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Supporting information for article:

Phase transitions in ferroelectric 4-aminopyridinium tetrachloro-antimonate(III) – revisited

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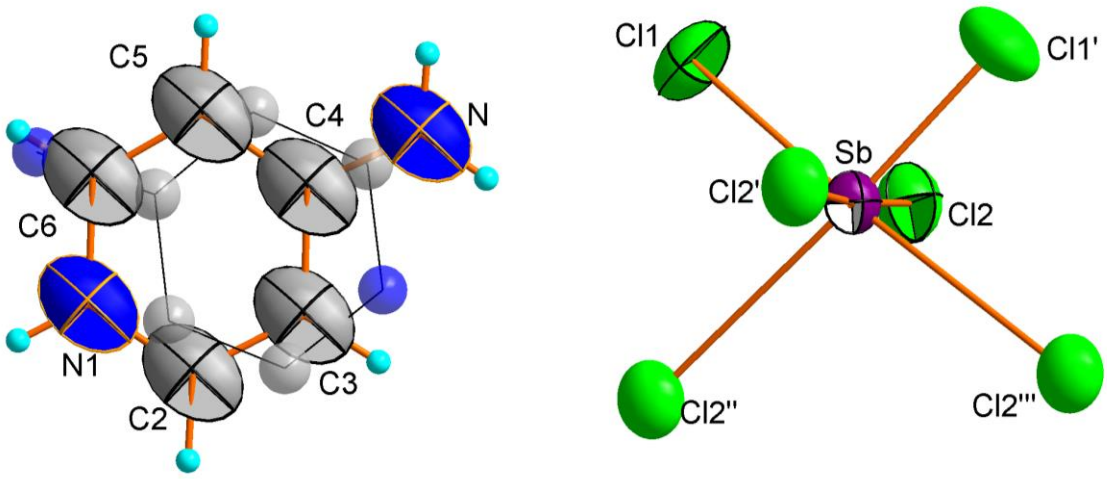


Figure S1

Atom numbering scheme in phase I, T=320K, the atoms from the asymmetric unit are drawn as octants; site occupation factor for 4-AP is 0.5, the ellipsoids are presented with 50% probability. The second disordered position is drawn as transparent section with reduced displacement parameters for the picture clarity.

