High Resolution X-ray and Neutron Diffraction Studies on Cocrystals of Chloranilic Acid and Lutidines

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SUPPORTING INFORMATION

Figures S1-S18

Tables S1-S21

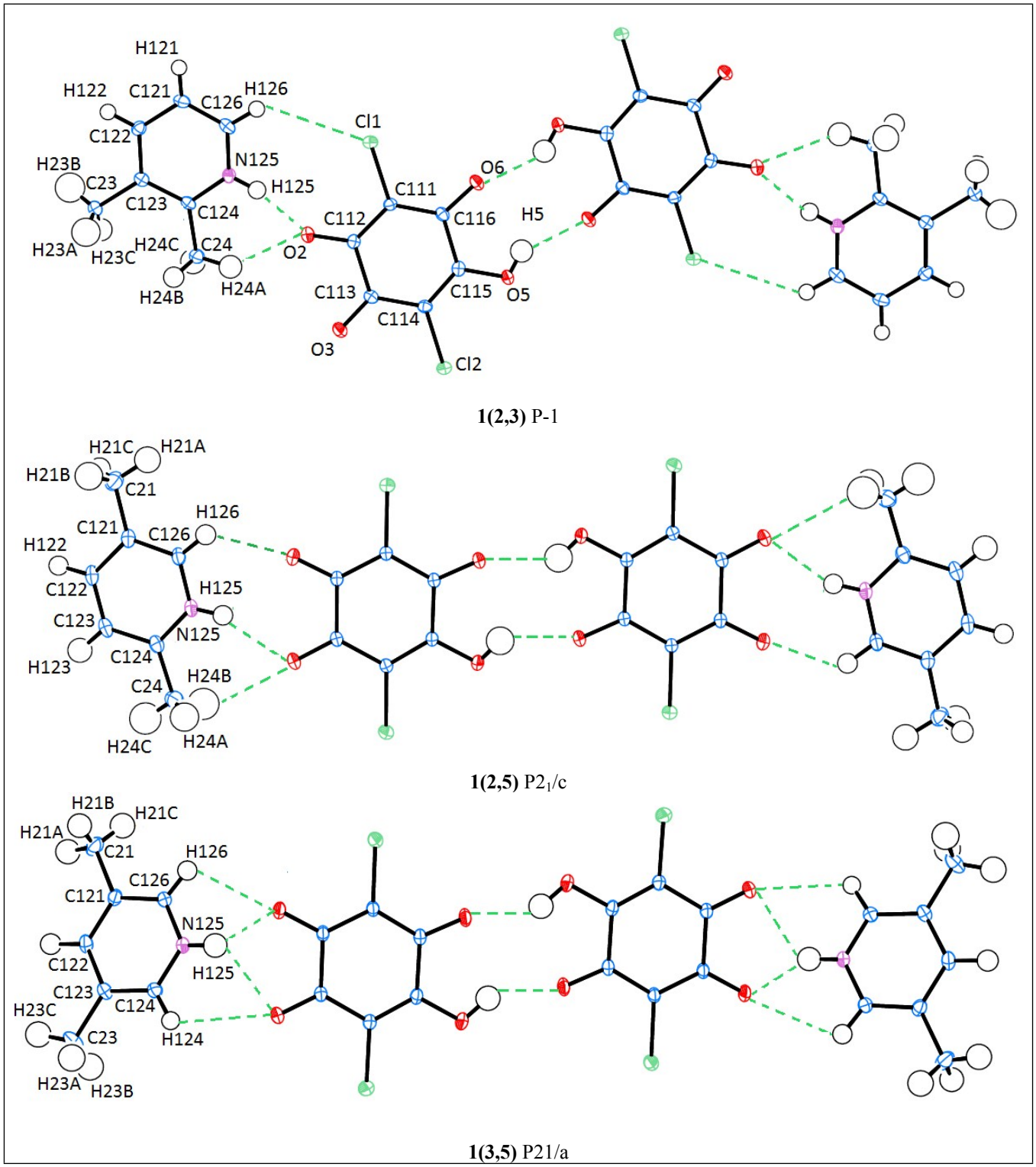
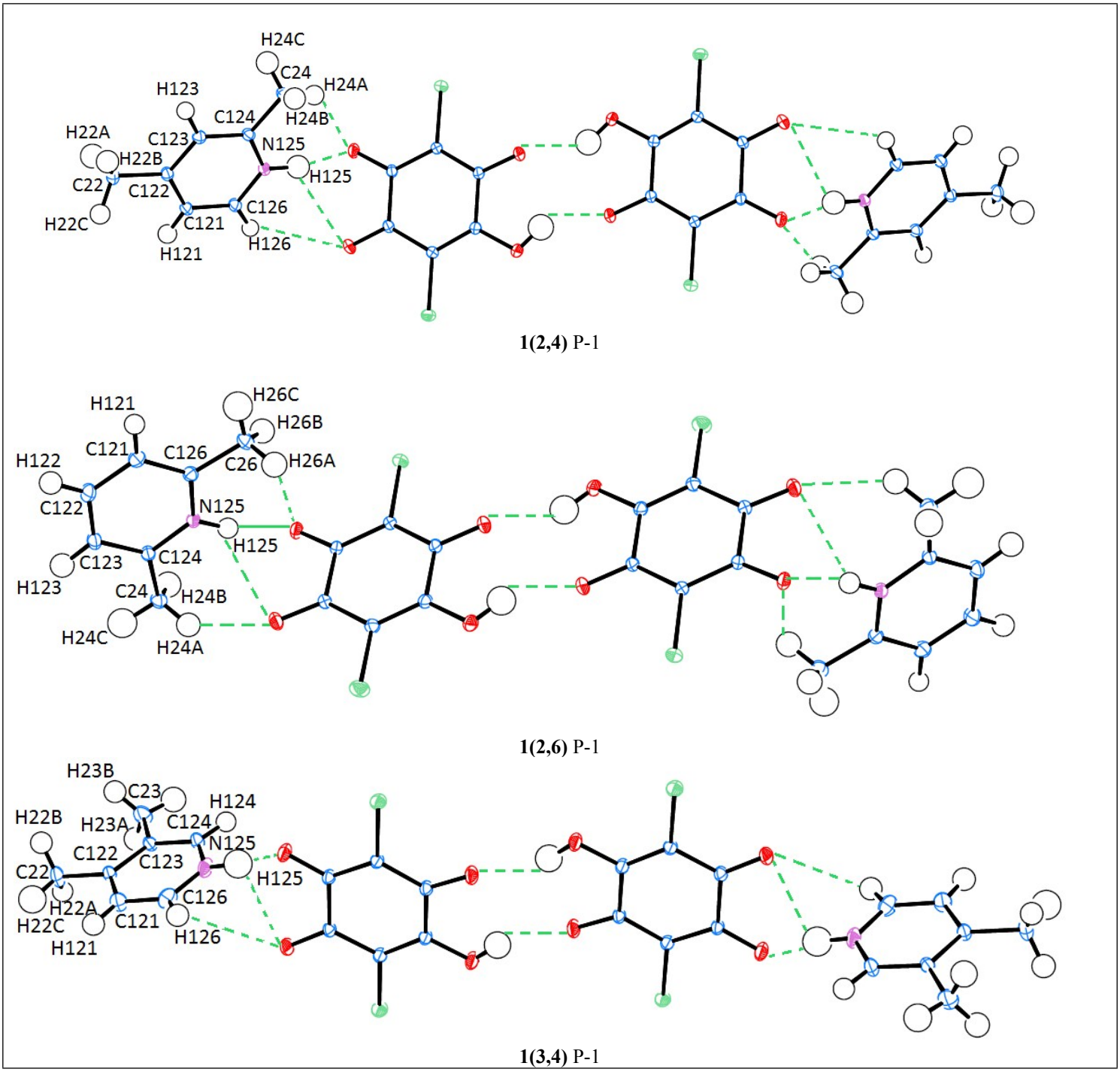


Figure S1. Ortep plots of the 1:1 chloranilic acid 2,3-, 2,5- and 3,5-lutidine molecular complexes showing their connection through intermolecular hydrogen bonds and the co-planar position of the lutidine ring relative to the chloranilic acid molecules. Ellipsoids are shown at the 50% probability level.



1(2,4) P-1

1(2,6) P-1

1(3,4) P-1

Figure S2. Ortep plots of the **1(2,4), 1(2,6)** and **1(3.4)** showing their connection through intermolecular hydrogen bonds and the twisted position of the [BH^+] ring relative to the [HCA^-] molecules. Ellipsoids are shown at the 50% probability level.

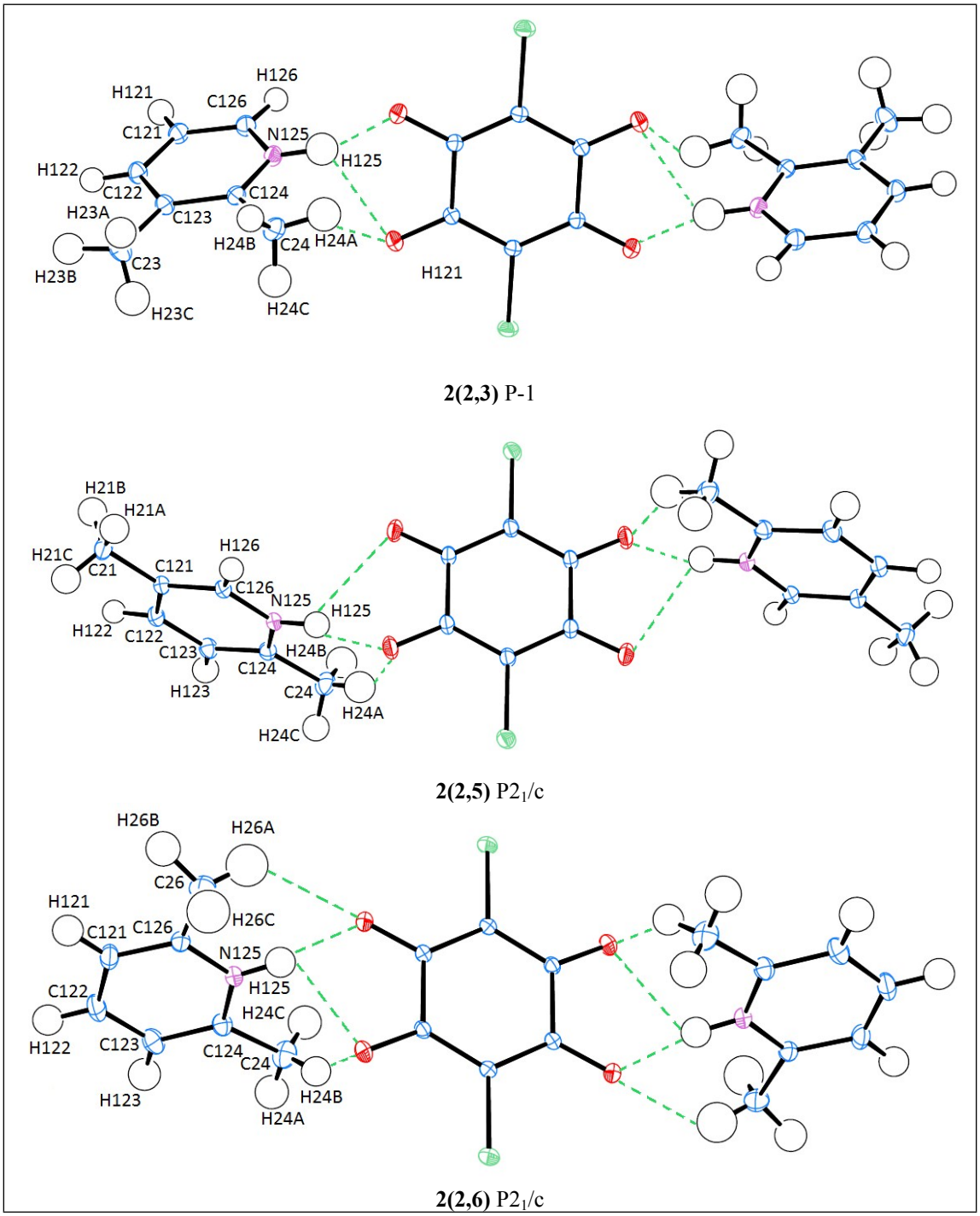


Figure S3. Ortep plots of the 2(2,3), 2(2,5) and 2(2,6) showing their connection through intermolecular hydrogen bonds and the twisted position of the $[BH^{+}]_2$ rings relative to the $[CA^{2-}]$ molecule. The ellipsoids are shown at the 50% probability level

