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8-(DI-METHYL-AMINO)-N,N-DI-METHYL-NAPHTHALEN-1-AMINIUM AND HYDROGENTEREPHTHALATE AS SYNTHONS FOR SUPRAMOLECULAR ARCHITECTURE

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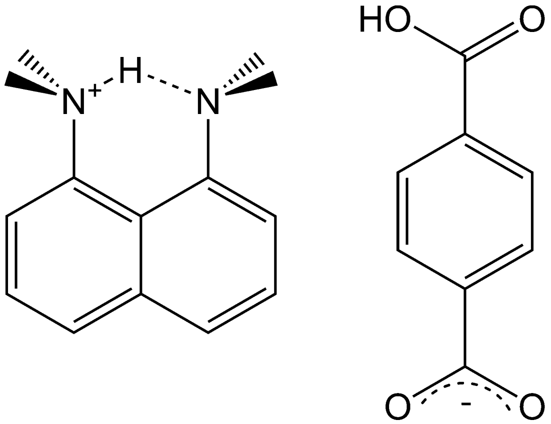
ABSTRACT

8-(dimethylamino)-N,N-dimethyl-naphthalen-1-aminium hydrogenterephthalate (PSH^+TPAH^-) and **8-(dimethylamino)-N,N-dimethylnaphthalen-1-aminium hydrogen-terephthalate hydrate ($PSH^+TPAH^-\cdot H_2O$)** were prepared by the direct reaction of N^1,N^1,N^8,N^8-tetra-methyl-naphthalene-1,8-di-amine, Proton Sponge (**PS**) © and terephthalic acid (**$TPAH_2$**) in a 1:1 stoichiometric relation. The structure of both salts is constructed on the base of 1D chains defined by hydrogen bonding of the anionic carboxylate end and the carboxylic acid of **$TPAH^-$** anion. Additionally for the structure of **$PSH^+TPAH^-\cdot H_2O$** the water molecules connect this 1D chains through hydrogen bonds, then defining a 1D-belt. In both cases the **PSH^+** provides balance of charge among the chains.

Keywords: Proton Sponge; hydrogenterephthalate; hydrogen-bonded chains.

1. INTRODUCTION

N^1,N^1,N^8,N^8-tetra-methyl-naphthalene-1,8-diamine, commonly named Proton Sponge (**PS**) © is a strong organic base, whose pK_B is equal to 1.8(1) in water at 25°C [1]. The base is soluble in most the commonly used laboratory organic solvents and can be considered as a monoprotic base, where the proton binds to one of the nitrogen atoms then defining a hydrogen bond to the other; as shown in Scheme 1; to produce the **PSH^+** cation [2]. In an opposite way, terephthalic acid (**$TPAH_2$**) is an organic diacid with pK_{A1} equal to 3.54 and pK_{A2} equal to 3.54 [3].



Scheme 1. 8-(dimethylamino)-*N*,*N*-dimethyl-naphthalen-1-aminium (PSH^+) and **hydrogenterephthalate ($TPAH^-$)** ions.

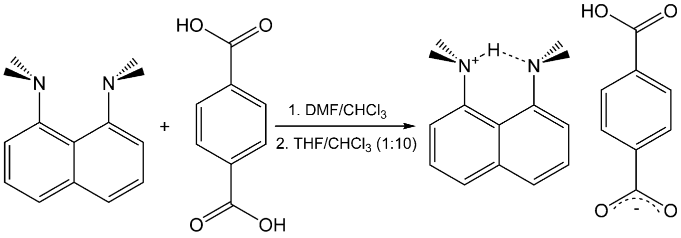
Terephthalic acid can be partially deprotonated to **$TPAH^-$** by bases to give a 1:1 salt like **$NH_4^+TPAH^-$** [4] or **ImH^+TPAH^-** [5] where **Im** corresponds to imidazole. **PSH^+** and **$TPAH^-$** are valuable building blocks for crystal engineering owing to their rigidity, charge, and the possibility to define multiple non-covalent inter-actions [4, 6].

In the present article we show how these two cations could be used to define different packing architectures by using their intermolecular bonding capacities.