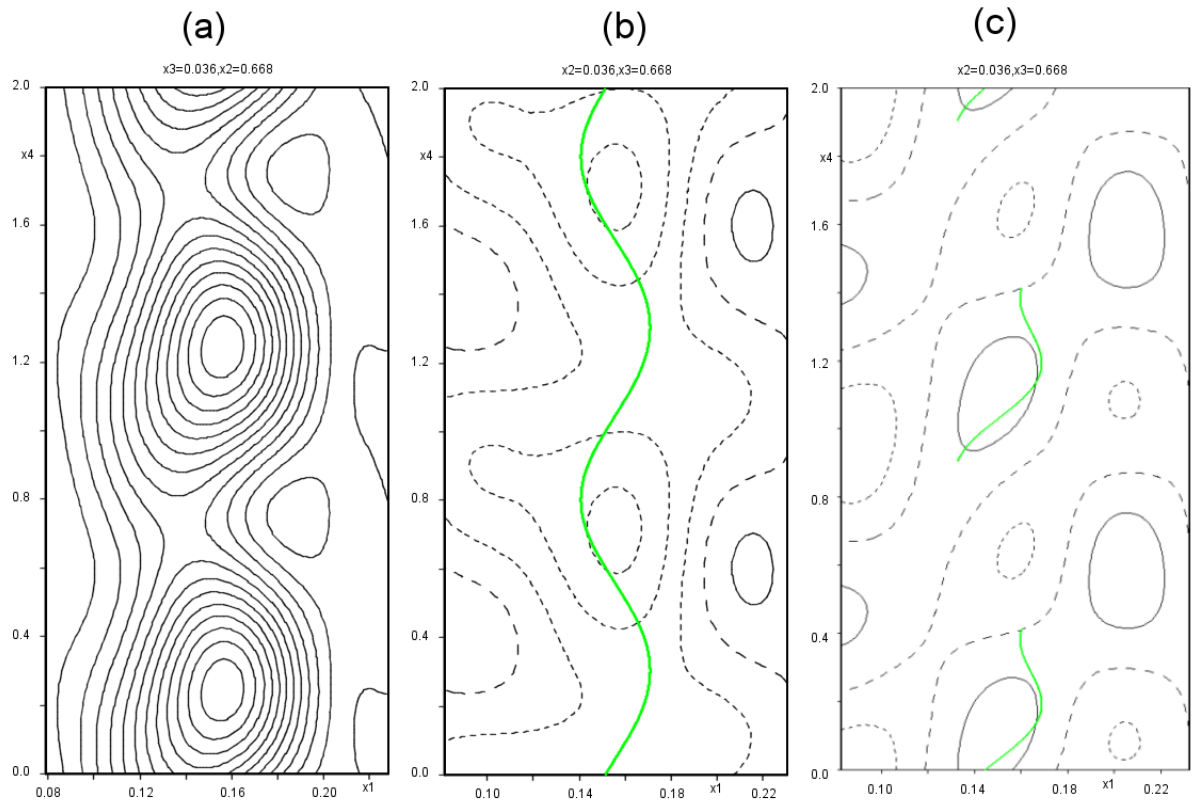
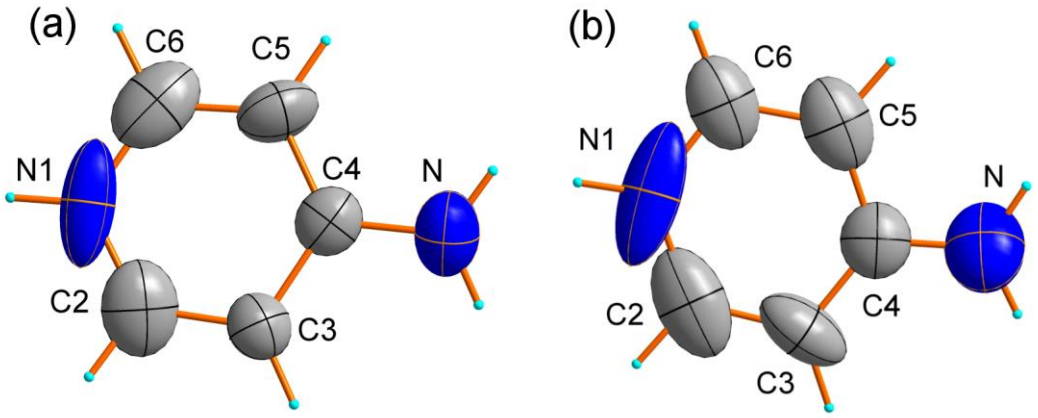


Figure S2

The x1-x4 sections through nitrogen amine atom from 4-AP at 290 K in phase II (a) the observed Fourier map, the contour step is 0.5 eÅ^{-3}; (b)- the difference F_c-F_o maps for harmonic modulation of 4-AP occupancy; (c) occupancy modelled with Crenel function, Δx_4=0.5. The contour step for the difference map is 0.1 eÅ^{-3}.



	harmonic	***crenel***
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, *S*, *all*	0.027, 0.095, 1.82	0.035, 0.116, 2.23
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, *main*	0.019, 0.063,	0.025, 0.0839

$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, *satellites*	0.046, 0.110	0.056, 0.14
No. of reflections (*main/sat.*)	2539	2539
No. of parameters	133	126
No. of restraints	0	0
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.50, -0.71	0.72, -0.83

Figure S3 The 4-AP in the ellipsoid representation at 290 K in phase II, (a) harmonic, (b) crenel model. The table below summarizes the final refinement parameters for both models.