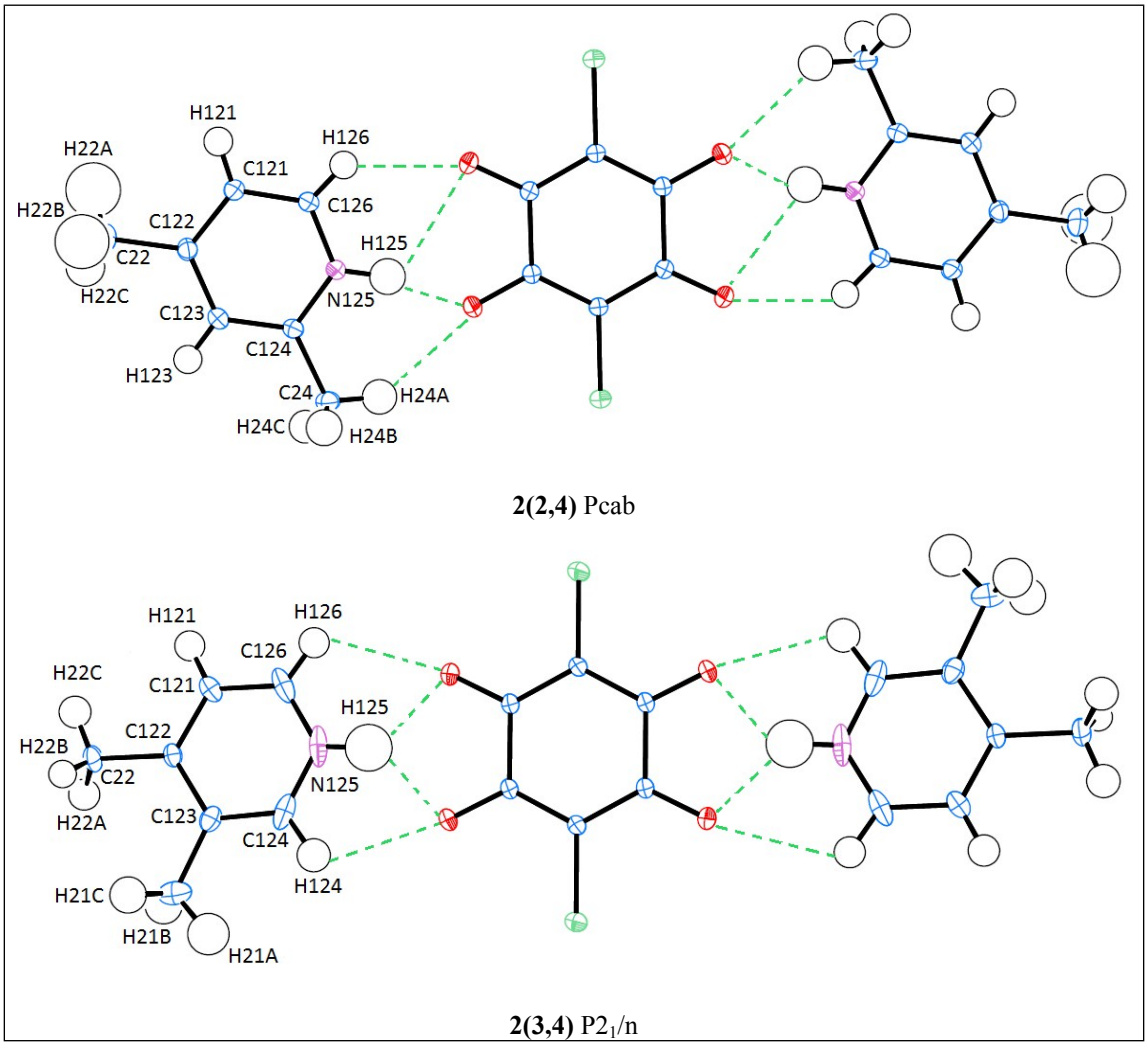
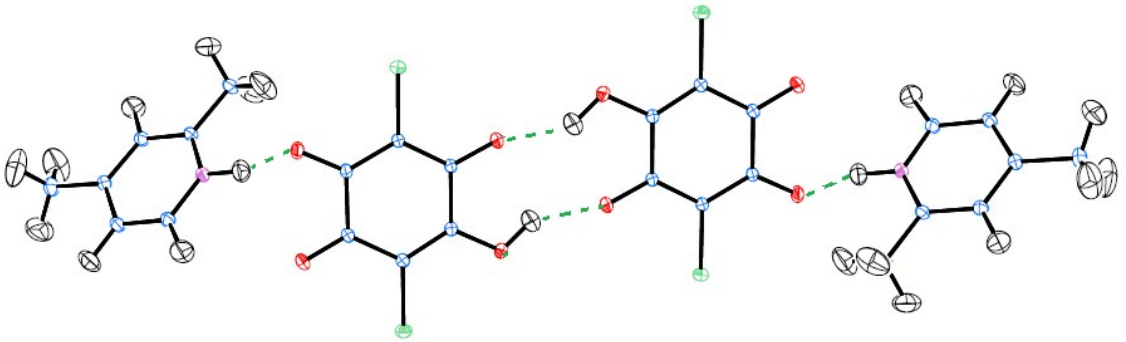
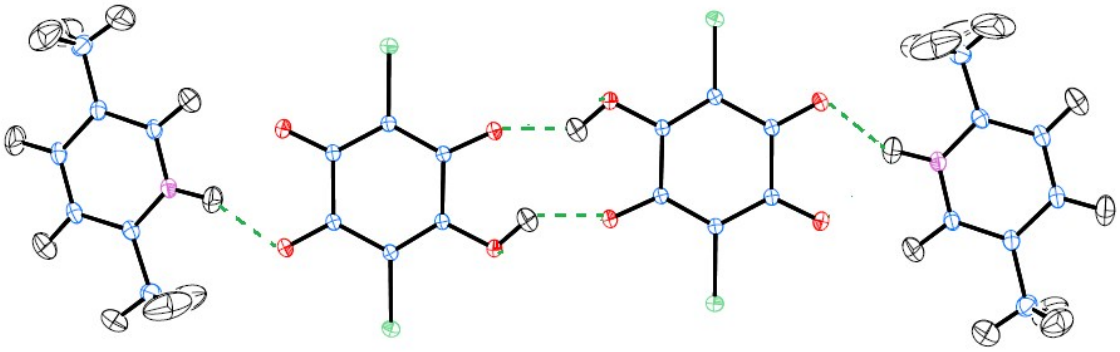


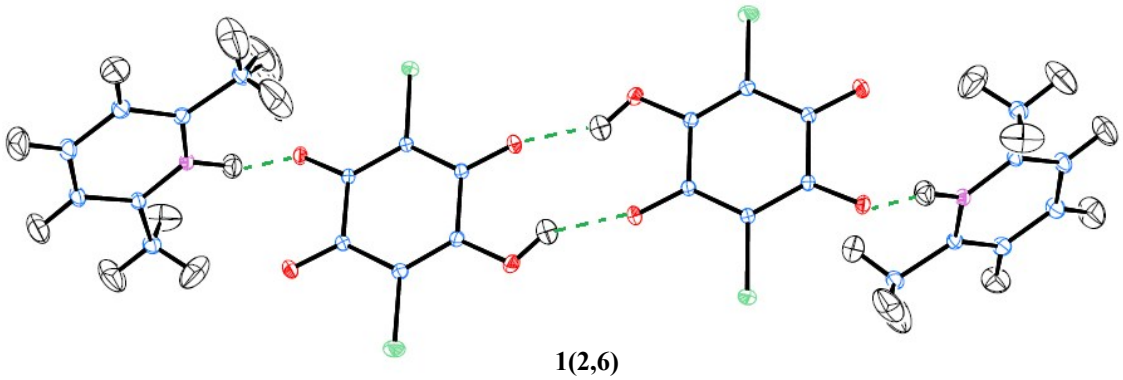
Figure S4. Ortep plots of the **2(2,4)** and **2(3,5)** showing their connection through intermolecular hydrogen bonds and the co-planar position of the $[BH^+]_2$ rings relative to the $[CA^{2-}]$ molecule. The ellipsoids are shown at the 50% probability level



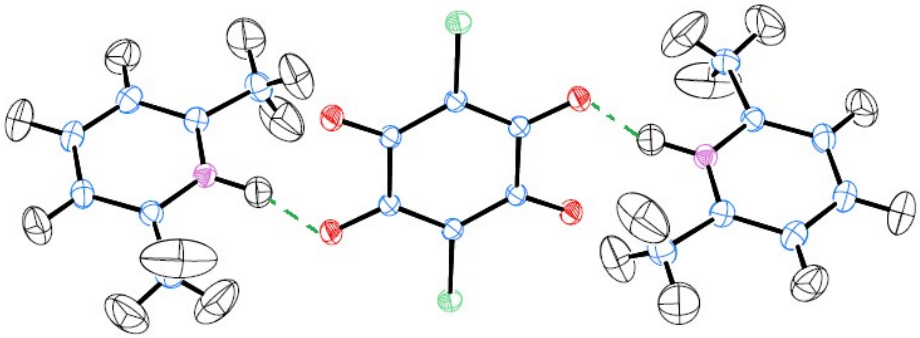
1(2,4)



1(2,5)



1(2,6)



2(2,6)

Figure S5. The lutidine - chloranilic acid salts showing the anisotropic thermal ellipsoids including H atoms from neutron diffraction (the same labelling scheme was used as in the X-ray diffraction data).

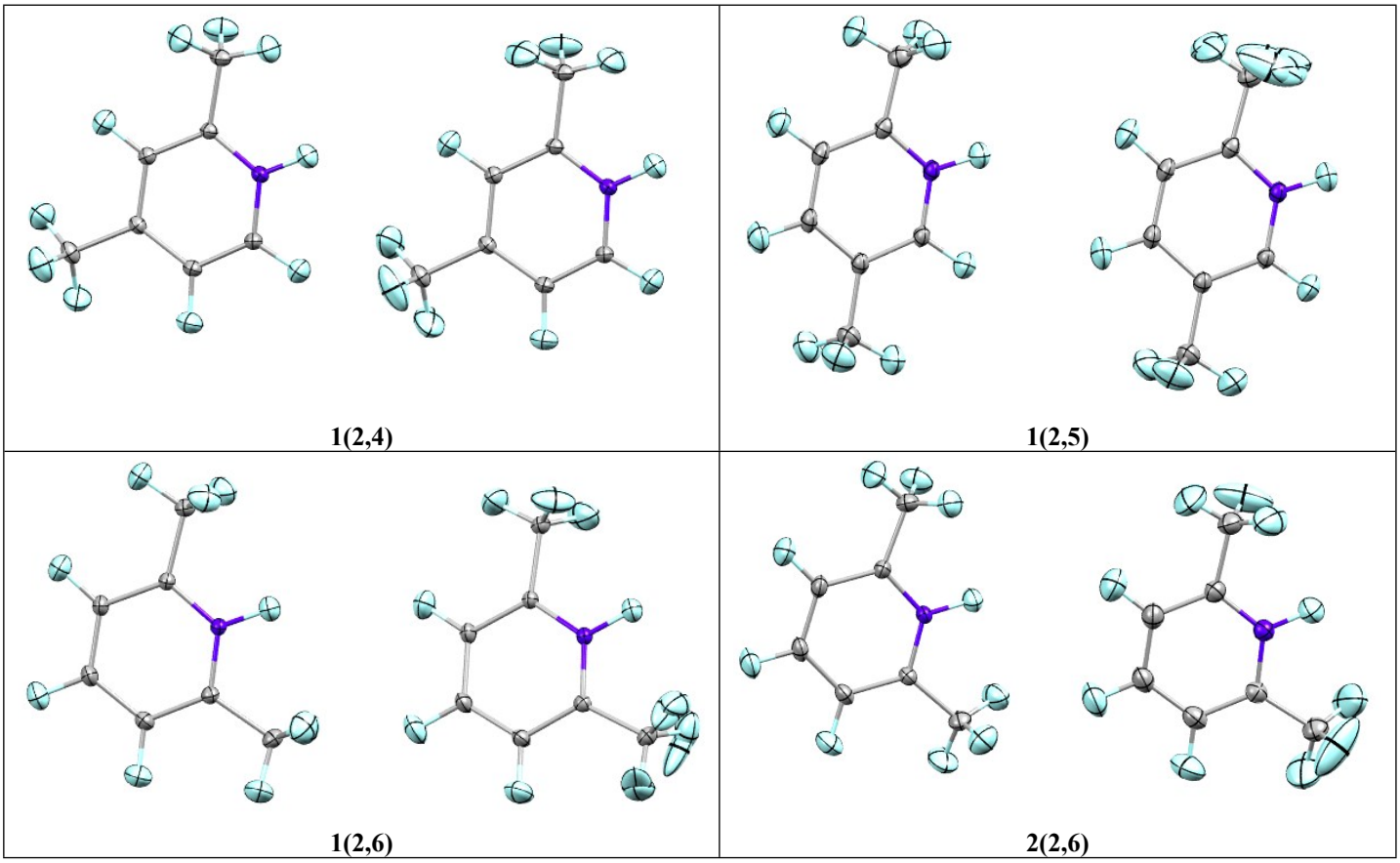


Figure S6. Adps illustration left - shade estimated, right - neutron diffraction, showing larger thermal motion for the hydrogen of the methyl groups in case of neutron data.

