

# Supramolecular Architecture of Chloranilate Salts with Organic Cations: $\pi$ -stacking vs. Hydrogen Bonding

Krešimir Molčanov\*, Lidija Androš Dubraja, Marijana Jurić

Ruder Bošković Institute, Bijenička cesta 54, HR-10002, Zagreb, Croatia

\* Corresponding author's e-mail address: kmolcano@irb.hr

RECEIVED: June 6, 2019 \* REVISED: November 19, 2019 \* ACCEPTED: November 19, 2019

THIS PAPER IS DEDICATED TO PROF. KATA MLINARIĆ-MAJERSKI ON THE OCCASION OF HER 70<sup>TH</sup> BIRTHDAY

**Abstract:** Four novel salts of chloranilic acid ( $H_2CA$ ; 3,6-dichloro-2,5-dihydroxy-1,4-quinone) with organic cations pyridinium ( $Hpy^+$ ), piperazinediium ( $H_2ppz^{2+}$ ), 4,4'-bipyridinediium ( $H_2bpy^{2+}$ ) and 1,10-phenanthroline ( $Hphen^+$ ) were prepared and structurally characterised: ( $Hpy$ ) $_2CA$  (**1**), ( $H_2ppz$ ) $CA$  (**2**), ( $H_2bpy$ ) $CA \cdot 4H_2O$  (**3**) and ( $Hphen$ ) $HCA \cdot MeOH$  (**4**). Supramolecular architecture is based on extensive hydrogen bonding and  $\pi$ -stacking. The central motive is chloranilate dianion which acts as an acceptor of two bifurcated hydrogen bonds. Topology and dimensionality of hydrogen bonded networks can be tuned by use of different cations: thus discrete motives, 1D chains and 2D layers were observed. Three different types of  $\pi$ -stacks are present: aromatic stacks, quinoid stacks and stacks of alternating quinoid and aromatic rings.

**Keywords:** chloranilic acid, crystal structure, crystal engineering, supramolecular chemistry.

## INTRODUCTION

CHLORANILIC ACID, 3,6-dichloro-2,5-dihydroxy-1,4-quinone ( $H_2CA$ , Scheme 1), is a member of a well-studied class of compounds, substituted 2,5-dihydroxyquinones (*anilic acids*).<sup>[1]</sup> Since its first preparation by Gräbe in 1891,<sup>[2]</sup> it has been widely used in organic chemistry and crystal engineering, due to its versatility: it is a good ligand towards transition metals,<sup>[3–8]</sup> strong hydrogen bond donor and acceptor<sup>[9]</sup> and is capable of forming strong stacking interactions.<sup>[10–12]</sup> Presence of two chlorine substituents enhances acidity of its OH groups, giving a moderately strong acid with  $pK_a$  values of 0.73 and 3.08.<sup>[13]</sup>

Deprotonation strongly affects electronic structure of the chloranilic acid: the neutral form is a *p*-quinone, while its mono- ( $HCA^-$ ) and dianion ( $CA^{2-}$ ) comprise delocalised  $\pi$ -electron systems. Molecular geometries<sup>[1,9,10]</sup> and IR spectra<sup>[7,8,14]</sup> agree well with the Scheme 1, and these structures were recently confirmed by X-ray charge density.<sup>[15]</sup> Thus, the neutral acid (Scheme 1, left) comprises a *p*-quinoid ring, and the dianion comprises two delocalised

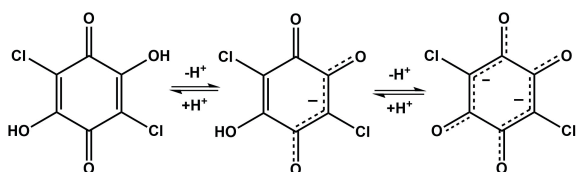
systems connected by two single C–C bonds (Scheme 1, right). The mono anion (Scheme 1, centre) has a delocalised system in the deprotonated part of the ring, while the protonated part resembles the half of a neutral molecule.

Chloranilic acid easily forms salts and co-crystals with organic cations involving a proton transfer, and a considerable number of these compounds is known.<sup>[9,16–30]</sup> The neutral chloranilic acid and its monoanion are strong hydrogen bond donors, and are also good hydrogen bond acceptors,<sup>[14,18]</sup> so in the solid state they form multiple hydrogen bonds. The dianion is a strong hydrogen bond acceptor,<sup>[1,14]</sup> and comprises six possible acceptor sites (Scheme 1), four strong (partially negatively charged O atoms) and two weaker ones (Cl atoms). Most commonly it acts as an acceptor of two bifurcated hydrogen bonds directed towards its O atoms, forming two  $R_1^2(5)$  rings (Figure 1).<sup>[9]</sup>