2. EXPERIMENTAL

Reagents. All reagents were used as provided from supplier (Aldrich) and 6 with no purification before use. Solvents were dried and freshly distilled according to standard drying procedures.

i.- Syntheses of 8-(dimethylamino)-N,N-di-methyl-naphthalen-1-amminium hydrogen terephthalate (PSH^+TPAH^-) and 8-(dimethylamino)-N,N-dimethylnaphthalen-1-amminium hydrogen terephthalate ($PSH^+TPAH^-\cdot H_2O$)
The compound was prepared by the direct reaction between terephthalic acid and Proton-sponge ©, 1,8-bis(dimethylamino)-naphthalene, in stoichiometric ratio 1:1 at room temperature according to Scheme 2. A colourless solution of 250 mg of the acid (1.504 mmol) in 20 mL DMF was added to a colourless solution of 323 mg (1.504 mmol) of the organic base dissolved in 10 mL of chloroform. The reaction was stirred at room temperature overnight. The solvent was then removed by evaporation under reduced pressure leaving a white crude solid, whose recrystallization in a $CHCl_3$/THF (10:1) mixture gave-off crystals of **PSH^+TPAH^-** and **$PSH^+TPAH^-\cdot H_2O$** in the same batch. This last one is believed to be produced from adventitious water incorporated during reaction or recrystallization.



Scheme 2. Synthetic route to **(PSH^+TPAH^-)**.

ii. Structural Determination: The crystal structure of **(PSH^+TPAH^-)** and **(PSH^+TPAH^-)$\cdot$$H_2O$**, at room temperature was determined by X-rays diffraction. Data collections were done on a SMART-APEX II CCD diffractometer using ω−scans as collection strategy. Data were reduced by using SAINT [7], while the structure was solved by direct methods, completed by Difference Fourier Synthesis and refined by least-squares using SHELXL [8, 9] Empirical absorption corrections were applied using SADABS [7]. Crystal data, data collection and structure refinement details are summarized in Table 1. For both structures the hydrogen atoms were positioned geometrically and refined using a riding model: C—H = 0.93-0.96 Å with $U_{iso}(H) = 1.2–1.5\ U_{eq}(C)$, except the ammonium hydrogen atom on **PSH^+** and the acid hydrogen atom on **$TPAH^-$** which were in the respective Fourier-difference maps and subsequently refined with a distant constraint of 0.82 Å and 0.85 Å respectively

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Table 1. Crystal data and structure refinement for **(PSH^+TPAH^-)** and **(PSH^+TPAH^-)**.

	(PSH^+TPAH^-)	**(PSH^+TPAH^-)·H_2O**
Chemical formula	$C_{14}H_{19}N_2{\cdot}C_8H_5O_4$	$C_{14}H_{19}N_2{\cdot}C_8H_5O_4{\cdot}H_2O$
FW/uma	380.43	398.45
Crystal System	Monoclinic	Triclinic
Space Group	$C2/c$	$P\bar{1}$
a (Å)	21.206(3)	9.5970(18)
b (Å)	9.7790(14)	10.762(2)
c (Å)	19.066 (3)	11.069(2)
α(°)	90	105.211(5)
β (°)	98.715(4)	102.258(6)
γ (°)	90	98.772(5)
V (Å^3)	3908.1(10)	1051.4(3)
Z	8	2
d (g cm^{-3})	1.293	1.259
μ (mm^{-1})	0.09	0.09
F000	1616	424
θ range	2.0 to 26.0°	2.0 to 26.0°
hkl range	$-12 \le h \le 12$	$-12 \le h \le 12$
	$-14 \le k \le 14$	$-14 \le k \le 14$
	$-24 \le l \le 24$	$-24 \le l \le 24$
N_{tot}, N_{uniq} (R_{int}), N_{obs}	12652, 3833 (0.054), 2976	8235, 4119 (0.018), 2979
Refined Parameters	265	282
GOF	1.03	1.02
R1, wR2 (obs)	0.054, 0.154	0.045, 0.128
Max. and min Δρ	0.45 and -0.21	0.25 and -0.21

3. RESULTS AND DISCUSSION

3.1. Structural Description. Figure 1 shows the molecular structure of the **PSH^+** cation and the **$TPAH^-$** anion. The geometry of the cation is highly like that previously described [10], including the intra-molecular hydrogen bond [6, 11] with ***D···A*** 2.584 (2) Å and 2.611 (2) Å for **PSH^+TPAH^-** and **$PSH^+TPAH^-{\cdot}H_2O$** respectively. In the same way, the distances and angles for the hydrogen terephthalate anion are highly like what previously described [4, 12]. As clear from the difference Fourier Map the acid hydrogen is in one of the carboxyl-ate moieties, which makes this anion a rigid ionic/dipole synthon for crystal engineering.