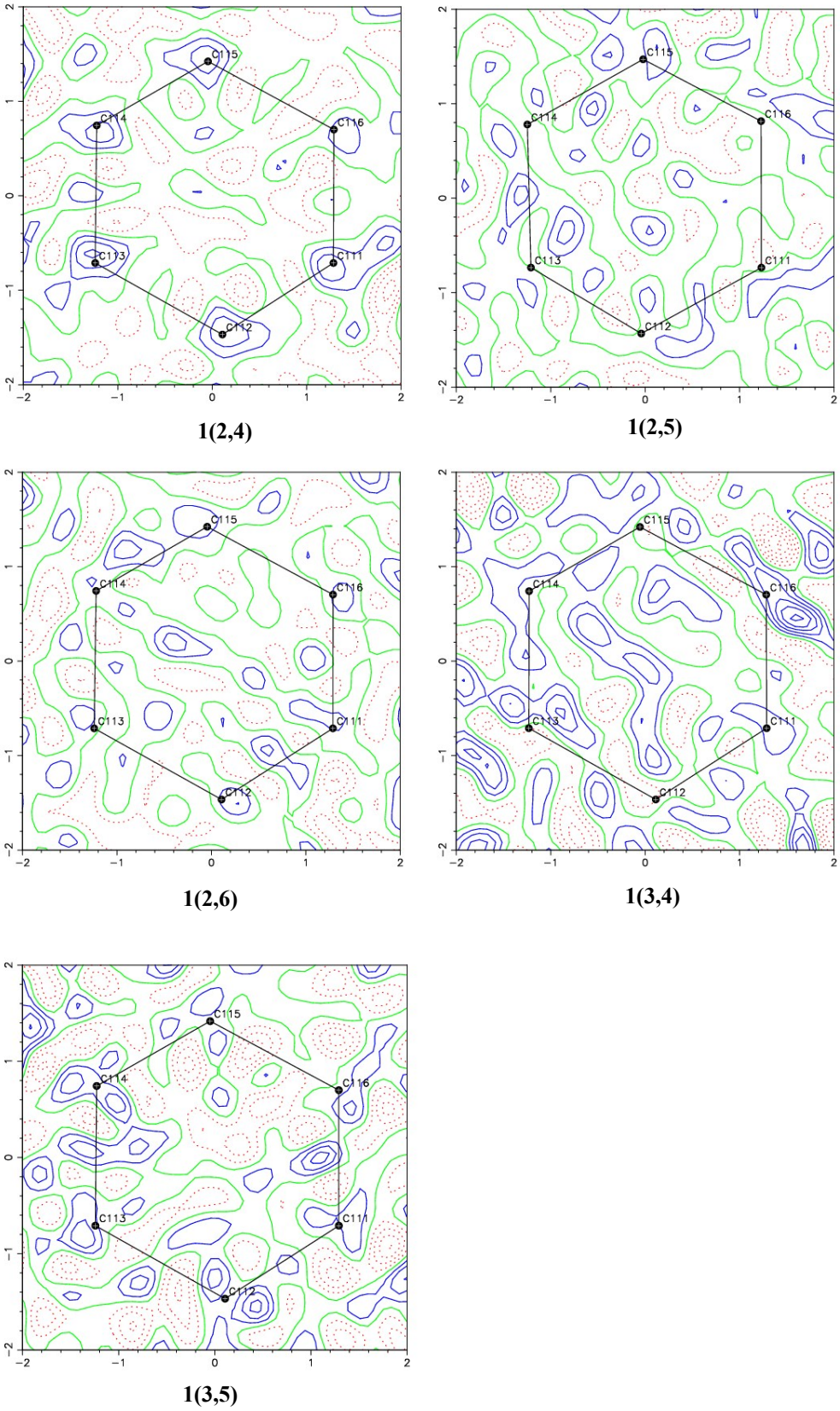


Figure S7. Residual electron density maps of [HCA^-] rings Contour levels at ±0.05e$Å^{-3}$

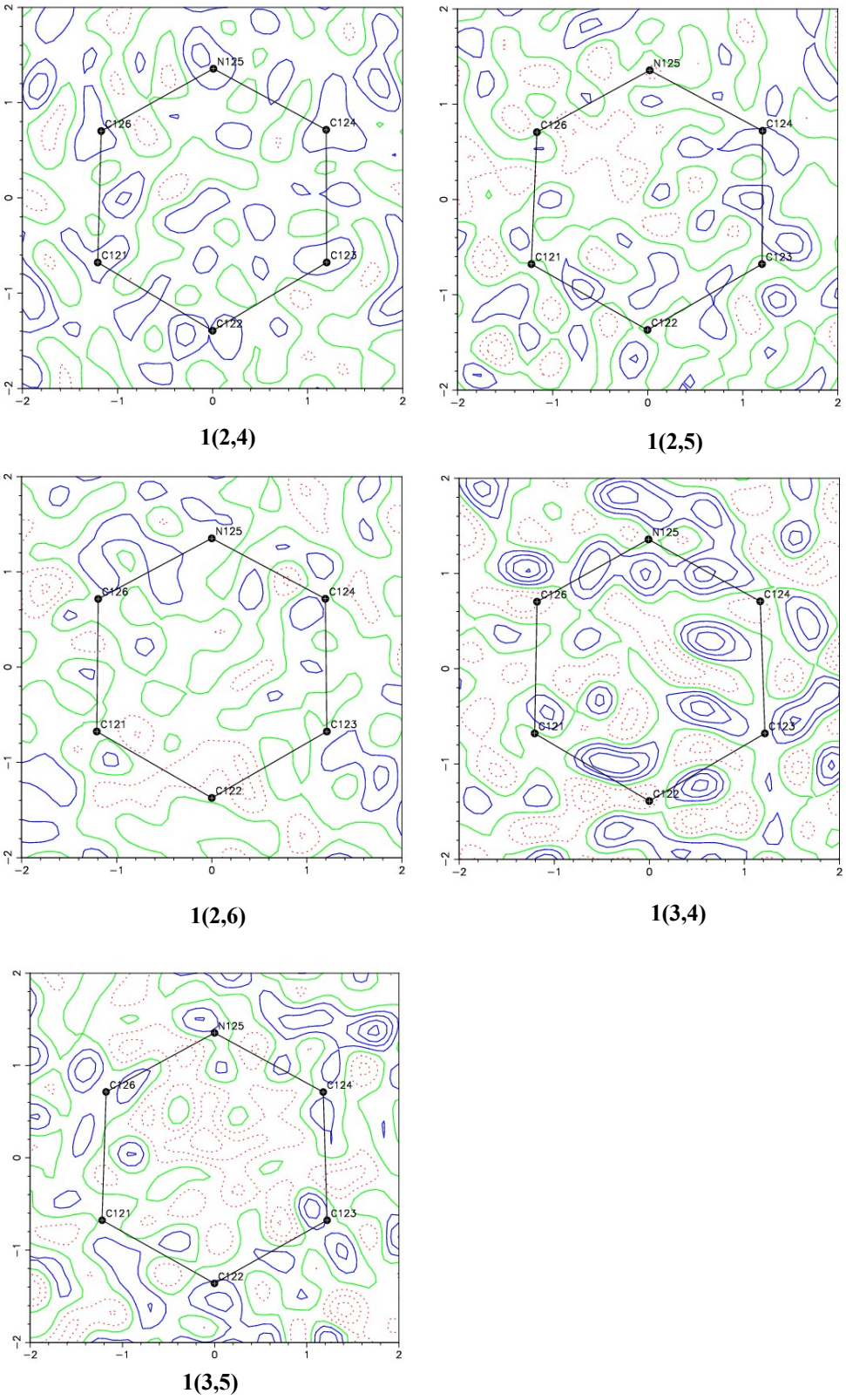
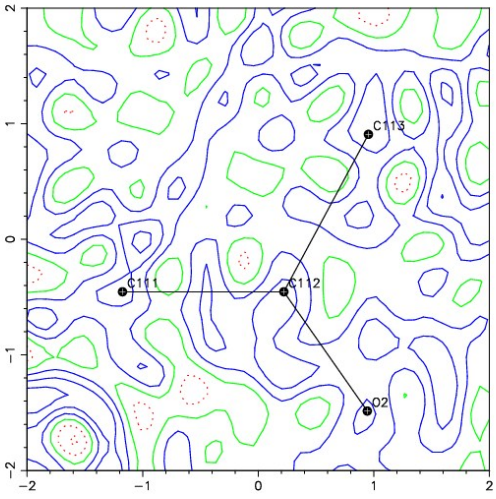
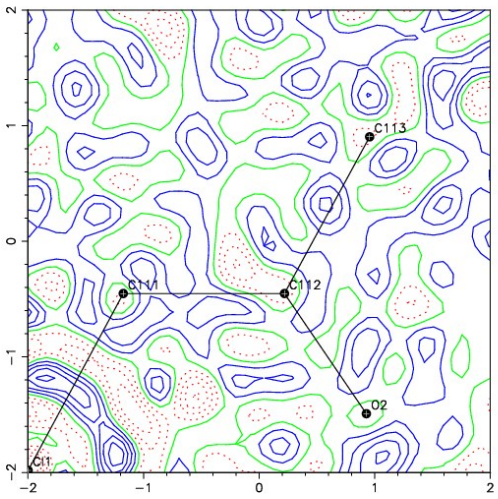


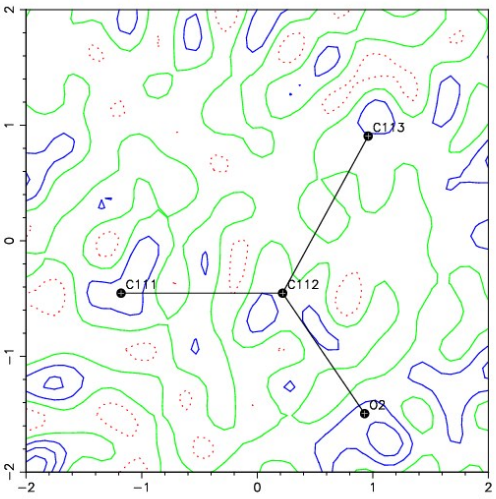
Figure S8. Residual electron density maps of [HB^+] rings Contour levels at ±0.05e$Å^{-3}$



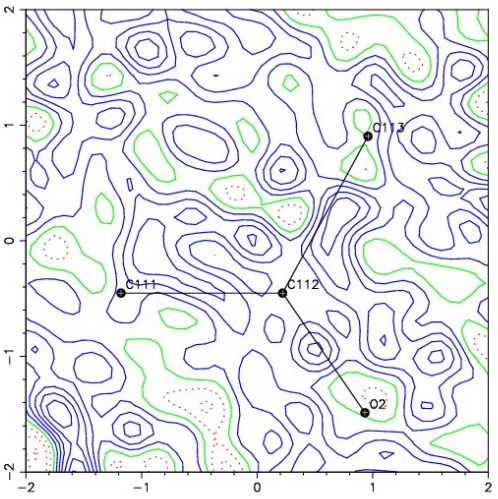
2(2,3)



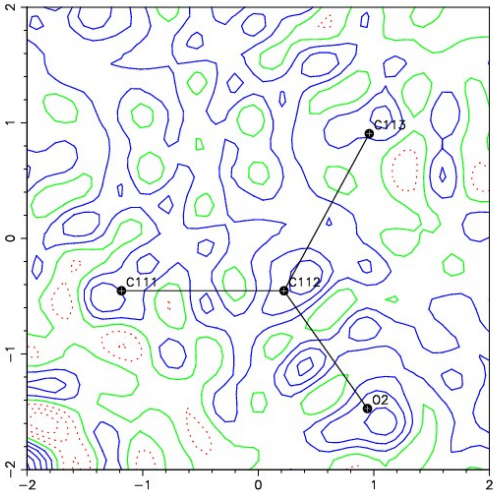
2(2,4)



2(2,5)



2(2,6)



2(3,4)

Figure S9. Residual electron density maps of [CA^{2-}] rings Contour levels at ±0.05e$Å^{-3}$