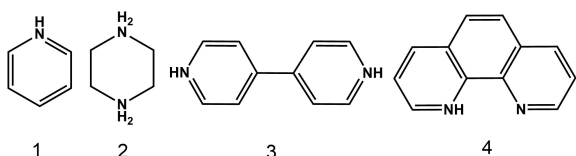
Hydrogen chloranilate monoanions in their simple alkali salts often form a rare type of face-to-face  $\pi$ -stacks with extremely short interplanar separations of about

3.3 Å;<sup>[10,11]</sup> this specific arrangement is a result of unique electronic structure of the anion, with alternating areas of positive and negative electrostatic potential.<sup>[12]</sup> This type of  $\pi$ -interaction has an energy exceeding 10 kcal mol<sup>-1</sup>, which is by an order of a magnitude stronger than common  $\pi$ -interactions between aromatic rings,<sup>[12,31]</sup> and was also found in salts of closely related hydrogen bromanilate dianion<sup>[32]</sup> and unsubstituted 2,5-dihydroxyquinonate.<sup>[33]</sup> This face-to-face stacking is the dominant interaction in the crystals, even where hydrogen bonding is present.<sup>[12]</sup> However, the dianions form only offset stacks with geometries and energies closer to aromatic stacking.<sup>[1,11]</sup>

Study of unusually strong  $\pi$ -interactions prompted us to extend our research to more salts of CA<sup>2-</sup> and HCA<sup>-</sup> with organic cations, to determine whether there is a competition or synergy between stacking and hydrogen bonding. Here we present four novel salts of CA<sup>2-</sup> and HCA<sup>-</sup> (Scheme 1) with pyridinium (Hpy<sup>+</sup>), piperazinediium (H<sub>2</sub>ppz<sup>2+</sup>), 4,4'-bipyridinediium (H<sub>2</sub>bpy<sup>2+</sup>) and 1,10-phenanthrolium (Hphen<sup>+</sup>) cations (Scheme 2).



**Scheme 1.** The dissociation of chloranilic acid. The dianion has two delocalised  $\pi$ -systems separated by single C–C bonds.



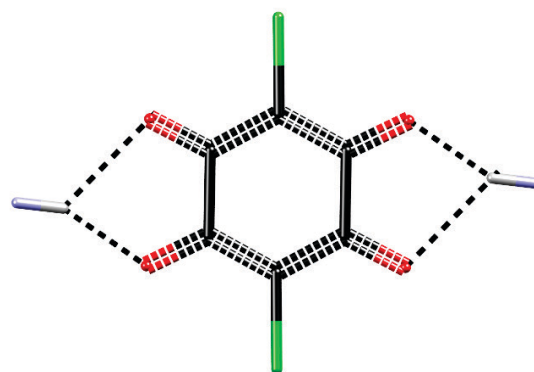
**Scheme 2.** Cations used in preparation of the studied salts: (1) pyridinium (Hpy)<sup>+</sup>, (2) piperazinediium (H<sub>2</sub>ppz)<sup>2+</sup>, (3) 4,4'-bipyridinediium (H<sub>2</sub>bpy)<sup>2+</sup> and (4) 1,10-phenanthrolium (Hphen)<sup>+</sup> cations.

## EXPERIMENTAL

### Preparation

All reagents used were purchased from commercial sources (Merck, Sigma-Aldrich, Kemika), were of p.a. grade and were used without further purification.

Chloranilic acid dihydrate was prepared by a known procedure;<sup>[34]</sup> its salts were prepared by dissolution of



**Figure 1.** The most common mode of hydrogen bonding of a chloranilate dianion: it acts as an acceptor of two bifurcated hydrogen bonds.

equimolar amounts (typically 0.01 mol) of chloranilic acid dihydrate and the organic base in water (*ca.* 10 mL, compounds **1**, **2** and **3**) and methanol (*ca.* 10 mL, compound **4**). Diffraction-quality single crystals were obtained by slow evaporation of aqueous or methanolic solutions at room temperature.

### X-ray Structural Analysis

Single-crystal X-ray measurements of compounds **1–4** were performed on an Oxford Diffraction Xcalibur Nova R diffractometer with a microfocus Cu-tube using mirror-monochromated CuK $\alpha$  radiation ( $\lambda = 1.54179$  Å). Program package CrysAlis PRO<sup>[35]</sup> was used for data reduction and multi-scan absorption correction.

The structures were solved using SHELXS97<sup>[36]</sup> and refined with SHELXL-2017.<sup>[36]</sup> The structures were refined using the full-matrix least squares refinement; all non-hydrogen atoms were refined anisotropically. Hydrogen atoms were located from difference Fourier maps and refined either as riding or geometrically restrained entities. For refinement of hydrogen atoms in water molecules, the following restraints were used:  $d(\text{O–H}) = 0.95$  Å;  $d(\text{H}\cdots\text{H}) = 1.50$  Å; hydrogen atoms bound to N and C were modelled as riding entities.

