it a promising synthon in the supramolecular synthesis of multicomponent molecular complexes. Reactions of dpa and acidic synthons with suitable different functional groups afford three 3D supramolecular frameworks by robust and predictable hydrogen-bonding interactions. The strength and directionality of the strong ionic N–H···O$^-$ hydrogen bonds between 2,2′-dipyridylamine and acidic components, described herein, are sufficient to give rise to proton transfer and formation of organic acid–base salts. It is worthy of notice that the N–H$^+$···N hydrogen bonding offers the intramolecular ring S(6) in the proton sponge dpaH$^+$ of supramolecular ammonium salts **1**–**3**.

Under similar reaction conditions, all crystallize in the triclinic space group *P*−1. However, large discrepancy has been observed among them. The robust hydrogen bonding interactions generate various ring motifs in the salt **1**, e.g. $R_2^1(5)$, $R_2^1(6)$, $R_2^3(7)$, $R_2^2(8)$, $R_2^2(11)$, $R_4^2(10)$, $R_4^2(18)$ and $R_4^4(26)$. Only one type of the $R_4^4(12)$ ring exists in ammonium carboxylate **2**. The ammonium picrate **3** does not form any of recognized types of ring motifs between cations and anions. From the three cases, we can draw the inference that variations in molecular shape on the acidic components lead to different architectures. Functional carboxyl group with two oxygen atoms can act as a bidentate potential hydrogen-bonding donor so that it has an advantage over the deprotonated picrate in constructing hydrogen bonding rings, which are well agreement with these results. As for the difference of ring motifs between **1** and **2**, the position of nitro group in the benzene ring may play an important role on it.

In conclusion, from this we can gather clues about the influence of different functional groups as well as the steric effect of electron-withdrawing groups on the overall packing, which offer the favorable and reliable information for the design of supramolecules.

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Appendix A. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic data center, CCDC Nos. 92890 for **1**, 92892 for **2**, and 92891 for **3**. Copies of this information may be obtained free of charge from the +44 1223 336 033 or Email: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk. Supplementary data associated with this article (details of crystallographic data and hydrogen bond information for the complex of 1-3) can be found, in the online version, at http://dx.doi.org/10.1016/j.molstruc.2013.07.056.

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