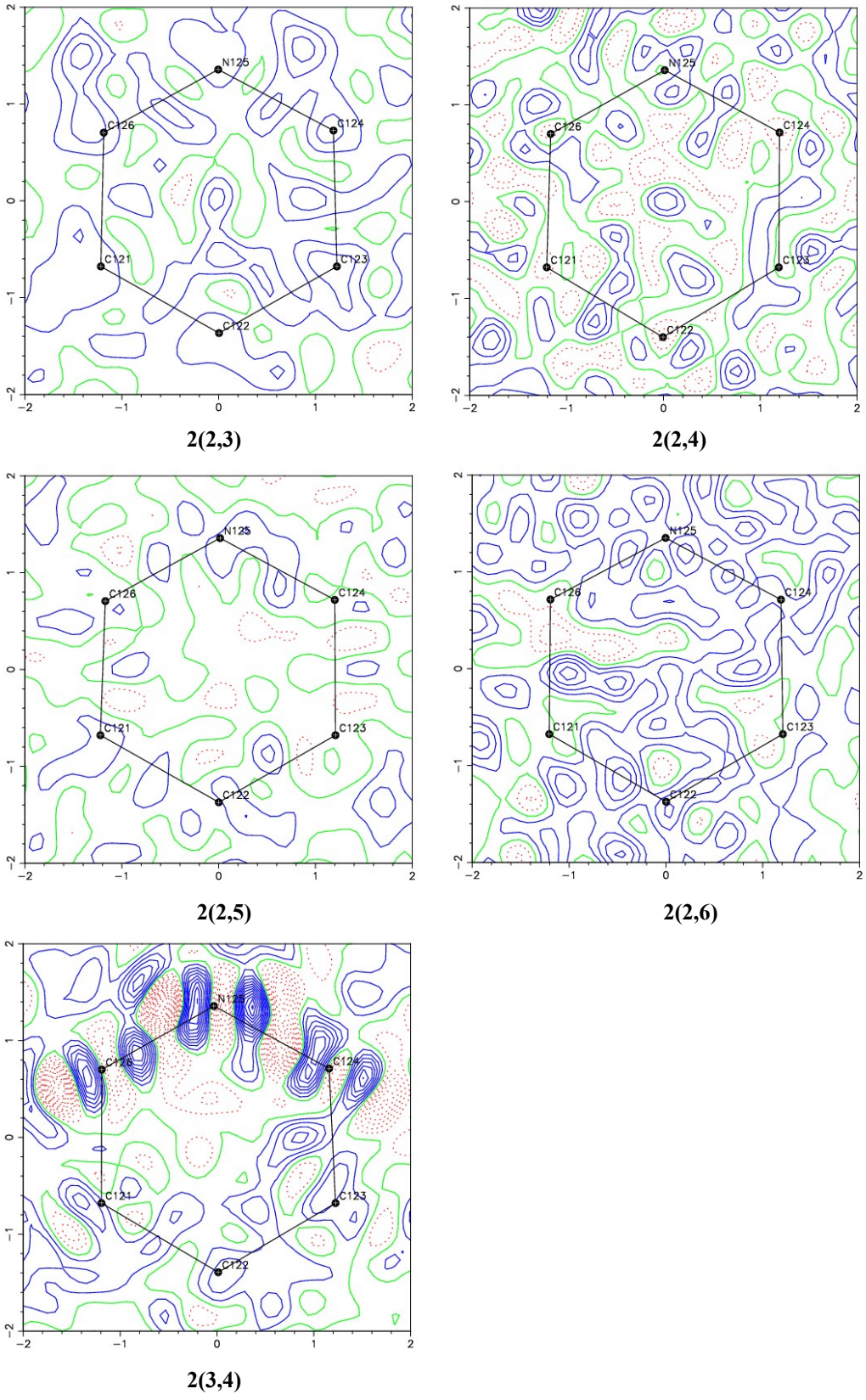


Figure S10. Residual electron density maps of $[BH^+]_2$ rings. Contour levels at ±0.05eÅ^{-3}

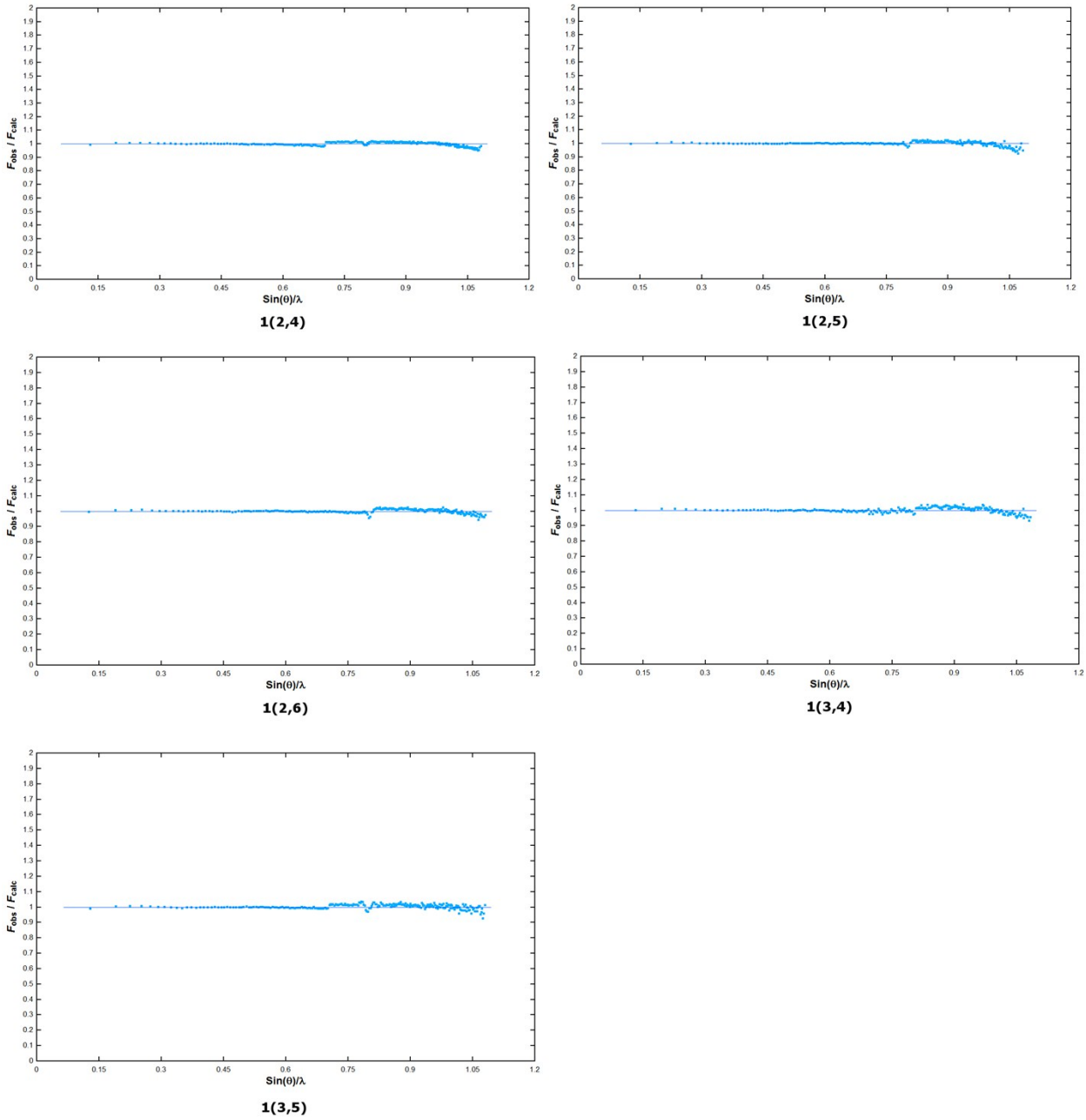


Figure S11. Scatter plots of the scale factor Fobs/Fcalc against sin(θ)/λ for $[BH^+][HCA^-]$ salts

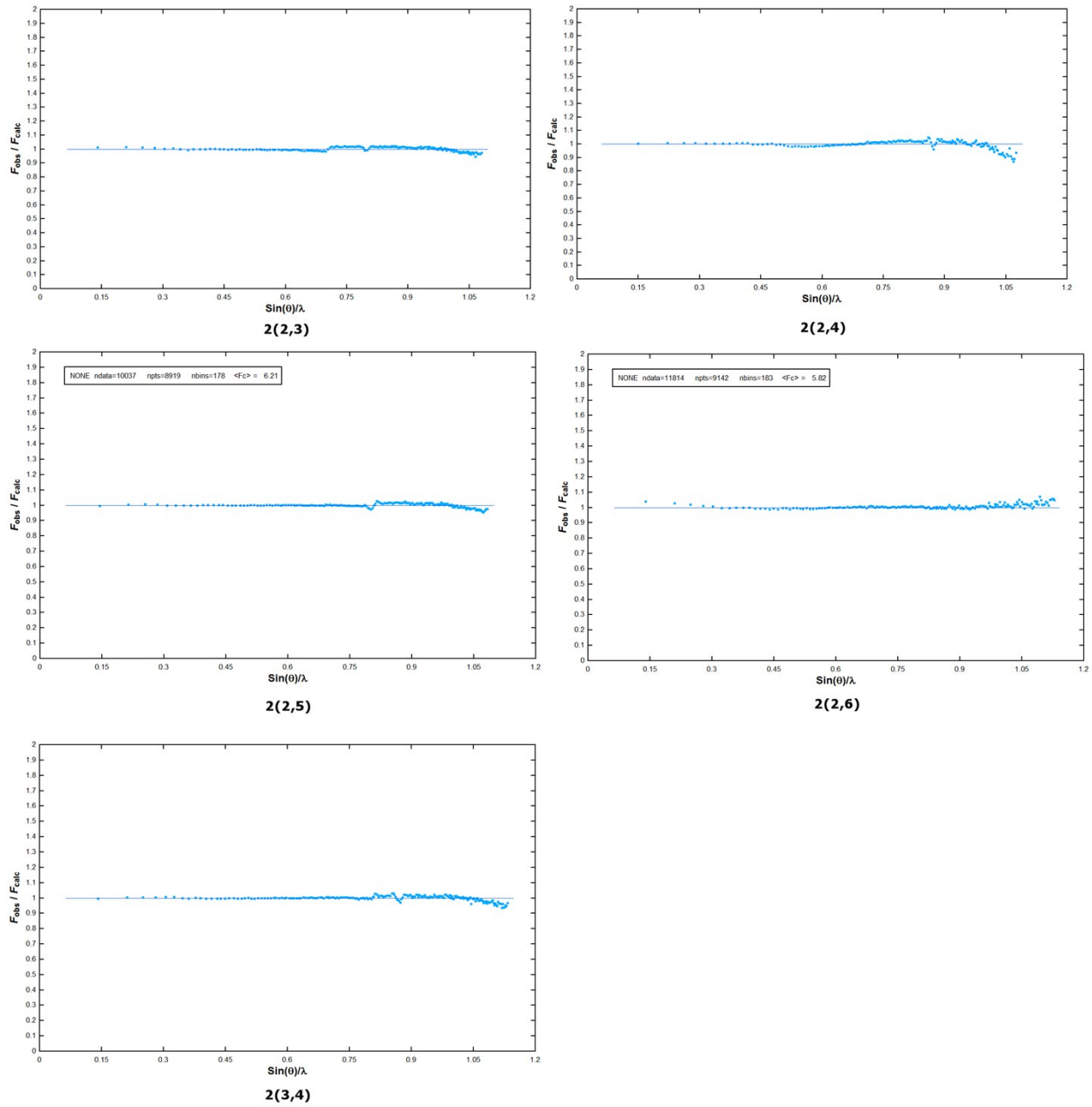


Figure S12. Scatter plots of the scale factor Fobs/Fcalc against sin(θ)/λ from final XD refinements for $[BH^{+}]_2[CA^{2-}]$ salts

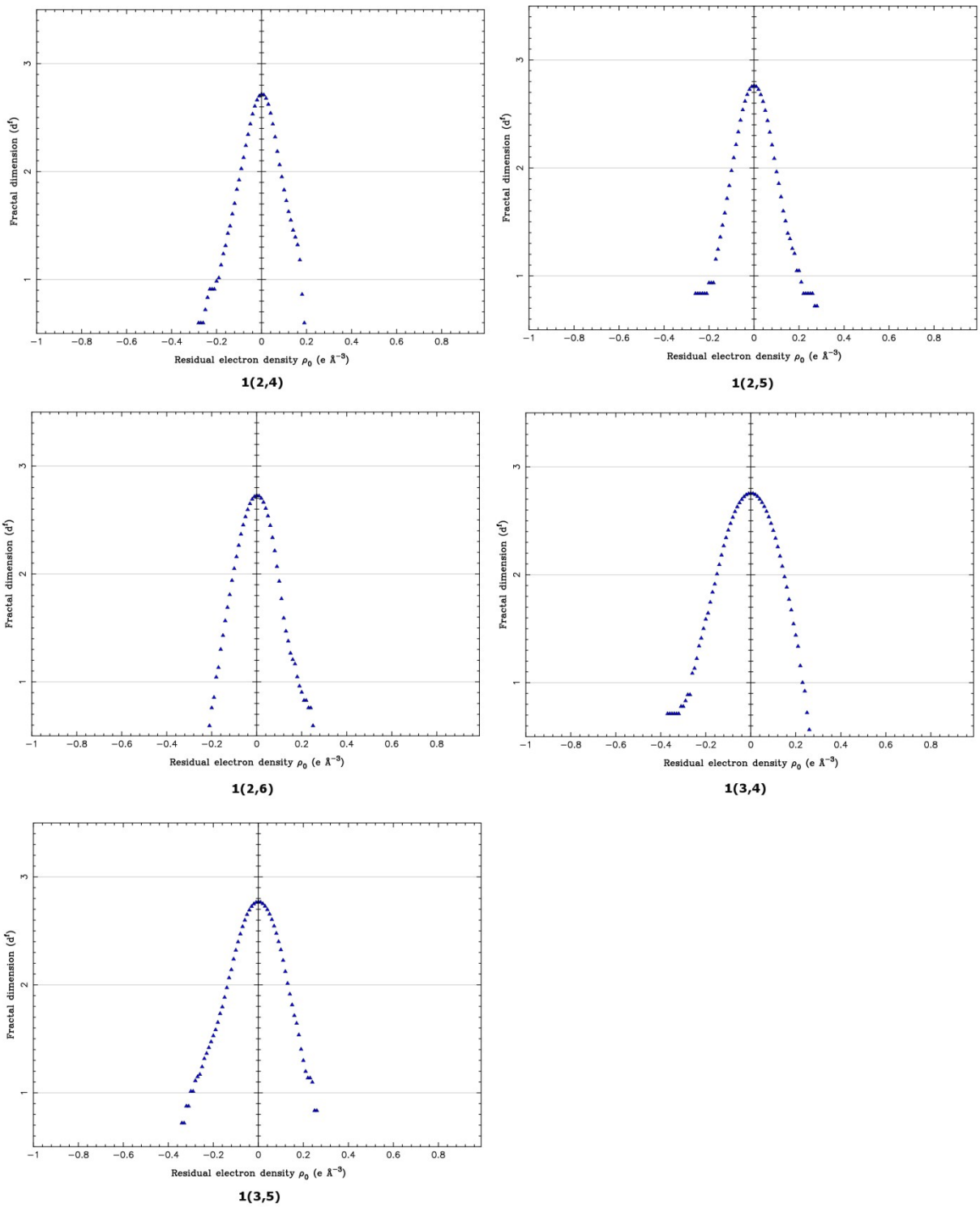


Figure S13. Residual density fractional dimension plots from final XD refinements for for [BH^+][CA^-] salts