Molecular geometry calculations were performed by PLATON,<sup>[37]</sup> and molecular graphics were prepared using ORTEP-3,<sup>[38]</sup> and CCDC-Mercury.<sup>[39]</sup> Crystallographic and refinement data for the structures reported in this paper are shown in Table 1.

Supplementary crystallographic data for this paper can be obtained free of charge via [www.ccdc.cam.ac.uk/conts/retrieving.html](http://www.ccdc.cam.ac.uk/conts/retrieving.html) (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033; or [deposit@ccdc.cam.ac.uk](mailto:deposit@ccdc.cam.ac.uk)). CCDC 1921368-1921371 contain the supplementary crystallographic data for this paper.

**Table 1.** Crystallographic, data collection and structure refinement details for compounds (Hpy)<sub>2</sub>CA (**1**), (H<sub>2</sub>ppz)CA (**2**), (H<sub>2</sub>bpy)CA·4H<sub>2</sub>O (**3**) and (Hphen)HCA·MeOH (**4**).

Compound	(Hpy) <sub>2</sub> CA ( <b>1</b> )	(H <sub>2</sub> ppz)CA ( <b>2</b> )	(H <sub>2</sub> bpy)CA·4H <sub>2</sub> O ( <b>3</b> )	(Hphen)HCA·MeOH ( <b>4</b> )
Empirical formula	C <sub>16</sub> H <sub>12</sub> Cl <sub>2</sub> N <sub>2</sub> O <sub>4</sub>	C <sub>10</sub> H <sub>12</sub> Cl <sub>2</sub> N <sub>2</sub> O <sub>4</sub>	C <sub>16</sub> H <sub>18</sub> Cl <sub>2</sub> N <sub>2</sub> O <sub>8</sub>	C <sub>19</sub> H <sub>14</sub> Cl <sub>2</sub> N <sub>2</sub> O <sub>5</sub>
Formula wt. / g mol <sup>-1</sup>	367.18	295.12	437.22	421.22
Colour	dark red	dark purple	purple	dark red
Crystal dimensions / mm	0.15 × 0.12 × 0.10	0.33 × 0.30 × 0.20	0.20 × 0.05 × 0.03	0.18 × 0.12 × 0.06
Space group	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$	<i>C</i> 2/ <i>c</i>	<i>P</i> $\bar{1}$
<i>a</i> / Å	4.0660(2)	5.8301(7)	7.0532(3)	7.426(5)
<i>b</i> / Å	9.9311(6)	6.7317(7)	16.5844(7)	10.901(5)
<i>c</i> / Å	10.6189(6)	8.0163(8)	15.5762(7)	11.183(5)
$\alpha$ / °	114.889(6)	88.642(9)	90	86.124(5)
$\beta$ / °	90.372(4)	79.680(9)	91.968(4)	83.291(5)
$\gamma$ / °	100.469(5)	67.789(11)	90	81.033(5)
Z	1	1	4	2
<i>V</i> / Å <sup>3</sup>	380.83(4)	286.22(6)	1820.92(14)	887.0(8)
<i>D</i> <sub>calc</sub> / g cm <sup>-3</sup>	1.601	1.712	1.595	1.577
$\lambda$ / Å	1.54179 (CuK $\alpha$ )	1.54179 (CuK $\alpha$ )	1.54179 (CuK $\alpha$ )	1.54179 (CuK $\alpha$ )
$\mu$ / mm <sup>-1</sup>	4.067	5.223	3.670	3.622
$\theta$ range / °	4.61–75.72	5.62–66.0	5.33–75.88	3.98–72.0
<i>T</i> / K	293(2)	293(2)	293(2)	293(2)
Diffractometer type	Xcalibur Nova	Xcalibur Nova	Xcalibur Nova	Xcalibur Nova
Range of <i>h, k, l</i>	–3 < <i>h</i> < 5; –12 < <i>k</i> < 10; –13 < <i>l</i> < 13	–7 < <i>h</i> < 7; –7 < <i>k</i> < 8; –9 < <i>l</i> < 8	–7 < <i>h</i> < 8; –20 < <i>k</i> < 19; –19 < <i>l</i> < 19	–9 < <i>h</i> < 9; –13 < <i>k</i> < 13; –11 < <i>l</i> < 13
Reflections collected	3150	1465	4012	6986
Independent reflections	1555	963	1860	3406
Observed reflections ( <i>I</i> ≥ 2 $\sigma$ )	1496	901	1578	2774
Absorption correction	Multi-scan	Multi-scan	Multi-scan	Multi-scan
<i>T</i> <sub>min</sub> , <i>T</i> <sub>max</sub>	0.7570; 1.0000	0.4484; 1.0000	0.6027; 1.0000	0.4677; 1.0000
<i>R</i> <sub>int</sub>	0.0279	0.0188	0.0214	0.0411
<i>R</i> ( <i>F</i> )	0.0487	0.0406	0.0688	0.0596
<i>R</i> <sub>w</sub> ( <i>F</i> <sup>2</sup> )	0.1371	0.1161	0.1790	0.1838
Goodness of fit	1.063	1.076	1.636	0.957
H atom treatment	Constrained	Constrained	Mixed	Mixed
No. of parameters, restraints	109, 0	82, 0	141, 9	264, 6
$\Delta\rho_{\max}$ , $\Delta\rho_{\min}$ (eÅ <sup>-3</sup> )	0.306; –0.335	0.285; –0.408	1.510; –0.476	0.434; –0.389