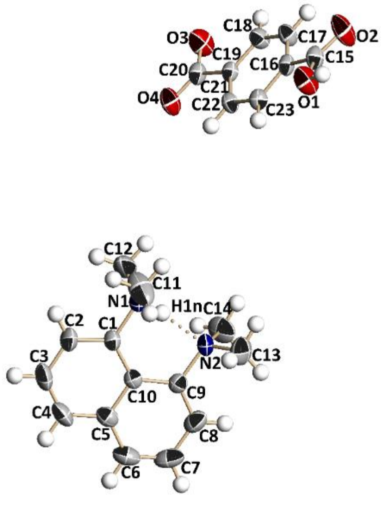

Figure 1. Molecular structure diagrams for the **PSH^+** cation and the **$TPAH^-$** anion from **PSH^+TPAH^-**. Full numbering scheme included for the non-hydrogen atoms and the hydrogen atoms involved in hydrogen bonding. Displacement ellipsoids at 50%. Hydrogen atoms are drawn as arbitrary radii spheres.

3.2. Packing Structure: Figure 2 shows the 1D chains defined by the hydrogen terephthalate **$TPAH^-$** anions along the [001] direction within the packing structure of **PSH^+TPAH^-**. The chain is stabilized by ion/dipole inter-actions with O1···O3^{i} (*i*: *x*, -*y*+2, *z*-1/2) of 2.4662 (19) Å, as the **PSH^+** provides balance of charge among the chains. This scheme of a 1D-chain is preserved for the hydrated salt, **$PSH^+TPAH^-{\cdot}H_2O$**, whereas depicted in Figure 3, there are chains of **$TPAH^-$** anions equivalent to those of the non-solvated salt (O1—H1T···O3^{i} 2.4519 (17) Å; *i*: *x*-1, *y*, *z*), but with water molecules bonding two vicinal ones, defining a sort of 1D-belt along the [100] direction. The strong hydrogen bonds defined by the anionic terephthalate oxygen atoms to the bridging water molecules are characterized by O5*w*···O4^{i}, 1.998 (3) Å (*i*: *x*-1, *y*, *z*) and O5*w*···O4^{ii} 2.084 (10) (*ii*: -*x*+2, -*y*+1, -*z*+1).

Table 2. Hydrogen-bond geometry (Å) for **(PSH^+TPAH^-)** and **(PSH^+TPAH^-)**.

(PSH^+TPAH^-)	
D*—H···*A	***D···A***
N1—H1*N*···N2	2.584(2)
O1—H1*T*···O3^{i}	2.4662(19)
(PSH^+TPAH^-)·H_2O	
O5*W*—H1*W*···O4^{ii}	2.848(2)
O5*W*—H2*W*···O4^{iii}	2.8924(19)
O1—H1*T*···O3^{ii}	2.4519(17)
N1—H1*N*···N2	2.611(2)

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

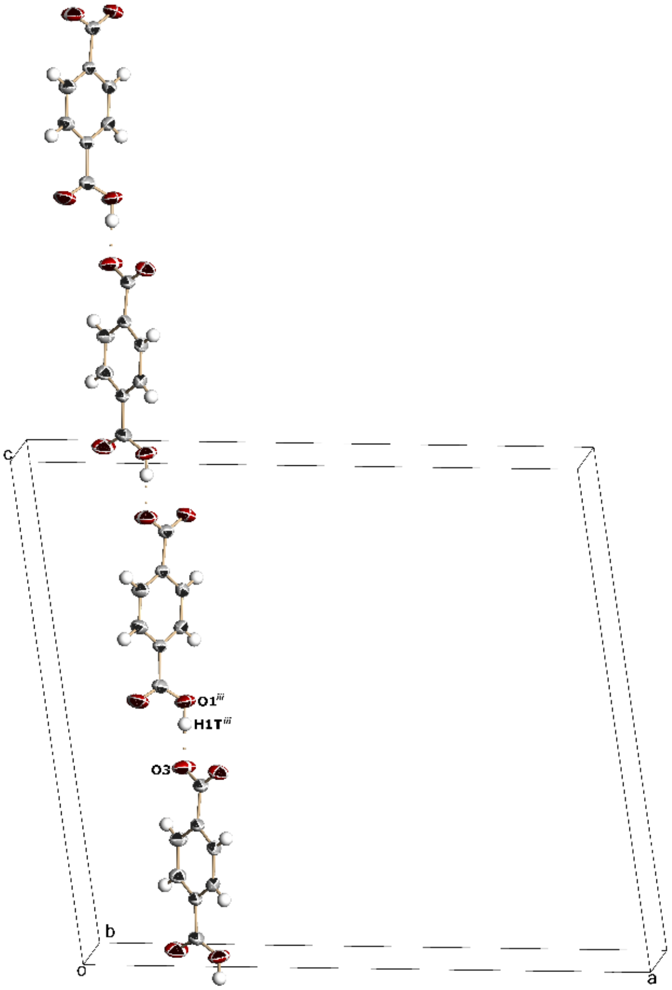

Figure 2. 1D hydrogen bonded hydrogen terephthalate chains along [001] in the packing of **PSH^+TPAH^-**. *Symmetry label iii: x, -y+2, z+1/2.*