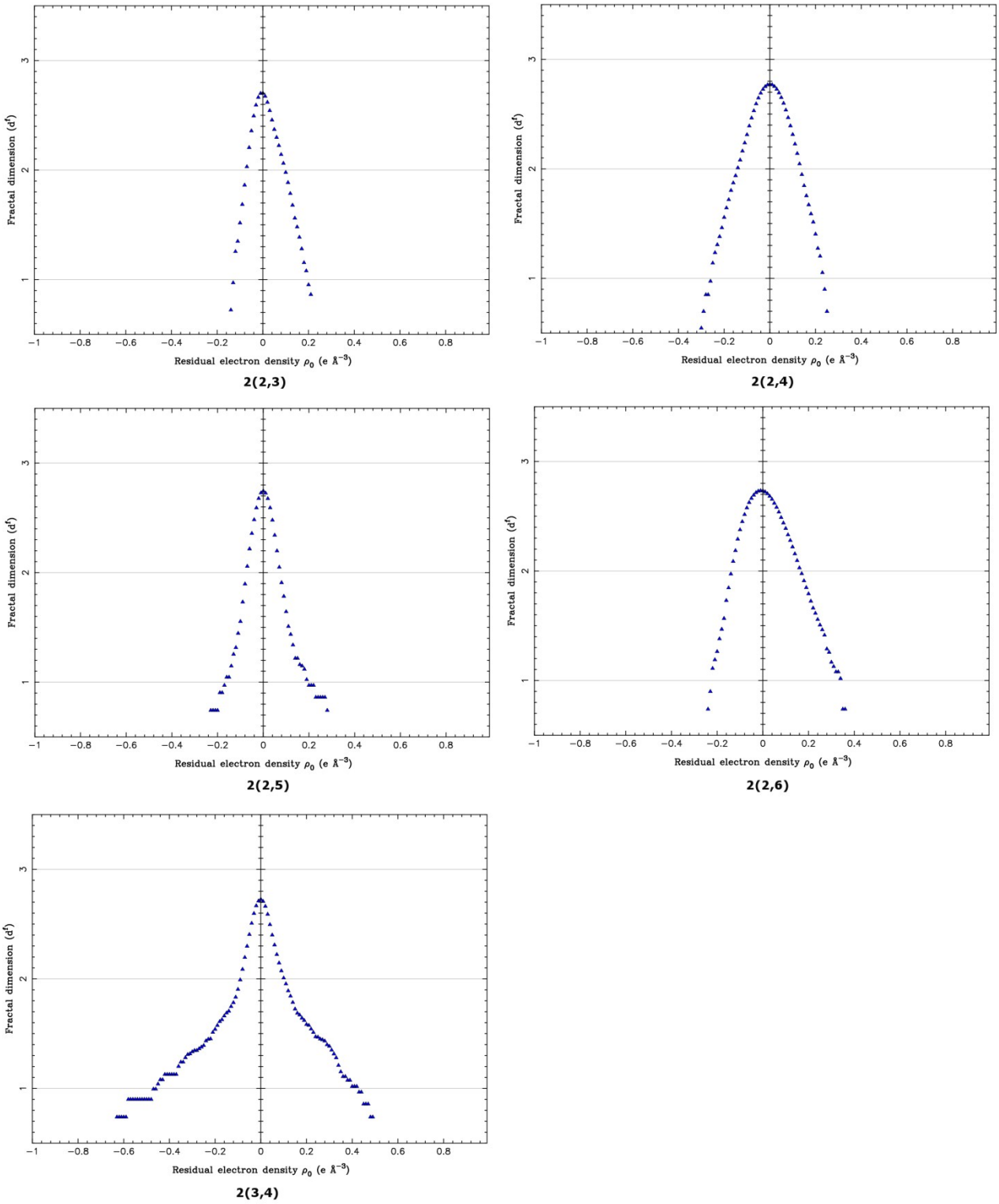


Figure S14. Residual density fractional dimension plots from final XD refinements for for $[BH^+]_2[CA^{2-}]$ salts

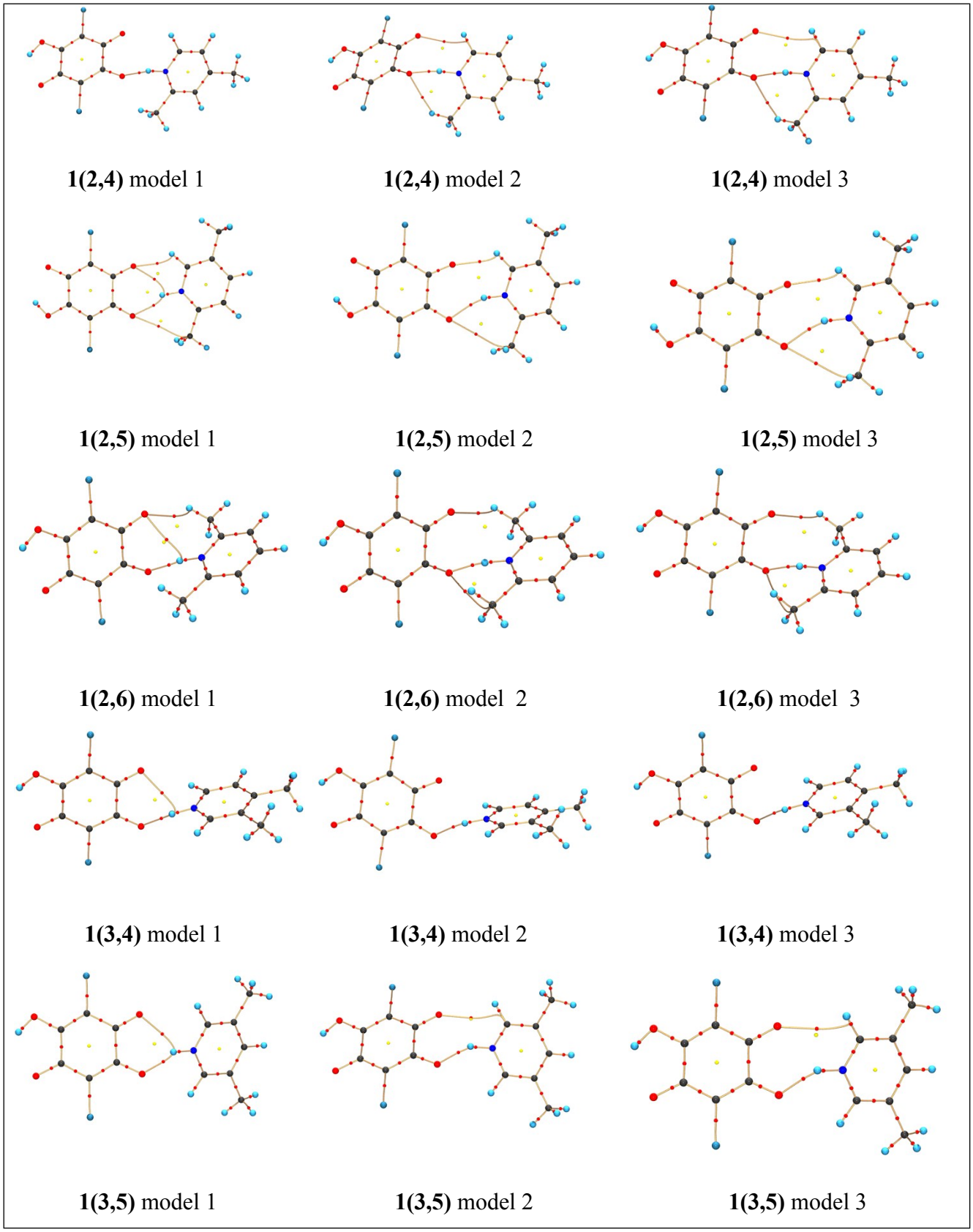


Figure S15. Molecular graphs of $[BH^+][HCA^-]$ salts showing the BCPs formed between the two molecules