**Table 2.** Bond lengths (Å) in chloranilate and hydrogen chloranilate anions of salts (Hpy)<sub>2</sub>CA (**1**), (H<sub>2</sub>ppz)CA (**2**), (H<sub>2</sub>bpy)CA·4H<sub>2</sub>O (**3**) and (Hphen)HCA·MeOH (**4**). Symmetry operators: *i*) 1-x, 1-y, 2-z; *ii*) 1-x, 2-y, 2-z; *iii*) -x, y, 3/2-z.

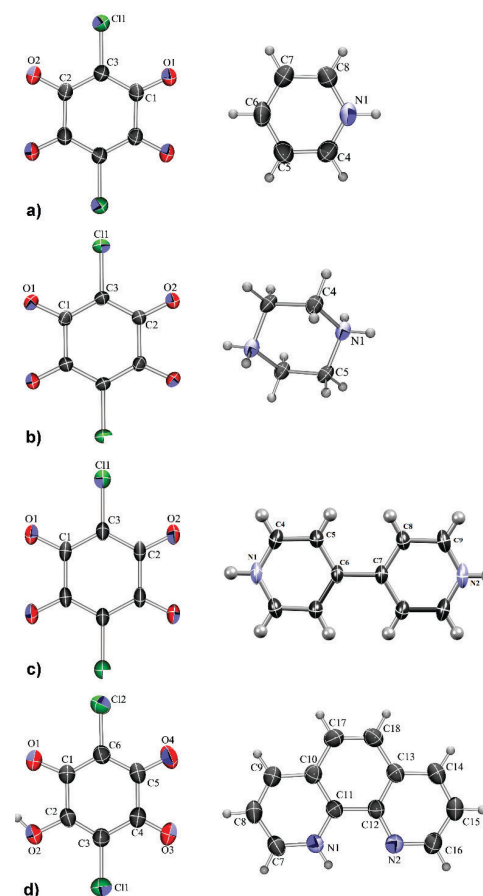
	<b>1</b>	<b>2</b>	<b>4</b>		<b>3</b>
C1–C2	1.539(2) <sup><i>i</i></sup>	1.541(4) <sup><i>ii</i></sup>	1.511(3)	C1–C1 <sup><i>iii</i></sup>	1.531(3)
C2–C3	1.414(3)	1.399(3)	1.354(3)	C1–C2	1.401(3)
C1–C3/C3–C4	1.390(2)	1.395(3)	1.453(3)		
O1–C1	1.259(2)	1.249(3)	1.247(3)	O1–C1	1.255(3)
O2–C2	1.242(2)	1.247(3)	1.320(3)	O2–C2	1.247(3)
Cl1–C3	1.7402(17)	1.738(3)	1.725(2)	Cl1–C3	1.740(3)
C4–C5			1.552(3)	C3–C3 <sup><i>iii</i></sup>	1.533(4)
C5–C6			1.408(3)	C2–C3	1.401(3)
C6–C1			1.397(3)		
O3–C4			1.217(3)		
O4–C5			1.237(3)		
Cl2–C6			1.735(2)		

## RESULTS AND DISCUSSION

In this paper we describe four novel salts of chloranilic acid (Scheme 2, Figure 2): pyridinium chloranilate (Hpy)<sub>2</sub>CA (**1**), piperazinedium chloranilate (H<sub>2</sub>ppz)CA (**2**), 4,4'-bipyridinedium chloranilate tetrahydrate (H<sub>2</sub>bpy)CA·4H<sub>2</sub>O (**3**) and 1,10-phenantrolinium hydrogen chloranilate methanol solvate (Hphen)HCA·MeOH (**4**). Asymmetric unit of **1** comprises a half of a centrosymmetric chloranilate dianion and a pyridinium cation in a general position; in **2** both the anion and the cation are centrosymmetric, while in **3** the cation and anion have a crystallographic symmetry *C*. In **4** hydrogen chloranilate mono anion, phenanthrolinium cation and methanol molecule are all located in a general position.

Bond lengths (Table 2) are in accord with previous studies of chloranilate salts,<sup>[1,9,10,15]</sup> and agree with  $\pi$ -electron delocalisation shown in Scheme 1. In all four studied anions there are two single C–C bonds; the dianion **4** also has one shortened single C–C bond (C3–C4) and one elongated double C=C bond (C2–C3); other two C–C (C5–C6 and C6–C1) bonds are delocalised. One C–O bond (C2–O2) is single, one is double (C4–O3), and other two (C5–O4 and C1–O1) are delocalised. In the three dianions there are four delocalised C–C bonds, and four delocalised C–O bonds.

