Supporting Information

Exceptions to the rule: new hydrogen bonded networks from an old reliable

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**General Information**

All reagents were obtained from Aldrich (Milwaukee, WI) or Alfa Aesar (Ward Hill, MA) and used without further purification unless otherwise stated. Single crystal X-ray diffraction data was obtained on an APEX II or a SMART APEX II diffractometer at 100 K unless otherwise stated. Powder x-ray diffraction (PXRD) was obtained on a Rigaku Ultima-IV diffractometer under ambient conditions. Melting points were determined on a Thermo-Scientific Mel-Temp apparatus, while Infra-red spectra were collected using a Thermo Nicolet Avatar 380 FT-IR.

Note: PXRD data is not reported for hexane-1,6-diammonium•(HPzDCA)₂, compound 7, as sufficient quantities of a pure phase could not be obtained.

**Compound 1: o-ethoxyanilinium•HPzDCA**

A 20 ml scintillation vial was charged with 70.0 mg (0.40 mmol) of pyrazole-3,5-dicarboxylic acid monohydrate, which was dissolved in 5.0 ml of a 3:2 EtOH-H₂O mixture. To this solution was then added 54.9 mg (52.2 µl, 0.40 mmol) of o-ethoxyaniline. The mixture was filtered and the filtrate was allowed to slowly evaporate to yield colorless single crystals of o-ethoxyanilinium•HPzDCA (65.0 mg, 56% yield), mp 218-220 °C.

**Compound 2: o-ethylanilinium•HPzDCA•H₂O**

A 20 ml scintillation vial was charged with 70.0 mg (0.40 mmol) of pyrazole-3,5-dicarboxylic acid monohydrate, which was dissolved in 5.0 ml of MeOH. To this solution was then added 48.5 mg (49.3 µl, 0.40 mmol) of o-ethylaniline. The mixture was filtered and the filtrate was allowed to slowly evaporate to yield colorless single crystals of o-ethylanilinium•HPzDCA•H₂O (36.8 mg, 33 % yield), mp 207-209 °C.

**Compound 3: 2,6-diethylanilinium•HPzDCA•H₂O**

A 20 ml scintillation vial was charged with 70.0 mg (0.40 mmol) of pyrazole-3,5-dicarboxylic acid monohydrate, which was dissolved in 5.0 ml of a 3:2 MeOH-H₂O mixture. To this solution was then added 59.7 mg (66.0 µl, 0.40 mmol) of 2,6-diethylaniline. The mixture was filtered and the filtrate was allowed to slowly evaporate to yield colorless single crystals of 2,6-diethylanilinium•HPzDCA•H₂O (73.5 mg, 60 % yield), mp 253-255 °C.

**Compound 4: 2-Isopropylanilinium•HPzDCA**

A 20 ml scintillation vial was charged with 70.0 mg (0.40 mmol) of pyrazole-3,5-dicarboxylic acid monohydrate, which was dissolved in 5.0 ml of a MeOH. To this solution was then added 54.1 mg
(56 µl, 0.40 mmol) of 2-isopropylaniline. The mixture was filtered and the filtrate was allowed to slowly evaporate to yield colorless single crystals of 2-Isopropylanilinium•HPzDCA (56.3 mg, 47 % yield), mp 173-175 °C.

**Compound 5: 1,4-bis(2-hydroxyethyl)piperazinium•(HPzDCA)$_2$**

A 20 ml scintillation vial was charged with 70.0 mg (0.40 mmol) of pyrazole-3,5-dicarboxylic acid monohydrate, which was dissolved in 5.0 ml of a 4:1 MeOH-H$_2$O mixture. To this solution was then added 70.0 mg (0.40 mmol) of 1,4-bis(2-hydroxyethanol)piperazine. The mixture was filtered and the filtrate was allowed to slowly evaporate to yield colorless single crystals of 1,4-bis(2-hydroxyethyl)piperazinium•HPzDCA (96.7 mg, 73 % yield), mp 250-252 °C.

**Compound 6: TMEDAH$_2$•(HPzDCA)$_2$**

A 20 ml scintillation vial was charged with 70.0 mg (0.40 mmol) of pyrazole-3,5-dicarboxylic acid monohydrate, which was dissolved in 5.0 ml of MeOH. To this solution was then added 46.5 mg (60.0 µl, 0.40 mmol) of $N,N,N',N'$-tetramethylethylenediamine (TMEDA). The mixture was filtered and the filtrate was allowed to slowly evaporate to yield colorless single crystals of TMEDAH$_2$•HPzDCA (74.1 mg, 68 % yield), mp 284-286 °C.