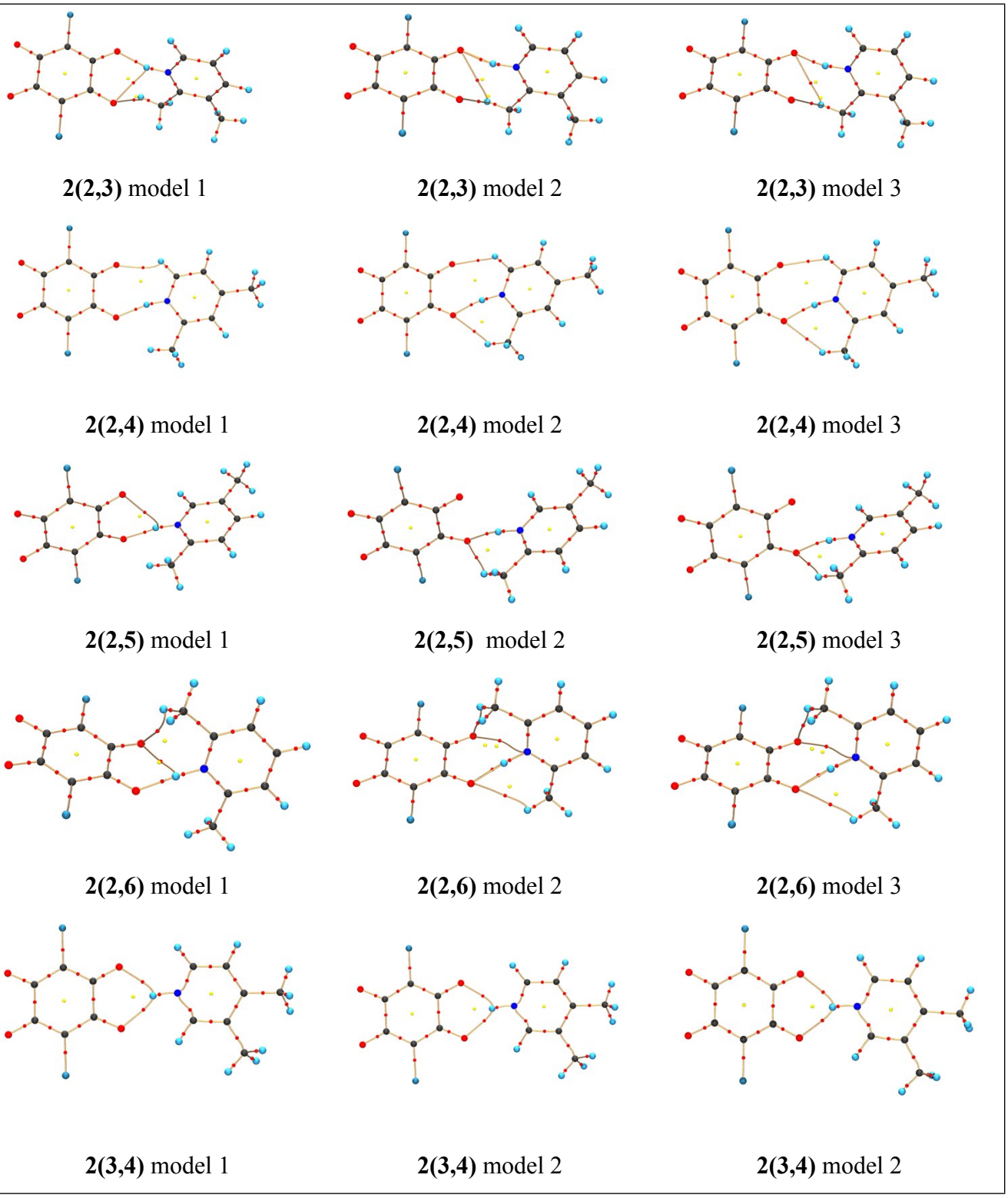


Figure S16. Molecular graphs of $[BH^{+}]_2[CA^{2-}]$ salts

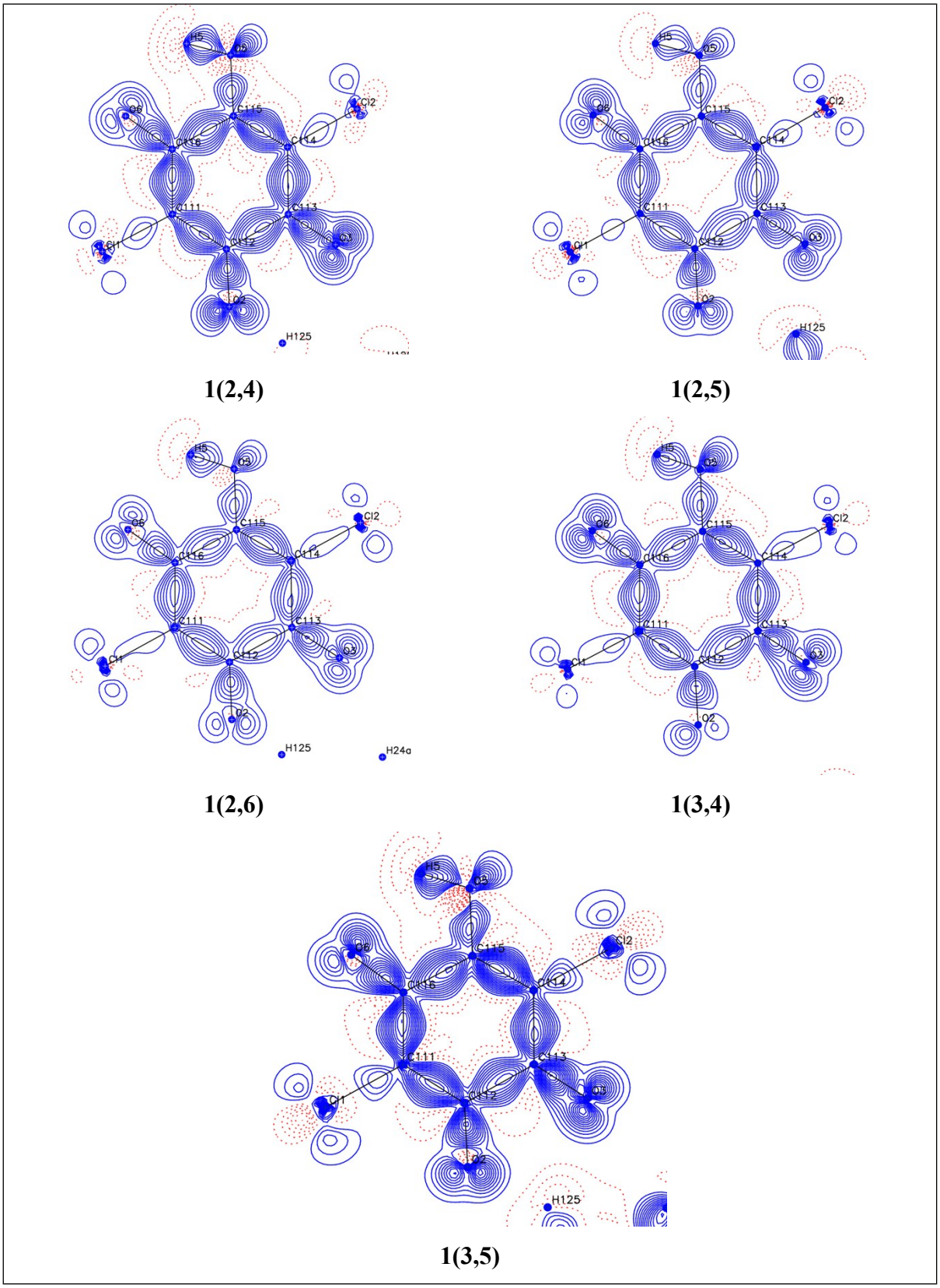


Figure S17. Deformation density maps in plane of [HCA$^-$] molecule (dashed red line – negative contours, solid blue line – positive contours). Contour levels at 0.08 eÅ$^-$

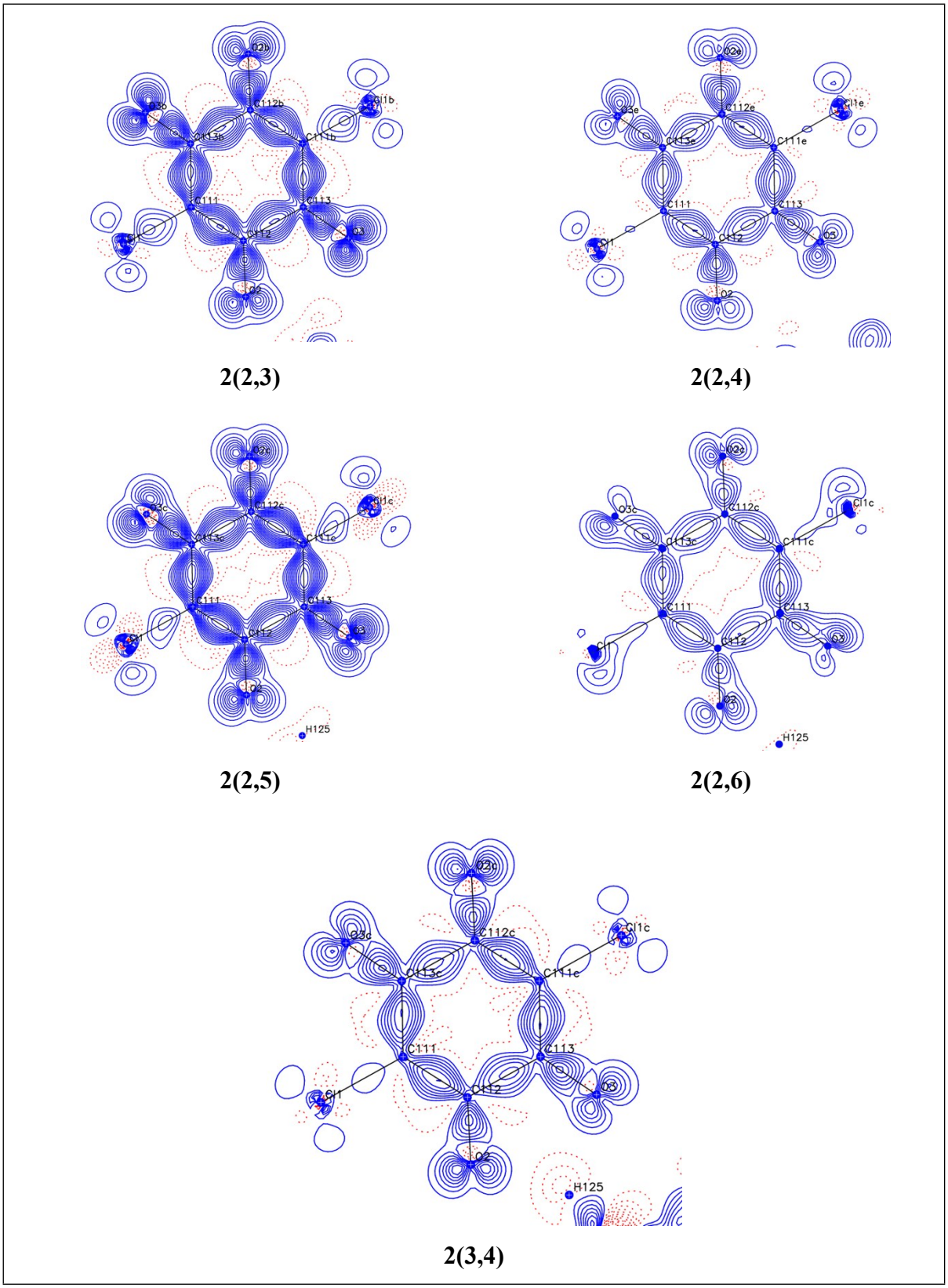


Figure S18. Deformation density maps in plane of [CA^{2-}] molecule (dashed red line – negative contours, solid blue line – positive contours). Contour levels at 0.08 $eÅ^{-3}$

Table S1. Crystallographic data of $[BH^+][HCA^-]$ salts: **1(2,3), 1(2,4)** and **1(2,5)**

Compound formula	$C_{13}H_{11}Cl_2NO_4$	$C_{13}H_{11}Cl_2NO_4$	$C_{13}H_{11}Cl_2NO_4$
Isomer	**1(2,3)**	**1(2,4)**	**1(2,5)**
M_r	316.13	316.13	316.1
Space group	P-1	P-1	$P2_1/c$
Crystal system	Triclinic	Triclinic	Monoclinic
a/ Å	3.8653(4)	5.0687(2)	7.7415(2)
b/ Å	711.5522(12)	11.2561(4)	11.0538(3)
c/Å	14.4711(14)	11.6281(3)	15.4495(3)
α/deg	98.976(6)	96.274(2)	90.00
β/deg	93.377(5)	91.960(2)	95.514(1)
γ/deg	91.025(6)	90.609(1)	90.00
V/Å^{-3}	636.91(7)	659.00(2)	1315.94(1)
Z	2	2	4
D_{calc}/g cm^{-3}	1.65	1.59	1.60
F(000)	324.0	324.0	648
Radiation	Mo Kα	Mo Kα	Mo Kα
λ/Å	0.71073	0.71073	0.71073
μ(Mo-K_a)/mm^{-1}	0.522	0.504	0.505
Crystal size/mm	0.18x0.21x0.34	0.17x0.20x0.41	0.12x0.31x0.39
θ range/deg	1.4 – 30.4	2.4-50.7	2.3-50.6
Max sin(θ)/ λ	0.72	1.1	1.1
No. of data used for merging	24317	281388	500656
No. of unique data	3793	13978	14004
hkl range	-5≤ h ≤5	-10≤ h ≤10	-16≤ h ≤16
	-16≤ k ≤16	-24≤ k ≤24	0≤ k ≤23
	0≤ l ≤20	0≤ l ≤25	0≤ l ≤33
R_{int}	0.0702	0.0194	0.0331
R_σ	0.0727	0.259	0.0291
Completeness (%)	98.1	98.4	98.8
Spherical atom refinement			
No. of data in refinement	3793	13978	14004
No. of refined parameters	206	225	225
Final R [$I > 2\sigma(I)$]	0.046	0.025	0.027
R_w [$I > 2\sigma(I)$]	0.091	0.076	0.082
Goodness of fit S	1.019	1.039	1.047
Extrema in residual map/eÅ^{-3}	-0.403 →0.438	-0.406→0.642	-0.403→0.608
Max shift/esd in last cycle	0.000	0.004	0.002
Multipole refinement			
No. of data in refinement	-	12502	11797
No. of refined parameters	-	543	543
Final R [$I > 3\sigma(I)$]	-	0.0164	0.0190
R_w [$I > 3\sigma(I)$]	-	0.0200	0.0205
Goodness of fit S	-	1.2038	1.1312
Extrema in residual map/ eÅ^{-3} (all data)	-	-0.310→0.183	-0.302→0.254
Max shift/esd in last cycle	-	0.0009	0.0003

Table S2. Crystallographic data for [BH^+][HCA^-] salts: **1(2,6), 1(3,4)** and **1(3,5)**

Compound formula	$C_{13}H_{11}Cl_2NO_4$	$C_{13}H_{11}Cl_2NO_4$	$C_{13}H_{11}Cl_2NO_4$
Isomer	**1(2,6)**	**1(3,4)**	**1(3,5)**
M_r	316.1	316.1	316.1
Space group	P-1	$P2_1/n$	$P2_1/a$
Crystal system	Triclinic	Monoclinic	Monoclinic
a/ Å	9.0071(3)	10.6010(2)	11.3192(4)
b/ Å	9.0326(3)	5.167(1)	10.2762(4)
c/Å	9.0768(3)	24.3363(4)	11.7534(4)
α/deg	93.526(2)	90.00	90.00
β/deg	104.359(2)	97.199(1)	100.198(2)
γ/deg	110.821(2)	90.00	90.00
V/Å^{-3}	659.48(8)	1322.75(2)	1345.54(5)
Z	2	4	4
D_{calc}/g cm^{-3}	1.59	1.59	1.56
F(000)	324.0	647.9	647.9
Radiation	Mo Kα	Mo Kα	Mo Kα
λ/Å	0.71073	0.71073	0.71073
μ(Mo-K_a)/mm^{-1}	0.504	0.503	0.494
Crystal size/mm	0.20x0.25x0.36	0.16x0.22x0.35	0.20x0.20x0.27
θ range/deg	2.3-50.5	2.4-50.6	2.7-50.4
Max sin(θ)/ λ	1.1	1.08	1.08
No. of data used for merging	284210	238608	276447
No. of unique data	14000	13865	14184
hkl range	-19≤ *h* ≤18	-22 ≤ *h* ≤22	-24≤ *h* ≤ 23
	-19≤ *k* ≤19	0≤ *k* ≤ 11	0≤ *k* ≤ 22
	0≤ *l* ≤19	0≤ *l* ≤ 52	0≤ *l* ≤25
R_{int}	0.0261	0.0240	0.0331
R_σ	0.0295	0.0403	0.0283
Completeness (%)	98.8	97.3	98.8
Spherical atom refinement			
No. of data in refinement	14000	13865	14184
No. of refined parameters	225	225	225
Final *R* [$I > 2\sigma(I)$]	0.026	0.033	0.034
R_w [$I > 2\sigma(I)$]	0.080	0.091	0.089
Goodness of fit *S*	1.038	1.020	1.032
Extrema in residual map/eÅ^{-3}	-0.384→0.715	-0.314→0.690	-0.529→0.672
Max shift/esd in last cycle	0.002	0.001	0.002
Multipole refinement			
No. of data in refinement	11968	10959	12092
No. of refined parameters	543	542	542
Final *R* [$I > 3\sigma(I)$]	0.0183	0.0268	0.0258
R_w [$I > 3\sigma(I)$]	0.0203	0.0240	0.0278
Goodness of fit *S*	1.0882	1.0935	1.5751
Extrema in residual map/ eÅ^{-3} (all data)	-0.239→0.235	-0.378→0.265	-0.342→0.269
Max shift/esd in last cycle	0.0003	0.0004	0.0004