Since the chloranilate dianion, CA<sup>2-</sup>, has four hydrogen bond accepting oxygen atoms, it typically acts as a bridge between hydrogen bond-donating cations, as we noticed previously.<sup>[9]</sup> Most commonly, this dianion accepts two bifurcated hydrogen bonds, forming a double  $R_1^2(5)$  motif shown in Figure 1. This type of hydrogen bonding is observed in compounds **1–3** (Table 3, Figure 3). In



**Figure 2.** ORTEP-3 drawings of anions (left) and cations (right) in compounds a) **1**, b) **2**, c) **3** and d) **4**. Displacement ellipsoids are drawn for the probability of 50 % and hydrogen atoms are shown as spheres of arbitrary radii.

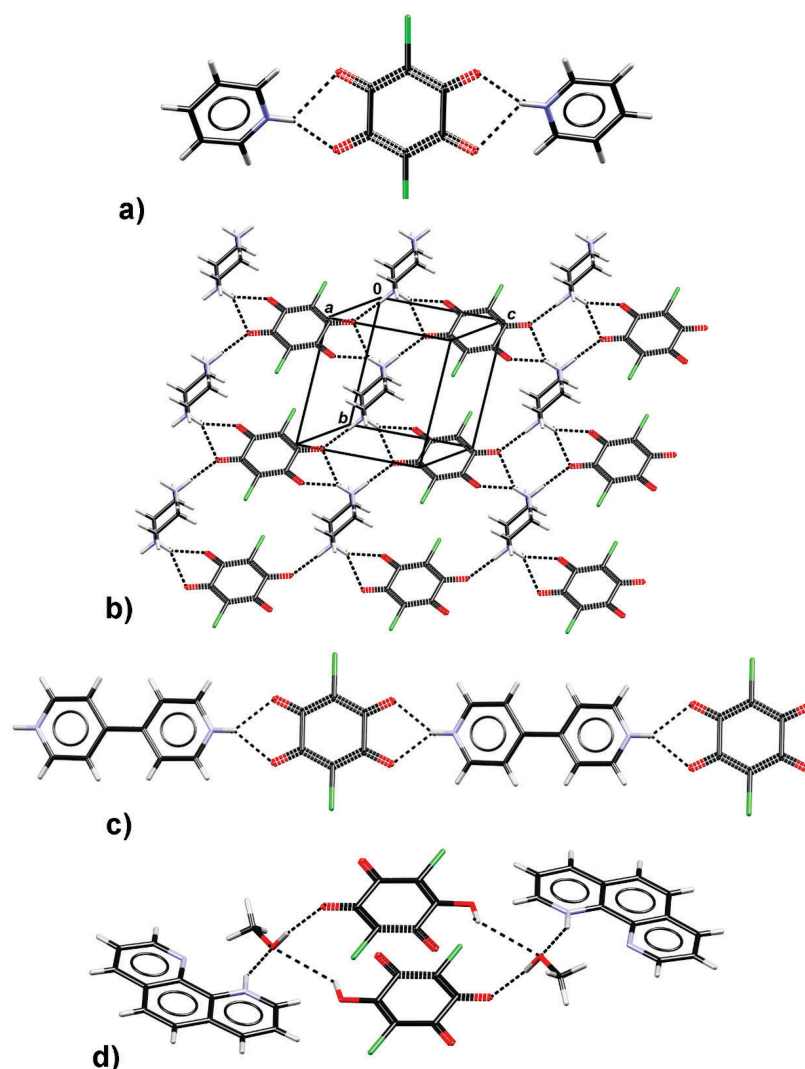


compound **4**, monoanion  $\text{HCA}^-$  is an acceptor of one and a donor of one hydrogen bond (Table 3); however, two anions are stacked (Table 4), forming a main centrosymmetric motif  $(\text{Hphen}\cdot\text{CA}\cdot\text{MeOH})_2$  (Figure 3 d) with a graph-set designation  $R_4^4(18)D_1^1(2)$ . The phenanthroline cation here acts as a hydrogen bond donor towards a methanol molecule, which acts as a hydrogen bond donor to one anion, and accepts a hydrogen bond from another one. This is in contrast to previously noted hydrogen-bonded dimers with an  $R_2^2(10)$  ring topology.<sup>[9]</sup>

