

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 R₂²(8), R₄²(10), R₄⁴(12), R₄²(18) and R₄⁴(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 picronic acid) afford three proton-transfer supramolecular ammonium salts, (2,4-dinitrobenzoate)···(2,2'-dipyridylammonium) (**1**), (3,4-dinitrobenzoate)···(2,2'-dipyridylammonium)···(H₂O) (**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.

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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 abstraction [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)·(H₂O) (**2**) and (picrate)·(2,2'-dipyridylammonium) (**3**), respectively (Scheme 1). The proton transfers from the acid to pyridyl nitrogen atom.

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)·(H₂O) (**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.

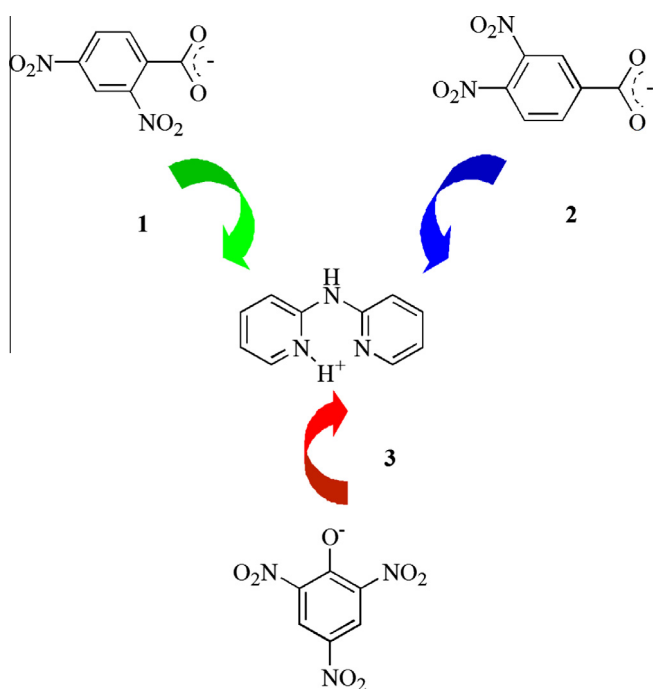
2.2. X-ray crystallography

Data collections were made by using graphite monochromated Mo K α diffraction ($\lambda = 0.71073 \text{ \AA}$) 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



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

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