Table S3. Crystallographic data of $[BH^+]_2[CA^{2-}]$ salts: **2(2,3), 2(2,4)** and **2(2,5)**

Compound formula	$C_{20}H_{20}Cl_2N_2O_4$	$C_{20}H_{20}Cl_2N_2O_4$	$C_{20}H_{20}Cl_2N_2O_4$
Isomer	**2(2,3)**	**2(2,4)**	**2(2,5)**
M_r	423.28	423.28	423.28
Space group	P-1	P cab	$P2_1/c$
Crystal system	Triclinic	Orthorhombic	Monoclinic
a/ Å	7.6305(2)	7.5644(5)	8.0870(3)
b/ Å	8.3081(2)	15.7136(10)	11.4214(5)
c/Å	8.4348(2)	16.6651(11)	10.3253(4)
α/deg	65.839(1)	90.00	90.00
β/deg	80.610(2)	90.00	100.451(2)
γ/deg	88.280(1)	90.00	90.00
V/Å^{-3}	480.94(3)	1980.88(2)	937.87(4)
Z	1	4	2
D_{calc}/g cm^{-3}	1.46	1.42	1.50
F(000)	220.0	880	440
Radiation	Mo Kα	Mo Kα	Mo Kα
λ/Å	0.71073	0.71073	0.71073
μ(Mo-K_a)/mm^{-1}	0.368	0.357	0.377
Crystal size/mm	0.20x0.25x0.35	0.18x0.24x0.36	0.21x0.42x0.50
θ range/deg	2.7-50.4	2.4-50.2	2.6-50.6
Max sin(θ)/ λ	1.08	1.08	1.1
No. of data used for merging	199231	388485	365776
No. of unique data	10130	9962	10032
hkl range	$-16 \le h \le 16$	$0 \le h \le 16$	$-17 \le h \le 17$
	$-15 \le k \le 17$	$0 \le k \le 33$	$0 \le k \le 24$
	$0 \le l \le 18$	$0 \le l \le 35$	$0 \le l \le 22$
R_{int}	0.0290	0.0540	0.0267
R_σ	0.0255	0.0328	0.0261
Completeness (%)	98.5	94.9	99.1
Spherical atom refinement			
No. of data in refinement	10130	9962	10032
No. of refined parameters	167	156	167
Final R [$I > 2\sigma(I)$]	0.027	0.037	0.025
R_w [$I > 2\sigma(I)$]	0.081	0.102	0.082
Goodness of fit S	1.063	1.035	1.056
Extrema in residual map/eÅ^{-3}	-0.28→0.654	-0.468→0.598	-0.415→0.584
Max shift/esd in last cycle	0.002	0.003	0.007
Multipole refinement			
No. of data in refinement	9384	8200	8919
No. of refined parameters	378	378	379
Final R [$I > 3\sigma(I)$]	0.0173	0.0291	0.0155
R_w [$I > 3\sigma(I)$]	0.0217	0.0277	0.0190
Goodness of fit S	1.3299	1.4468	1.1711
Extrema in residual map/ eÅ^{-3} (all data)	-0.148→0.216	-0.305→0.253	-0.250→0.271
Max shift/esd in last cycle	0.0004	0.0006	0.0009

Table S4. Crystallographic data of $[BH^+]_2[CA^{2-}]$ salts: **2(2,6),** and **2(3,4)**

Compound formula	$C_{20}H_{20}Cl_2N_2O_4$	$C_{20}H_{20}Cl_2N_2O_4$
Isomer	**2(2,6)**	**2(3,4)**
M_r	423.28	423.28
Space group	$P2_1/c$	$P2_1/n$
Crystal system	Monoclinic	Monoclinic
a/ Å	7.1427(3)	7.0429(2)
b/ Å	9.3025(4)	9.3113(2)
c/Å	14.7753(6)	14.6210(3)
α/deg	90.00	90.00
β/deg	94.526(2)	90.303(1)
γ/deg	90.00	90.00
V/Å^{-3}	978.28(2)	958.81(0)
Z	2	2
D_{calc}/g cm^{-3}	1.44	1.47
F(000)	439.9	439.9
Radiation	Mo Kα	Mo Kα
λ/Å	0.71073	0.71073
μ(Mo-K_a)/mm^{-1}	0.361	0.369
Crystal size/mm	0.15x0.21x0.35	0.18x0.26x0.36
θ range/deg	2.6-53.4	2.6-53.9
Max sin(θ)/ λ	1.1	1.1
No. of data used for merging	168711	312677
No. of unique data	11814	11674
hkl range	$-16 \le h \le 16$	$-15 \le h \le 15$
	$0 \le k \le 20$	$0 \le k \le 20$
	$0 \le l \le 33$	$0 \le l \le 33$
R_{int}	0.0470	0.0231
R_σ	0.0466	0.0254
Completeness (%)	99.9	99
Spherical atom refinement		
No. of data in refinement	11814	11674
No. of refined parameters	167	167
Final *R* [$I > 2\sigma(I)$]	0.035	0.033
R_w^2 [$I > 2\sigma(I)$]	0.094	0.103
Goodness of fit *S*	1.017	
Extrema in residual map/eÅ^{-3}	-0.300→0.690	-0.874→0.739
Max shift/esd in last cycle	0.003	0.002
Multipole refinement		
No. of data in refinement	9143	10232
No. of refined parameters	378	379
Final *R* [$I > 3\sigma(I)$]	0.0280	0.0240
R_w [$I > 3\sigma(I)$]	0.0263	0.0335
Goodness of fit *S*	1.1554	2.0459
Extrema in residual map/ eÅ^{-3} (all data)	-0.242→0.367	-0.666→0.471
Max shift/esd in last cycle	0.0009	0.0002

Table S5. Crystallographic data of **3, 4** and **5**

Compound formula	$C_{20}H_{28}Cl_2N_2O_8$	$C_{20}H_{28}Cl_2N_2O_8$	$C_{20}H_{26}Cl_2N_2O_7$
Isomer	**3**	**4**	**5**
M_r	495.34	229.7	477.33
Space group	P-1	$P2_1/c$	$P2_1/n$
Crystal system	Triclinic	Monoclinic	Monoclinic
a/ Å	7.9413(3)	10.0360(20)	10.6104(4)
b/ Å	8.9010(4)	7.6591(17)	17.7659(7)
c/Å	9.0838(3)	13.9480(39)	12.3211(5)
α/deg	71.310(2)	90	90
β/deg	70.3580(10)	99.620(14)	108.6810(10)
γ/deg	76.061(2)	90	90
V/Å^{-3}	566.42(4)	1057.06(26)	2200.21(15)
Z	1	4	4
D_{calc}/g cm^{-3}	1.45	1.44	1.44
F(000)	260.0	480.0	1000.0
Radiation	Mo Kα	Mo Kα	Mo Kα
λ/Å	0.71073	0.71073	0.71073
μ(Mo-K_a)/mm^{-1}	0.336	0.347	0.340
Crystal size/mm	0.20x0.22x0.31	0.15x0.18x0.27	0.19x0.24x0.29
θ range/deg	2.4-51.3	2.1-26.5	2.1-50.4
Max sin(θ)/ λ	1.09	0.62	1.08
No. of data used for merging	241193	9350	426309
No. of unique data	12071	2162	23247
hkl range	$-15\leq h\leq 17$	$-12\leq h\leq 12$	$-22\leq h\leq 21$
	$-17\leq k\leq 19$	$-9\leq k\leq 9$	$0\leq k\leq 38$
	$0\leq l\leq 19$	$-17\leq l\leq 17$	$0\leq l\leq 26$
R_{int}	0.0260	0.0616	0.0279
R_σ	0.0272	0.0626	0.0296
Completeness (%)	96	99.3	99.1
Spherical atom refinement			
No. of data in refinement	12071	2162	23247
No. of refined parameters	201	184	373
Final R $[I > 2\sigma(I)]$	0.029	0.0429	0.033
R_w^2 $[I > 2\sigma(I)]$	0.087	0.0991	0.096
Goodness of fit *S*	1.029	1.04	1.046
Extrema in residual map/ eÅ^{-3}	-0.287→0.6030	-0.41→0.29	-0.591→0.592
Max shift/esd in last cycle	0.001	0.001	0.002

Table S6. Crystallographic data of **6**, **7**, **8** and [HCA^-] 2,6-di-tert-butil-4-methylpyridine

Compound formula	$C_{16}H_{11}Cl_3NO_6$	$C_{16}H_{12}Cl_3NO_6$	$C_{29}H_{23}Cl_5N_2O_{10}$	$C_{20}H_{25}Cl_2NO_4$
Isomer	**6**	**7**	**8**	**9**
M_r	420.6	420.6	736.8	414.31
Space group	P-1	$P2_1/c$	P-1	$P2_1/n$
Crystal system	Triclinic	Monoclinic	Triclinic	Monoclinic
a/ Å	8.0154(3)	18.330(5)	8.4477(3)	11.7516(11)
b/ Å	9.3997(3)	4.9542(1)	10.5046(3)	11.5488(12)
c/Å	11.8524(5)	19.8433(5)	18.2834(4)	15.4398(15)
α/deg	71.632(2)	90	99.0840(16)	90
β/deg	88.044(2)	110.869(1)	93.6611(17)	95.931(6)
γ/deg	86.436(2)	90	91.1015(12)	90
V/Å^{-3}	845.75(5)	1684.62(7)	1598.14(8)	2084.2(4)
Z	2	4	2	4
D_{calc}/g cm^{-3}	1.65	1.66	1.53	1.32
F(000)	428.0	856.0	752.0	871.9
Radiation	Mo Kα	Mo Kα	Mo Kα	Mo Kα
λ/Å	0.71073	0.71073	0.71073	0.71073
μ(Mo-K_a)/mm^{-1}	0.577	0.579	0.513	0.336
Crystal size/mm	0.20x0.22x0.31	0.17x0.22x0.27	0.27x0.21x0.17	0.18x0.21x0.32
θ range/deg	1.8-30.2	1.2-30.3	1.1-30.1	2.1-31.5
Max sin(θ)/ λ	0.70	0.70	0.70	0.74
No. of data used for merging	42591	9339	74680	113946
No. of unique data	4974	4949	9370	6935
hkl range	-11≤ *h* ≤11	-25≤ *h* ≤24	-11≤ *h* ≤11	-16≤ *h* ≤17
	-12≤ *k* ≤13	0≤ *k* ≤6	-14≤ *k* ≤14	–16≤ *k* ≤16
	0≤ *l* ≤16	0≤ *l* ≤27	0≤ *l* ≤25	–22≤ *l* ≤22
R_{int}	0.0438	0.0314	0.0468	0.079
R_σ	0.0380	0.0274	0.0570	0.0809
Completeness (%)	98.8	98.7	99.4	100
Spherical atom refinement				
No. of data in refinement	4974	4949	9370	6935
No. of refined parameters	283	283	496	340
Final *R* [$I > 2\sigma(I)$]	0.033	0.024	0.034	0.041
R_w [$I > 2\sigma(I)$]	0.078	0.064	0.082	0.086
Goodness of fit *S*	1.04	1.064	1.050	1.006
Extrema in residual map/ eÅ^{-3}	-0.526→0.609	-0.300→0.654	-0.270→0.378	-0.315→0.550
Max shift/esd in last cycle	0.000	0.001	0.001	0.001

Table S7. Crystallographic data of $[BH^+][HCA^-]/[BH^+]_2[CA^{2-}]$ salts: **1(2,4), 1(2,5)**, **1(2,6)** and **2(2,6)** determined using neutron diffraction.