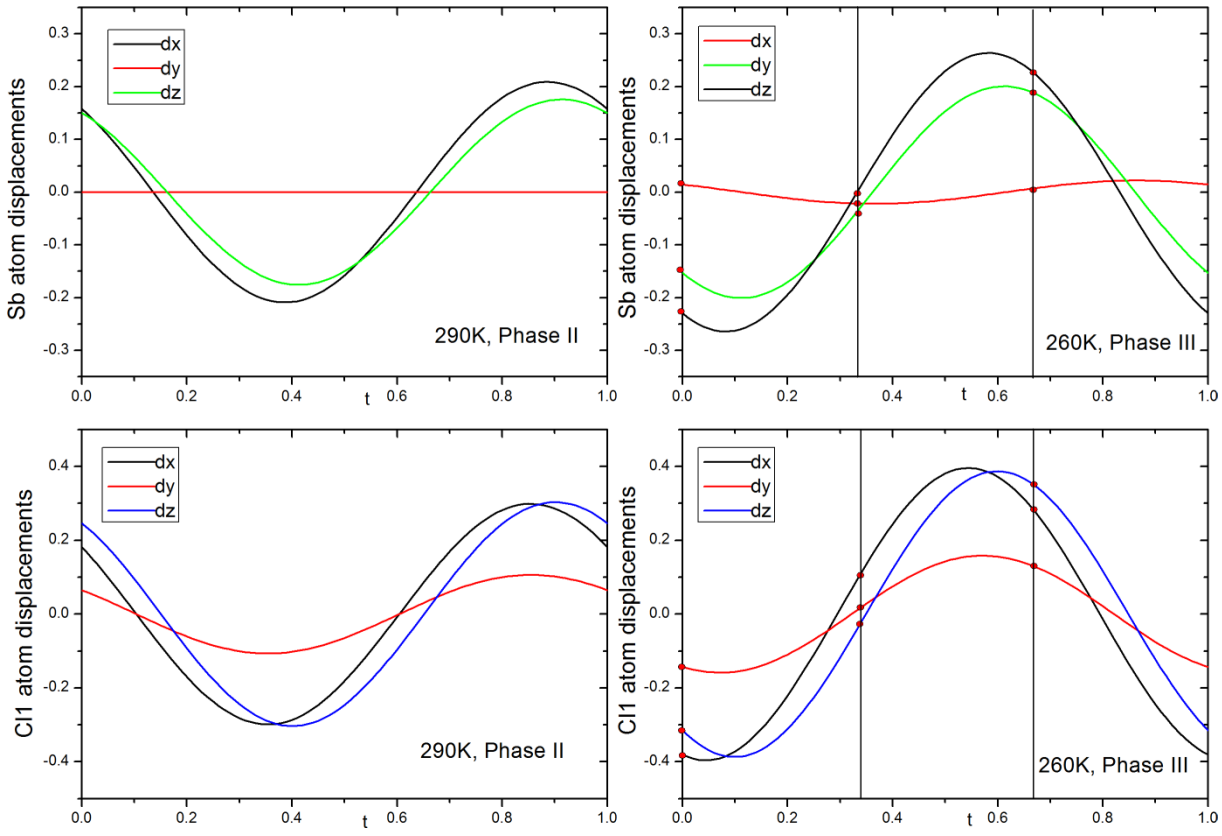


Figure S4

Sb and apical Cl1 atoms displacements in the modulated phase II and III.