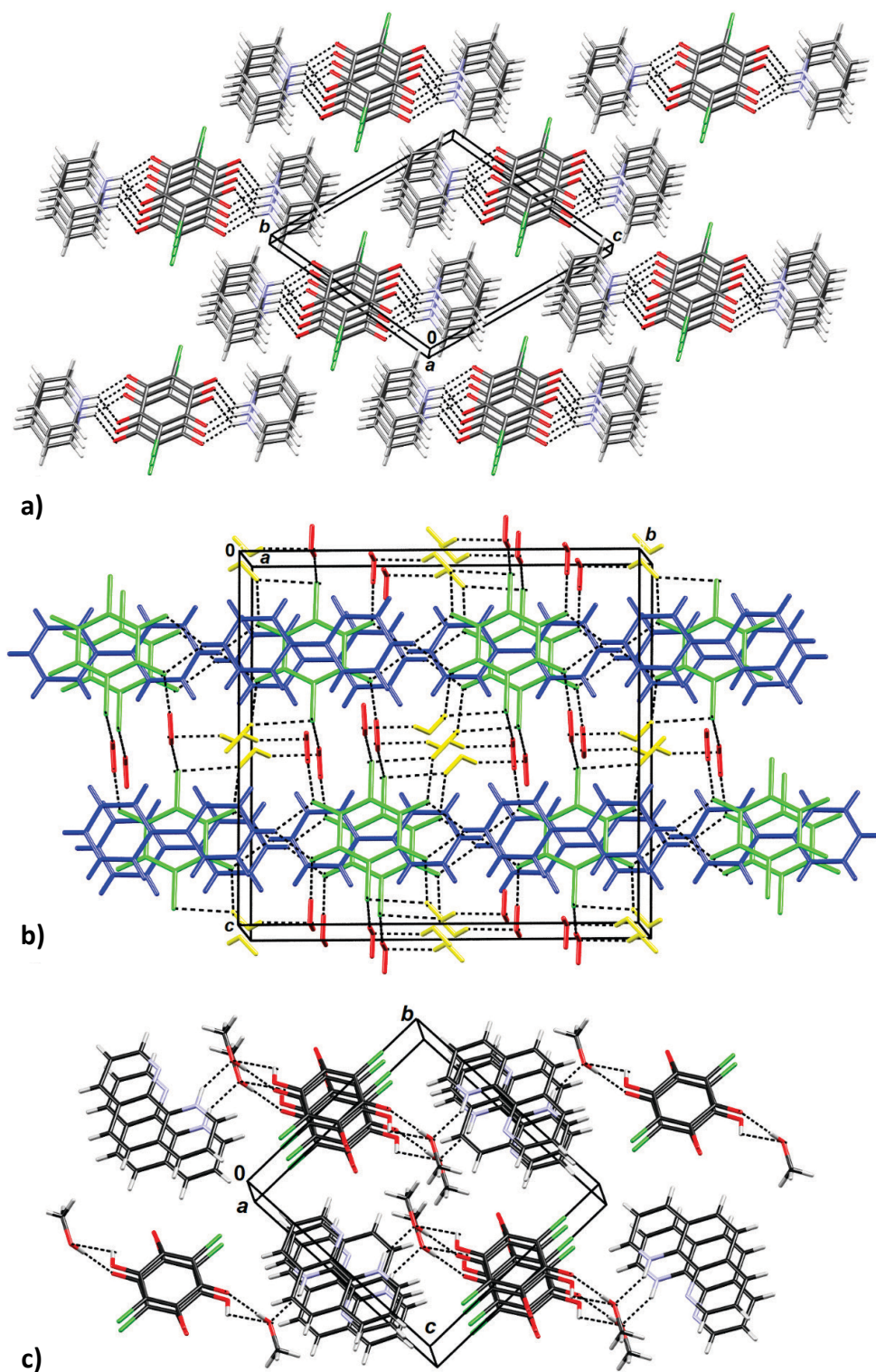
Dimensionality of the hydrogen-bonding pattern thus depends on the cation. Pyridinium and phenanthroline are donors of a single hydrogen bond (Table 3), and form discrete motifs (Figures 3 a and d). Cation 4,4'-bipyridinium is donor of two hydrogen bonds, and forms chains parallel to [010] with graph-set designation

$C_2^2(16)$  (Figure 3 c, Table 3). Piperazinedium, which is a donor of four hydrogen bonds (of which two are bifurcated), forms layers parallel to the plane (101) (Figure 3 b, Table 3), which can be described as two crossed  $C_2^2(12)$  chains; additionally ring-like motifs  $R_2^2(8)$  can be recognised.

Besides hydrogen bonding,  $\pi$ -stacking is also present in all structures except in compound **2** (Table 4); planar chloranilate moiety and aromatic rings are commonly involved in stacking interactions,<sup>[31]</sup> while non-planar piperazinedium cations of **2** do not stack. In compound **1** the main hydrogen-bonded units  $\text{Hpy}^+$  and  $\text{CA}^{2-}$  (Figure 3 a) form stacks which extend in the direction [100] (Figure 4 a). Weak  $\text{C}\cdots\text{O}$  hydrogen bonds (Table 3) connect these stacks into a 3D array. Two types of  $\pi$ -interactions are present:  $\text{CA}\cdots\text{CA}$  and  $\text{Hpy}\cdots\text{Hpy}$  (Figure 4 a and Table 4).