**Compound 7: Hexane-1,6-diammonium•(HPzDCA)$_2$**

A 20 ml scintillation vial was charged with 70.0 mg (0.40 mmol) of pyrazole-3,5-dicarboxylic acid monohydrate, which was dissolved in 5.0 ml of a 3:2 MeOH-H$_2$O mixture. To this solution was then added 46.5 mg (52.2 µl, 0.40 mmol) of 1,6-diaminohexane. The mixture was filtered and the filtrate was allowed to slowly evaporate to yield colorless single crystals of hexane-1,6-diammonium•(HPzDCA)$_2$ (8.74 mg, 8 % yield), mp 134-136 °C.
Figure S1. Infra-Red spectrum of $o$-ethoxyanilinium•HPzDCA

Figure S2. Infra-Red spectrum of $o$-ethylanilinium•HPzDCA•H$_2$O
Figure S3. Infra-Red spectrum of 2,6-diethylanilinium•HPzDCA•H2O

Figure S4. Infra-Red spectrum of 2-isopropylanilinium•HPzDCA
Figure S5. Infra-Red spectrum of 1,4-bis(2-hydroxyethylpiperazinium)•(HPzDCA)₂

Figure S6. Infra-Red spectrum of TMEDAH₂•(HPzDCA)₂
Figure S7. Infra-Red spectrum of hexane-1,6-diaminonium•(HPzDCA)$_2$

Figure S8. PXRD of o-ethoxyanilinium•HPzDCA
**Figure S9.** PXRD of o-ethylanilinium•HPzDCA•H$_2$O

**Figure S10.** PXRD of 2,6-diethylanilinium•HPzDCA•H$_2$O
Figure S11. PXRD of 2-isopropylanilinium•HPzDCA

Figure S12. PXRD of 1,4-bis(2-hydroxyethyl)piperazinium•(HPzDCA)$_2$
**Figure S13.** PXRD of TMEDA<sub>2</sub>•(HPzDCA)<sub>2</sub>

**Figure S14.** Structural features of: a) hydrogen bonded network of hexane-1,6-diaminonium•(HPzDCA)<sub>2</sub> (compound 7); b) Overlay of layers of 7 showing the occupation of intralayer voids by adjacent layers. (Hydrogen bonds within the “green” layer are colored grey, while those in the “yellow” layer are colored red.)

**Table S1.** Summary of Crystallographic Data for Compound 7.
Empirical formula \( \text{C}_{16} \text{H}_{24} \text{N}_{6} \text{O}_{8} \)

Formula weight 428.41

Temperature 100(2) K

Wavelength 0.71073 Å

Crystal system Triclinic

Space group P-1

Unit cell dimensions
\[
a = 4.5537(6) \text{ Å} = 79.342(4)^\circ.
\]
\[
b = 9.3845(11) \text{ Å} = 85.338(5)^\circ.
\]
\[
c = 11.1398(14) \text{ Å} = 85.904(4)^\circ.
\]

Volume 465.52(10) Å\(^3\)

Z 1

Density (calculated) 1.528 Mg/m\(^3\)

Absorption coefficient 0.124 mm\(^{-1}\)

\(F(000)\) 226

Crystal size 0.23 x 0.20 x 0.14 mm\(^3\)

Theta range for data collection 1.86 to 29.74\(^\circ\).

Index ranges
\(-6 \leq h \leq 6, -13 \leq k \leq 13, -15 \leq l \leq 15\)

Reflections collected 12441

Independent reflections 2637 [R(int) = 0.0318]

Completeness to theta = 25.00\(^\circ\) 99.8 \%

Absorption correction Semi-empirical from equivalents

Max. and min. transmission 0.9827 and 0.9725

Refinement method Full-matrix least-squares on \(F^2\)

Data / restraints / parameters 2637 / 0 / 138

Goodness-of-fit on \(F^2\) 1.061

Final R indices [I>2sigma(I)] \(R1 = 0.0364, wR2 = 0.0935\)

R indices (all data) \(R1 = 0.0446, wR2 = 0.0980\)

Largest diff. peak and hole 0.433 and -0.280 e.Å\(^{-3}\)