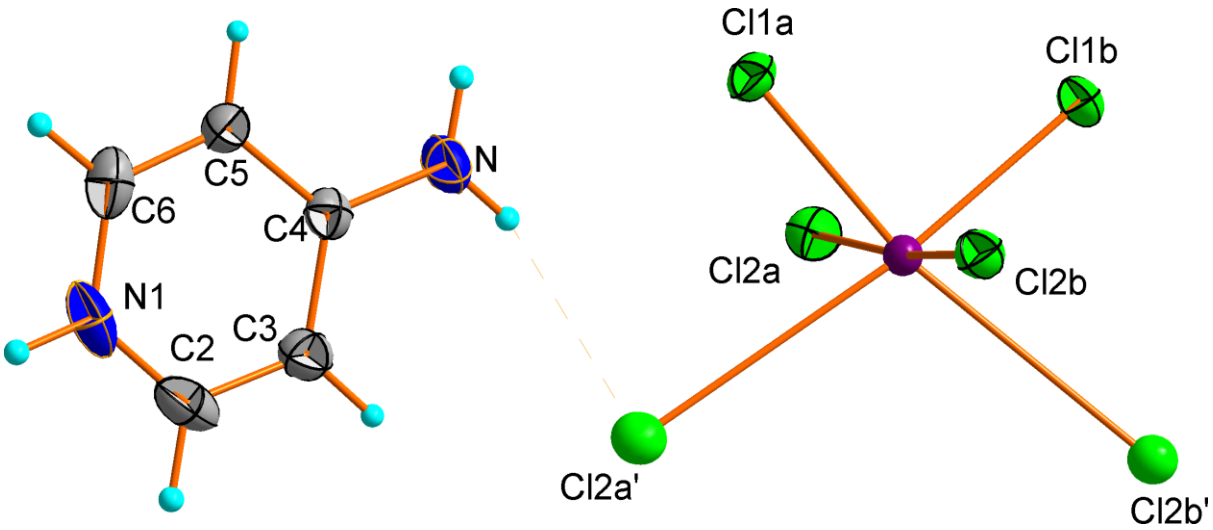


Figure S5

Atom numbering scheme in phase V, T=200 K, the atoms from the asymmetric unit are drawn as octants; site occupation factor for 4-AP is 1.

Table S1 The geometry of the N-H···Cl hydrogen-bonds in modulated phase II in the harmonic model, for different t values

N-H2···Cl2$^{x-1/2,-y+3/2,\ z-1/2}$

	D…H (Å)	H… A (Å)	D-A (Å)	D-H…A angle (°)
t=0.000	0.87(2)	2.653(16)	3.498(18)	164(2)
t=0.100	0.87(2)	2.600(14)	3.443(16)	163(2)
t=0.200	0.87(2)	2.552(15)	3.393(17)	162(2)
t=0.300	0.87(3)	2.528(18)	3.368(19)	162(2)
t=0.400	0.87(3)	2.537(18)	3.38(2)	163(2)
t=0.500	0.87(2)	2.574(16)	3.422(18)	165(2)
t=0.600	0.87(2)	2.624(14)	3.476(16)	166(2)
t=0.700	0.87(2)	2.670(15)	3.522(17)	166(2)
t=0.800	0.87(3)	2.695(18)	3.544(19)	165(2)
t=0.900	0.87(3)	2.689(19)	3.54(2)	165(3)
t=1.000	0.87(2)	2.653(16)	3.498(18)	164(2)

N1-H1···Cl2$^{x-1,1-y,z-3/2}$

	D… H (Å)	H… A (Å)	D…A	D-H… A angle (°)
t=0.000	0.87(4)	2.33(3)	3.20(2)	179(4)
t=0.100	0.87(3)	2.26(2)	3.13(2)	176(3)
t=0.200	0.87(3)	2.20(2)	3.07(2)	174(3)
t=0.300	0.87(4)	2.17(3)	3.04(3)	176(4)
t=0.400	0.87(4)	2.18(3)	3.05(3)	179(5)
t=0.500	0.87(3)	2.24(3)	3.11(3)	174(4)
t=0.600	0.87(3)	2.33(2)	3.19(2)	169(3)
t=0.700	0.87(3)	2.40(2)	3.25(2)	167(3)
t=0.800	0.87(4)	2.42(3)	3.28(3)	169(4)
t=0.900	0.87(4)	2.40(3)	3.26(3)	174(4)
t=1.000	0.87(4)	2.33(3)	3.20(2)	179(4)

Table S2 The geometry of the N-H···Cl hydrogen-bonds in commensurate phase III,

			D-H (Å)	H… A (Å)	D-A (Å)	D-H… A angle (°)
N_a	H1_a	Cl1_a$^{(I)}$				
		t=0.333	0.872(5)	2.547(4)	3.399(7)	165.8(3)
		t=0.667	0.871(5)	2.607(4)	3.449(7)	163.1(3)
N1_a	H1N1_a	Cl2_a$^{(II)}$				
		t=0.33	0.872(9)	2.399(15)	3.26(2)	167.9(6)
		t=0.667	0.871(9)	2.386(17)	3.25(2)	175.0(7)
N_b	H1_b	Cl2_a$^{(III)}$				
		t=0	0.880(5)	2.712(5)	3.569(8)	165.0(2)
N_b	H2_b	Cl2_a$^{(IV)}$				
		t=0	0.881(6)	2.615(9)	3.456(13)	159.7(3)
N1_b	H1n1_b	Cl2_b$^{(V)}$				
		t=0	0.886(9)	2.392(13)	3.25(2)	162.0(6)

(I) x-1/2,-y+3/2,z-1/2; (II) x-1,-y+1,z-3/2; (III) x-1/2,-y+3/2,z-3/2; (IV) x-1,-y+1,z-3/2; (V) x,-y+1,z-1/2