On the colossal and highly anisotropic thermal expansion exhibited by imidazolium salts

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Supplementary General Experimental Section

Preparation of 1-ethyl-2,3-dimethylimidazolium salts Edimim[Cl] and Edimim[Br]: 1,2-dimethylimidazole (9.38 g, 97.5 mmol) was dissolved in 150 mL acetonitrile and ethyl iodide (11.68 g, 107.25 mmol) was added drop wise to the stirred solution cooled in an ice bath. After addition of the iodoethane, the reaction mixture was warmed up and the mixture refluxed for 24h. The reaction was cooled down and the solvent removed under vacuum. The remaining solids were re-crystallized in a mixture of acetone: acetonitrile yielding white crystals 15.80 g, 79% yield. 1-ethyl-2,3-dimethylimidazolium iodide (5 g, 19.84 mmol) was dissolved in 500 mL of distilled water and passed through an anion exchange column Amberlite IRA-400 column (OH- form) to yield a iodide free solution of 1-ethyl-2,3-dimethylimidazolium hydroxide (test by the Volhard method). The hydroxide solution was neutralized with concentrated hydrochloric acid (36%, Vetec) and hydrobromic acid (47%, Vetec) for chloride and bromide compounds, respectively top PH 7 and water removed in rotary evaporator with the remaining water removed under vacuum at 100ºC. The solids were then dissolved in dichloromethane and dried over anhydrous Na_2CO_3, filtered and the solvent removed under vacuum, yielding 4.80 g (96%) and 4.70 g (94% yield) of 1-ethyl-2,3-dimethylimidazolium chloride and bromide samples. Further purification of the final products was made by recrystallization from ethyl acetate/hexane.

Powder data solution and refinement:

The diffraction patterns at 100 and 350 K were indexed using DICVOL04[s1] and the whole-pattern matching and intensity extraction were performed with DAjust software.[s2] The intensities were introduced in the direct-space solution program TALP[s3] to obtain the candidate solution that was finally refined with the restrained Rietveld refinement program RIBOLS[s4] using distance restraints taken from MOGUL[s5]. H atoms were placed in calculated positions and constrained to the respective C atoms. Finally, sequential refinements against the whole data were performed using the FullProf suite[s6] in order to

follow the evolution of the crystallographic data with the temperature. The thermal expansion tensors and the volume thermal expansion coefficients were obtained via linear fits using the PASCal program (Supplementary Fig .3). [s7]

DFT calculations and Computational details:

We have carried out density functional first-principles simulations based on a numerical atomic orbital method as implemented in the SIESTA[s8] code. All the calculations have been performed within the efficient implementation[s9] of the Van der walls (vdw) density functional of Dion et al. [s10] This fully non-local vdw correlation has been recently tested on imidazolium-based ionic liquids[s11], showing spectacular improvements in the interatomic geometries, equilibrium volume and internal geometry with respect to the local density (LDA) and generalized gradient approximation (GGA) at a very modest computational cost.

Core electrons were replaced by ab-initio norm conserving pseudopotentials, generated using the Troullier-Martins scheme[s12], in the Kleinman-Bylander fully non-local separable representation. [s13] In order to avoid the spiky oscillations close to the nucleus we have included small partial core corrections[s14] for all the atoms. The reference configuration and cutoff radii for each angular momentum shell and the matching radius between the full core charge density and the partial core charge density for the nonlinear core corrections (NLCCs) for the pseudopotentials used in this work can be found in Suplementary Table 11 for H, C, N, Cl and Br.

The one-electron Kohn-Sham eigenstates were expanded on a basis of strictly localized numerical atomic orbitals. [s15] We used a double-ζ plus polarization for the valence states of all the atoms. The atomic shells explicitly included in the simulations are the 1s, 2p for H; 2s, 2p, 3d for C and N; 4s, 4p, 4d for Cl and Br. All the parameters that define the shape and range of the basis functions were obtained by a variational optimization of the enthalpy (with a pressure P=0.1 GPa), using the coordinates of Edimim[Cl] and Edimim[Br] obtained by Rietveld refinement from synchrotron powder diffraction data at 100 K as the reference configuration.