The structure of $\mathbf{NH_4^+TPAH^-}$ [4, 13, 14] show the same pattern of the packing structure, with a 1D chain of $\mathbf{TPAH^-}$ anions in one direction whose charge is counterbalanced by ammonium cations. The introduction of solvating molecules or the modification of the amine slightly modify the pattern, but this is essentially preserved [15, 16], as occurs going from $\mathbf{PSH^+TPAH^-}$ to $\mathbf{PSH^+TPAH^-{\cdot}H_2O}$. This occurs even if a n highly rigid ammonium salt is used [5].

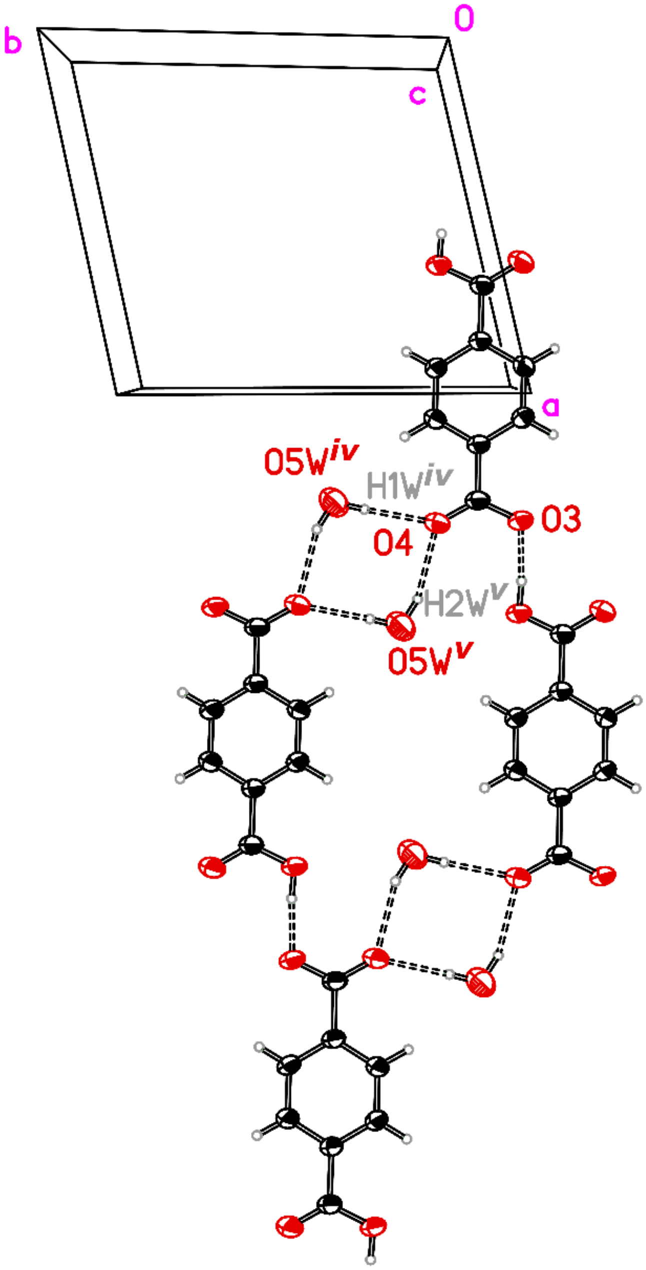

Figure 3. 1D hydrogen bonded hydrogen terephthalate/water belts along [100] in the packing of $\mathbf{PSH^+TPAH^-{\cdot}H_2O}$. *Symmetry labels iv: x+1, y, z; v: 2-x, -y, -z.*

CONCLUSION

$\mathbf{PSH^+}$ and $\mathbf{TPAH^-}$ ions can give rise to different packing structure via hydrogen bonding interactions. A simple experience shows that experimental conditions could strongly affect the structure.

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