**Figure 3.** Hydrogen bonded motifs in compounds (a)  $(\text{Hpy})_2\text{CA}$  (**1**), (b)  $(\text{H}_2\text{ppz})\text{CA}$  (**2**), (c)  $(\text{H}_2\text{bpy})\text{CA}\cdot 4\text{H}_2\text{O}$  (**3**) and (d)  $(\text{Hphen})\text{HCA}\cdot\text{MeOH}$  (**4**).



**Figure 4.** Crystal packing of (a)  $(\text{Hpy})_2\text{CA}$  (**1**), (b)  $(\text{H}_2\text{bpy})\text{CA}\cdot 4\text{H}_2\text{O}$  (**3**) and (c)  $(\text{Hphen})\text{HCA}\cdot \text{MeOH}$  (**4**) show  $\pi$ -stacking of main motives. In b) molecules are colour-coded for clarity:  $\text{CA}^{2-}$  is green,  $\text{Hbpy}^+$  is blue, while two symmetry-independent water molecules are red and yellow, respectively.

**Table 3.** Geometric parameters of hydrogen bonds (Å, °) in compounds (Hpy)<sub>2</sub>CA (**1**), (H<sub>2</sub>ppz)CA (**2**), (H<sub>2</sub>bpy)CA·4H<sub>2</sub>O (**3**) and (Hphen)HCA·MeOH (**4**).

	$d(D-H) / \text{Å}$	$d(H\cdots A) / \text{Å}$	$d(D\cdots A) / \text{Å}$	$\angle(D-H\cdots A) / ^\circ$	Sym. op. on A
<b>1</b>					
N1–H1...O1	0.86	1.87	2.661(2)	153	1 + x, y, -1 + z
N1–H1...O2	0.86	2.26	2.864(2)	128	2 - x, 1 - y, 1 - z
C4–H4...O2	0.93	2.59	3.040(3)	110	2 - x, 1 - y, 1 - z
C5–H5...O2	0.93	2.49	3.409(2)	169	x, y, z
<b>2</b>					
N1–H1A...O1	0.89	1.97	2.746(3)	144	-x, 1-y, 2-z
N1–H1B...O1	0.89	2.23	2.896(2)	131	-1+x, y, z
N1–H1B...O2	0.89	2.02	2.832(3)	151	1-x, 1-y, 1-z
C5–H5A...O2	0.97	2.48	3.385(3)	154	-x, 1-y, 1-z
C5–H5B...O2	0.97	2.40	3.149(3)	133	-1+x, y, z
<b>3</b>					
N1–H1...O2	0.86	2.08	2.794(3)	140	-x, 1 - y, 1 - z
N2–H2...O1	0.86	2.07	2.794(3)	140	-x, 1 - y, 1 - z
O3–H3A...O1	0.94(2)	2.05(6)	2.879(3)	146(7)	x, y, z
O3–H3B...Cl1	0.95(2)	2.64(4)	3.579(3)	168(7)	-1/2 - x, 1/2 - y, 1 - z
O3–H3B...O3	0.95(2)	2.48(5)	2.831(3)	102(3)	-1/2 - x, 1/2 - y, 1 - z
O4–H4A...O3	0.96(3)	2.08(3)	2.755(4)	126(3)	1/2 + x, 1/2 + y, z
O4–H4B...Cl1	0.96(3)	2.55(3)	3.318(4)	137(2)	x, y, z
O4–H4B...O2	0.96(3)	2.23(3)	2.961(5)	133(3)	x, y, z
<b>4</b>					
N1–H1...O5	0.86	1.96	2.749(3)	152	x, y, z
O5–H5...O4	0.82	1.91	2.721(3)	173	x, y, z
C7–H7...O2	0.93	2.40	3.282(4)	158	2 - x, -1 - y, -z
C9–H9...O1	0.93	2.48	3.355(4)	158	2 - x, -y, -z
C14–H14...O4	0.93	2.42	3.265(4)	150	1 - x, -y, 1 - z
C16–H16...O3	0.93	2.55	3.408(4)	154	1 - x, -1 - y, 1 - z

**Table 4.** Geometric parameters of  $\pi$ -interactions (Å, °) in compounds (Hpy)<sub>2</sub>CA (**1**), (H<sub>2</sub>bpy)CA·4H<sub>2</sub>O (**3**) and (Hphen)HCA·MeOH (**4**). Symmetry operators: *i*) 1-x, 1-y, 2-z; *ii*) -x, y, 3/2-z; *iii*) -x, y, 1/2-z.