The electronic density, Hartree, and exchange correlation potentials, as well as the corresponding matrix elements between the basis orbitals, were calculated in a uniform

real space grid. An equivalent plane wave cut-off of 350 Ry was used to represent the charge density. For the Brillouin zone integrations we use a Monkhorst-Pack sampling[s16] of 4 × 2 × 4, equivalent to a real-space cut-off of 10 Å. [s17]

Starting from the experimental coordinates obtained by synchrotron powder diffraction data at 100 K, a full optimization of the crystal lattice parameters and atomic positions was carried out, until a maximum component of the force on any atom was smaller than 0.01 eV/Å and the maximum component of the stress tensor was smaller than 0.0001 eV/Å^3.

The intramolecular geometries and distances of the [Edimim]$^+$ cation obtained by DFT calculations lie in the expected range comparable to those found in experimental data (overestimation within the range from 3 to 4 %). The intermolecular distances and orientations are in good agreement with the experimental results, thus confirming that the vdw functional does not introduce any unwanted features in the description of the low temperature structure. All the computation for the isolated Edimim[X] (X =Cl and Br) and the corresponding charged constituents were executed in cubic supercells of 25 Å side, with a compensating uniform background of the opposite charge to avoid the divergence of the electrostatic potential in charged periodic systems. The used correction energy for the isolated ions was proposed initially by Leslie and Gillanand[s18] also for G. Makov and M. Payne[s19].

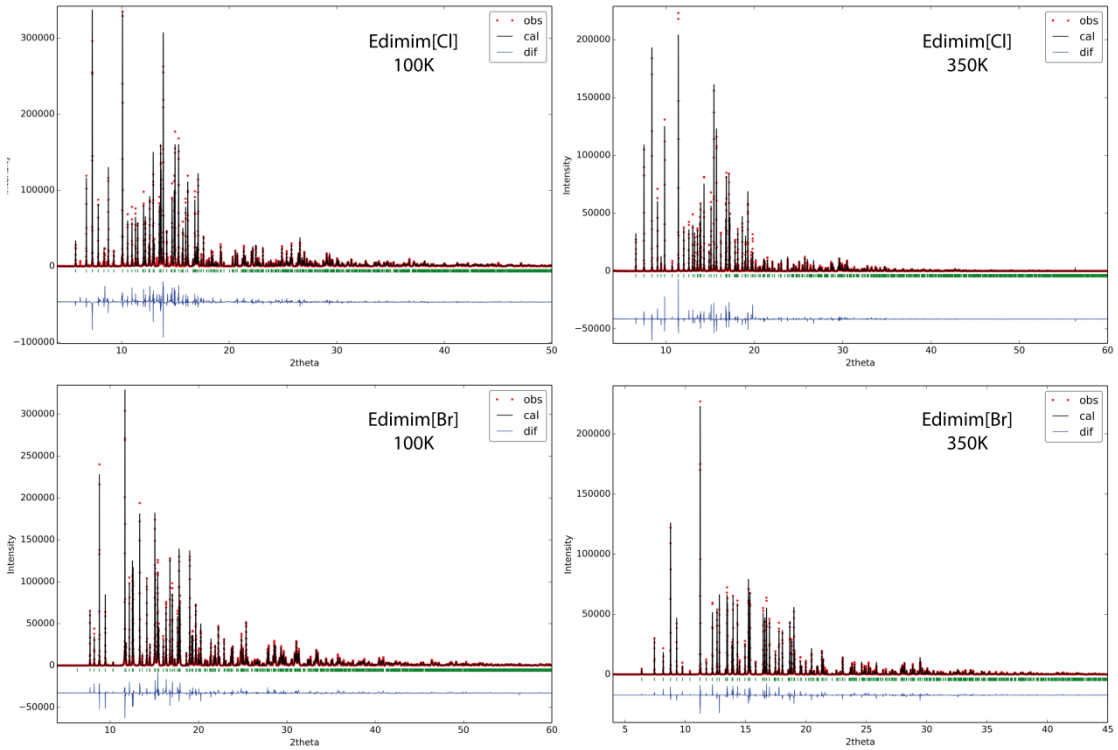


Figure S1. Observed (red points) and calculated (blue solid line) powder diffraction patterns for Edimim[Cl] at (a) 100 K and (b) 350 K, and Edimim[Br] at (c) 100 K and (d) 350 K. Positions of the Bragg reflections are represented by vertical bars. The observed-calculated difference patterns are depicted at the bottom of each figure.

The crystal structures of 1-ethyl-2,3-dimethylimidazolium chloride, Edimim[Cl], and bromide, Edimim[Br], imidazolium salts have been determined using synchrotron powder X-ray diffraction techniques. Both compounds crystallize in the same centrosymmetric space group $P2_1/a$ (nº 14) without structural transitions in the temperature range studied.