Compound formula	$C_{13}H_{11}Cl_2NO_4$	$C_{13}H_{11}Cl_2NO_4$	$C_{13}H_{11}Cl_2NO_4$	$C_{20}H_{20}Cl_2N_2O_4$
Isomer	**1(2,4)**	**1(2,5)**	**1(2,6)**	**2(2,6)**
M_r	316.13	316.1	316.1	423.28
Space group	P-1	$P2_1/c$	P-1	$P2_1/c$
Crystal system	Triclinic	Monoclinic	Triclinic	Monoclinic
a/ Å	5.0687(2)	7.7415(2)	9.0071(3)	7.1427(3)
b/ Å	11.2561(4)	11.0538(3)	9.0326(3)	9.3025(4)
c/Å	11.6281(3)	15.4495(3)	9.0768(3)	14.7753(6)
α/deg	96.274(2)	90.00	93.526(2)	90.00
β/deg	91.960(2)	95.514(1)	104.359(2)	94.526(2)
γ/deg	90.609(1)	90.00	110.821(2)	90.00
V/Å^{-3}	659.00(2)	1315.94(1)	659.48(8)	978.28(2)
Z	2	4	2	2
D_{calc}/g cm^{-3}	1.59	1.60	1.59	1.44
F(000)	200	388.0	200	238.5
Radiation	Neutrons	Neutrons	Neutrons	Neutrons
λ/Å	0.94840	0.94840	0.94840	0.94840
μ(Mo-K_a)/mm^{-1}	0.142	0.142	0.142	0.166
Crystal size/mm	1.8x2x5	1.9x1.9x6	2x2x7	2.1x2.1x6
θ range/deg	3.2-62.1	3.0-61.7	3.1-61.7	3.5-61.9
Max sin(θ)/ λ	0.93	0.92	0.92	0.93
No. of data used for merging	20076	34129	19566	18005
No. of unique data	7496	7915	7396	5216
hkl range	$-8\leq h\leq 1$	$-2\leq h\leq 12$	$-16\leq h\leq 16$	$-5\leq h\leq 12$
	$-20\leq k\leq 20$	$-20\leq k\leq 20$	$-16\leq k\leq 13$	$-17k\leq 16$
	$-21\leq l\leq 21$	$-28\leq l\leq 28$	$-12\leq l\leq 16$	$-27\leq l\leq 23$
R_{int}	0.0422	0.0484	0.0294	0.0666
R_σ	0.0529	0.0584	0.0486	0.1004
Completeness (%)	83.9	89.7	83.5	79
Spherical atom refinement				
No. of data in refinement	7496	7915	7396	5216
No. of refined parameters	281	309	309	218
Final *R* $[I > 2\sigma(I)]$	0.029	0.038	0.034	0.089
R_w $[I > 2\sigma(I)]$	0.059	0.089	0.078	0.223
Goodness of fit *S*	1.055	1.103	1.106	0.990
Extrema in residual map/ fmÅ^{-3}	-0.852→0. 852	-1.039→0.775	-0.994→0.969	-2.213→4.152
Max shift/esd in last cycle	0.002	0.001	0.001	0.000

Table S8. Bond lengths of H_2CA molecules.[43]

Chloranilic acid (H2CA)	Bond lengths (Å)
Cl1-C111	1.717
C111-C112	1.349
C112-C113	1.508
C113-C114	1.450
C112-O2	1.322
C113-O3	1.224
O5-H5	0.819

Table S9. Bond lengths of [HCA^-] molecules

Bond	**1(2,3)**	**1(2,4)**	**1(2,5)**	**1(2,6)**	**1(3,4)**	**1(3,5)**
Cl1-C111	1.7392(18)	1.7293(3)	1.7330(3)	1.7317(3)	1.7336(4)	1.7337(5)
Cl2-C114	1.7258(18)	1.7275(3)	1.7243(3)	1.7210(3)	1.7269(4)	1.7255(5)
C111-C112	1.400(2)	1.3978(4)	1.4097(5)	1.4006(4)	1.3956(6)	1.4066(6)
C112-C113	1.545(2)	1.5448(4)	1.5506(5)	1.5466(4)	1.5664(6)	1.5473(6)
C113-C114	1.460(2)	1.4559(4)	1.4513(5)	1.4554(4)	1.4517(6)	1.4531(6)
C114-C115	1.353(2)	1.3586(4)	1.3596(5)	1.3569(5)	1.3522(6)	1.3587(6)
C115-C116	1.516(2)	1.5155(4)	1.5152(5)	1.5143(5)	1.5194(6)	1.5170(6)
C116-C111	1.413(2)	1.4127(4)	1.4051(5)	1.4157(4)	1.4136(6)	1.4081(6)
C112-O2	1.246(2)	1.2554(3)	1.2442(5)	1.2547(4)	1.2485(5)	1.2484(5)
C113-O3	1.216(2)	1.2250(4)	1.2289(5)	1.2236(4)	1.2254(5)	1.2254(5)
C115-O5	1.328(2)	1.3238(4)	1.3241(4)	1.3252(4)	1.3247(5)	1.3244(5)
C116-O6	1.246(2)	1.2460(4)	1.2534(4)	1.2481(4)	1.2502(5)	1.2503(5)
O5-H5	0.80(3)	0.910(12)	0.809(14)	0.896(12)	0.870(13)	0.888(14)

Table S10. Bond lengths of [CA^{2-}] molecules

Bond	**2(2,3)**	**2(2,4)**	**2(2,5)**	**2(2,6)**	**2(3,4)**
Cl1-C111	1.7444(3)	1.7381(4)	1.7427(3)	1.7374(3)	1.7378(3)
C111-C112	1.3953(4)	1.3947(5)	1.3968(4)	1.3987(5)	1.4050(4)
C112-C113	1.5458(4)	1.5426(5)	1.5472(4)	1.5443(5)	1.5468(4)
C112-O2	1.2595(4)	1.2588(5)	1.2612(3)	1.2586(5)	1.2506(4)
C113-O3	1.2388(3)	1.2411(5)	1.2422(4)	1.2428(4)	1.2494(4)

Table S11. The intermolecular hydrogen bonds in the supramolecular synthon units of hydrated salts

D-H···A	D-H/Å	H···A/ Å	D···A/ Å	D-H···A/ º
3				
O111-H1A···O2	0.869(12)	2.2190(12)	2.9708(4)	149.4(11)
O111-H1A···O3	0.869(12)	2.222(13)	2.9082(4)	137.7(10)
4				
N125-H125···O2	0.98(3)	1.77(3)	2.691(3)	155(2)
N125-H125···O3	0.98(3)	2.24(3)	2.899(3)	123(2)
5				
N125-H125···O2	0.931(14)	1.984(14)	2.7733(5)	141.5(11)
N125-H125···O3	0.931(14)	2.079(14)	2.8203(5)	135.6(10)

Table S12. The intermolecular hydrogen bonds in the supramolecular synthon units of mixed salts

D-H···A	D-H/Å	H···A/ Å	D···A/ Å	D-H···A/ º
6				
N125-H125···O2	0.91(3)	1.85(3)	2.7188(17)	161(2)
N125-H125···O3	0.91(3)	2.43(3)	3.0344(19)	124.3(18)
7				
N125-H125···O2	0.896(18)	1.999(19)	2.7909(12)	146.7(17)
N125-H125···O3	0.896(18)	2.139(19)	2.8099(13)	131.1(16)
8				
N125-H125···O2	0.896(18)	1.911(18)	2.7559(16)	156.5(17)
N125-H125···O3	0.896(18)	2.352(19)	2.9791(17)	127.0(15)

Table S13. Comparison between the hydrogen bond lengths of **1(2,4)** determined by neutron and X-ray diffraction

Method	D-H/Å	H···A/ Å	D···A/ Å	D-H···A/ º
Neutron diffraction				
N125-H125···O2	1.0631(10)	1.6496(11)	2.6972(6)	167.45(9)
N125-H125···O3	1.0631(10)	2.5677(10)	3.1955(5)	117.11(7)
X-ray diffraction				
N125-H125···O2	0.990(11)	1.720(10)	2.6962(4)	168.0(10)
N125-H125···O3	0.991(11)	2.604(11)	3.1956(4)	118.3(8)

Table S14. Comparison between the hydrogen bond lengths of **1(2,5)** determined by neutron and X-ray diffraction

Method	D-H/Å	H···A/ Å	D···A/ Å	D-H···A/ º
Neutron diffraction				
N125-H125···O2	1.0448(15)	2.2481(16)	2.9204(9)	120.49(10)
N125-H125···O3	1.0448(15)	1.9518(16)	2.9477(8)	158.22(12)
X-ray diffraction				
N125-H125···O2	0.828(9)	2.333(9)	2.9202(5)	128.4(8)
N125-H125···O3	0.828(9)	2.174(9)	2.9461(5)	155.4(9)

Table S15. Comparison between the hydrogen bond lengths of **1(2,6)** determined by neutron and X-ray diffraction

Method	D-H/Å	H···A/ Å	D···A/ Å	D-H···A/ º
Neutron diffraction				
N125-H125···O2	1.0700(12)	1.6115(13)	2.6633(6)	166.37(11)
N125-H125···O3	1.0700(12)	2.5324(13)	3.1007(7)	112.30(8)
X-ray diffraction				
N125-H125···O2	0.899(10)	1.773(10)	2.6622(4)	169.7(9)
N125-H125···O3	0.899(9)	2.61799)	3.0999(4)	114.3(7)

Table S16. Comparison between the hydrogen bond lengths of **2(2,6)** determined by neutron and X-ray diffraction

Method	D-H/Å	H···A/ Å	D···A/ Å	D-H···A/ º
Neutron diffraction				
N125-H125···O2	1.080(3)	1.604(4)	2.646(2)	160.3(3)
N125-H125···O3	1.080(3)	2.399(4)	3.052(2)	117.6(2)
X-ray diffraction				
N125-H125···O2	0.916(12)	1.747(13)	2.6458(5)	166.5(12)
N125-H125···O3	0.916(12)	2.519(13)	3.0495(5)	117.3(10)

Table S17. Summary of the multipole model refinements of $[BH^+][HCA^-]$/$[BH^+]_2[HCA^{2-}]$ salts

Form	R_{val}	Form	R_{val}
1(2,4)		**2(2,3)**	
1	1.72	1	1.78
2	1.66	2	1.73
3	1.65	3	1.73
4	1.64		
5	1.64		
1(2,5)		**2(2,4)**	
1	1.96	1	2.98
2	1.91	2	2.93
3	1.90	3	2.91
1(2,6)		**2(2,5)**	
1	1.9	1	1.64
2	1.85	2	1.56
3	1.83	3	1.55
1(3,4)	2.74	**2(2,6)**	
1	2.69	1	2.88
2	2.68	2	2.83
3		3	2.8
1(3,5)		**2(3,4)**	
1	2.66	1	2.45
2	2.60	2	2.41
3	2.58	3	2.40

Table S18. The intermolecular interactions formed by chloranilic acid molecules in **1**

D-H···A	D-H/Å	H···A/ Å	D···A/ Å	D-H···A/ º
1(2,3)				
O5-H5···O6[1]	0.80(3)	2.05(3)	2.7212(19)	142(2)
1(2,4)				
O6-H6···O5[2]	0.910(11)	1.923(11)	2.7193(4)	145.0(10)
	0.9910(16)	*1.8371(16)*	*2.7213(9)*	*146.86(13)*
1(2,5)				
O5-H5···O6[3]	0.809(14)	2.045(14)	2.6970(5)	137.5(13)
	0.9883(15)	*1.8638(17)*	*2.6976(10)*	*140.10(13)*
1(2,6)				
O5-H5···O6[4]	0.896(12)	1.924(12)	2.7225(4)	147.5(11)
	0.9878(15)	*1.8528(13)*	*2.7248(8)*	*145.47(13)*
1(3,4)				
O5-H5···O6[5]	0.868(12)	1.952(12)	2.7143(7)	145.8(12)
1(3,5)				
O5-H5···O6[6]	0.888(14)	1.951(14)	2.7378(5)	146.9(13)

[1] –x,-y,-z ; [2] 1-x,1-y,-z ; [3] 2-x, -y, -z ; [4] –x,1-y,-z ; [5] 1-x,-y,-z ; [6] 1-x, 1-y, 1-z

Table S19. The crystal packing density of $[BH^+][HCA^-]$/$[BH^+]_2[HCA^{2-}]$ salts

Form	Density	Form	Density
1(2,3)	1.65	**2(2,3)**	1.46
1(2,4)	1.59	**2(2,4)**	1.42
1(2,5)	1.60	**2(2,5)**	1.50
1(2,6)	1.59	**2(2,6)**	1.44
1(3,4)	1.59	**2(3,4)**	1.47
1(3,5)	1.56		

Table S20. The lattice energy calculations using the experimental charge density approach of $[BH^+][HCA^-]$ salts.

	E_L (kJ/mole)	E_{int} (kJ/mole)	Sum (kJ/mole)
1(2,4)			
1	-241.07	-229.69	-335.91
2	-252.60	-334.94	-420.07
3	-255.63	-335.74	-423.5
4	-251.9	-332.57	-417.97
5	-254.76	-331.91	-420.71
1(2,5)			
1	-238.81	-253.6	-365.61
2	-248.15	-296.50	-396.4
3	-242.47	-302.41	-544.88
1(2,6)			
1	-170.44	-221.44	-281.16
2	-176.08	-313.1	-332.63
3	-179.56	-323.28	-341.2
1(3,4)			
1	-235.32	-222.00	-346.32
2	-259.37	-289.98	-404.36
3	-267.46	-291.76	-413.34
1(3,5)			
1	-218.35	-200.70	-318.7
2	-234.87	-267.50	-368.62
3	-242.66	-270.10	-337.71

Table S21. The lattice energy calculations using the experimental charge density approach of $[BH^+]_2[HCA^{2-}]$ salts

	E_L (kJ/mole)	E_{int} (kJ/mole)	Sum (kJ/mole)
2(2,3)			
1	-503.36	-459.77	-963.13
2	-486.29	-531.15	-1017.44
3	-478.25	-535.36	-1013.61
2(2,4)			
1	-592.75	-275.08	-867.83
2	-708.65	-291.49	-1000.14
3	-687.04	-470.76	-1157.8
2(2,5)			
1	-544.90	-403.04	-947.94
2	-496.84	-515.64	-1012.48
3	-496.63	-516.75	-1013.38
2(2,6)			
1	-543.55	-406.96	-950.51
2	-523.17	-534.89	-1058.06
3	-515.19	-541.89	-1057.08
2(3,4)			
1	-414.60	-427.76	-842.36
2	-387.22	-459.41	-846.63
3	-380.68	-471.87	-852.55