$\pi\cdots\pi$	$Cg^{(a)}\cdots Cg / \text{Å}$	$\alpha^{(b)}$	$\beta^{(c)}$	$Cg\cdots\text{plane}(Cg2) / \text{Å}$	Offset / Å	Symm. op. on Cg2
<b>1</b>						
C1→C2 <sup>i</sup> ...C1→C2 <sup>i</sup>	4.0660(10)	0.00(8)	31.5	3.4655(7)	2.127	-1+x, y, z
N1→C8...N1→C8	4.0661(12)	0.03(10)	29.0	3.5549(8)	1.974	-1+x, y, z
<b>3</b>						
C1→C1 <sup>ii</sup> ...N1→C4 <sup>iii</sup>	4.1265(14)	7.24(11)	33.6	3.4386(10)	2.461	-1/2-x, 1/2-y, 1-z
C1→C1 <sup>ii</sup> ...N2→C9 <sup>iii</sup>	4.1226(14)	0.36(11)	36.5	3.3050(10)	2.454	-1/2-x, 1/2-y, 1-z
<b>4</b>						
N1→C11...N2→C16	3.805(3)	0.98(10)	25.4	3.4483(8)	1.635	2-x, -y, 1-z
N1→C11...N2→C16	3.626(3)	0.98(10)	21.1	3.3819(8)	1.308	1-x, -y, 1-z
N1→C11...C10→C17	3.618(3)	0.08(10)	20.2	3.3947(8)	1.251	2-x, -y, 1-z
C1→C6...C1→C6	3.697(3)	0.00(9)	26.8	3.3011(8)	1.665	2-x, -1-y, -z

<sup>(a)</sup> Cg = centre of gravity of the aromatic ring;

<sup>(b)</sup>  $\alpha$  = angle between planes of two interacting rings;

<sup>(c)</sup>  $\beta$  = angle between Cg...Cg line and normal to the plane of the first interacting ring.

In compound **3** the hydrogen-bonded chains stack in the direction [100], forming layers parallel to the plane (110) (Figure 4 b). The stacks here are mixed, with alternating  $CA^{2-}$  and  $H_2bpy^{2+}$  moieties (i.e. sequence  $CA \cdots H_2bpy \cdots CA \cdots H_2bpy$ , Table 4). Water molecules are inserted between the layers, connecting them by hydrogen bonds into a 3D network (Table 3).

Components of compound **4** stack in the direction [100], forming separate stacks of  $HCA^-$  moieties and  $Hphen^+$  moieties (Figure 4 c, Table 4). Hydrogen chloranilate anions form offset stacks with geometry similar to stacking of aromatic rings (Table 4), rather than stronger face-to-face stacks which we have observed recently.<sup>[10–12]</sup> It can be concluded that the type of stack which will form depends mainly on steric factors: face-to-face stacks form in simple alkali salts, which are free from steric strain and competing interactions; in the presence of sterically larger organic cations, which engage in multiple hydrogen bonds, offset stacks are preferred.<sup>[9]</sup> This is an instance of the 'Gulliver effect':<sup>[40]</sup> energy of face-to-face stacking interaction ( $> 10 \text{ kcal mol}^{-1}$ ) is comparable, or slightly stronger than, medium strong hydrogen bonding; however, an arrangement with a larger number of hydrogen bonds is more favourable than one featuring face-to-face stacking, but has fewer hydrogen bonds. Multiple  $C-H \cdots O$  hydrogen bonds (Table 3) link the  $(Hphen-HCA \cdot MeOH)_2$  units into a 3D network.

## CONCLUSIONS

In this paper we have described four novel salts of chloranilic acid with organic cations pyridinium, piperazinedium, 4,4'-bipyridinedium and 1,10-phenanthroline. The commonly observed hydrogen bonding mode of the  $CA^{2-}/HCA^-$ , as an acceptor of two bifurcated hydrogen bonds (Figure 1) can be considered as a predictable and reliable 'supramolecular synthon'.<sup>[41]</sup> Dimensionality and topology of the hydrogen bonded network is strongly affected by the cation.

Three types of  $\pi$ -stacking is observed: aromatic $\cdots$ aromatic, quinoid $\cdots$ quinoid and mixed stacks with alternating aromatic and quinoid rings. Quinoid rings stack in an offset fashion, indicating relatively weak stacking interactions.

There is also an apparent competition between strong face-to-face  $\pi$ -stacking and hydrogen bonding in structures containing the  $HCA^-$  monoanion; the latter prevail due to a 'Gulliver effect'. Another reason for destabilisation of face-to-face stacks is that larger organic cations (compared to alkali cations) are less effective in compensating negative charges of the  $HCA^-$  anions, increasing electrostatic repulsion. Steric effects of the large cations may also play a role. However, hydrogen bonds act

in an apparent synergy with weaker, offset  $\pi$ -interactions, which are found in three of the studied structures, and also in many of previously described compounds.<sup>[9]</sup>

**Acknowledgment.** The financing by the Croatian Science Foundation (grant IP-2014-09-4079) is gratefully acknowledged.

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