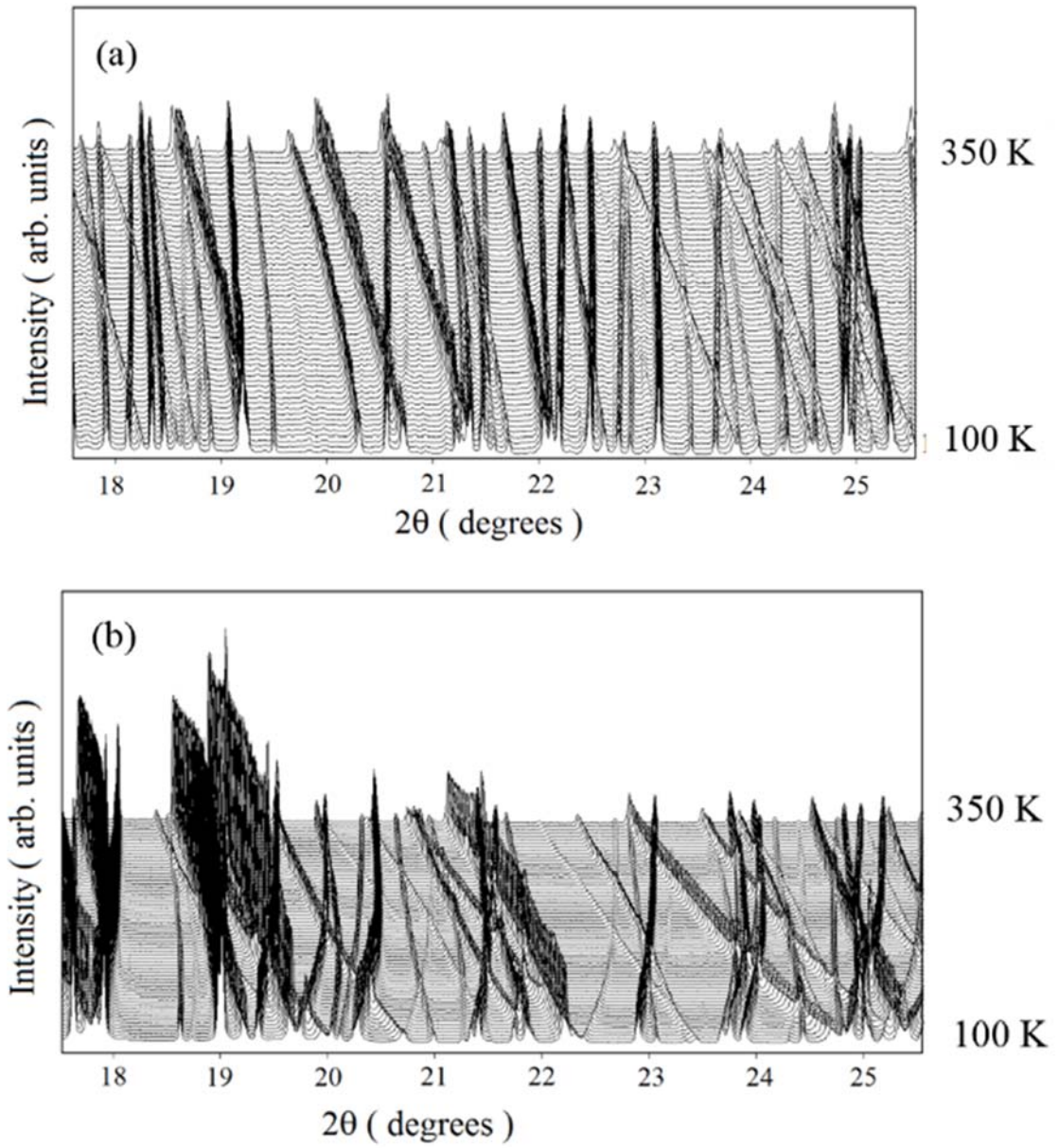


Figure S2. Thermal evolution of Synchrotron powder data collection between 100 and 350 K from 17.5 to 26 ° for (a) chloride and (b) bromide salts.

Comparison of the synchrotron Powder diffraction patterns of both salts from 100-350 K shows that no phase transition occurs. The peak positions of most reflections change considerably from pattern to pattern (with some values increasing and others decreasing) with no significant peak broadening effects. This is related with the colossal and highly anisotropic thermal expansion exhibited by these imidazolium salts.

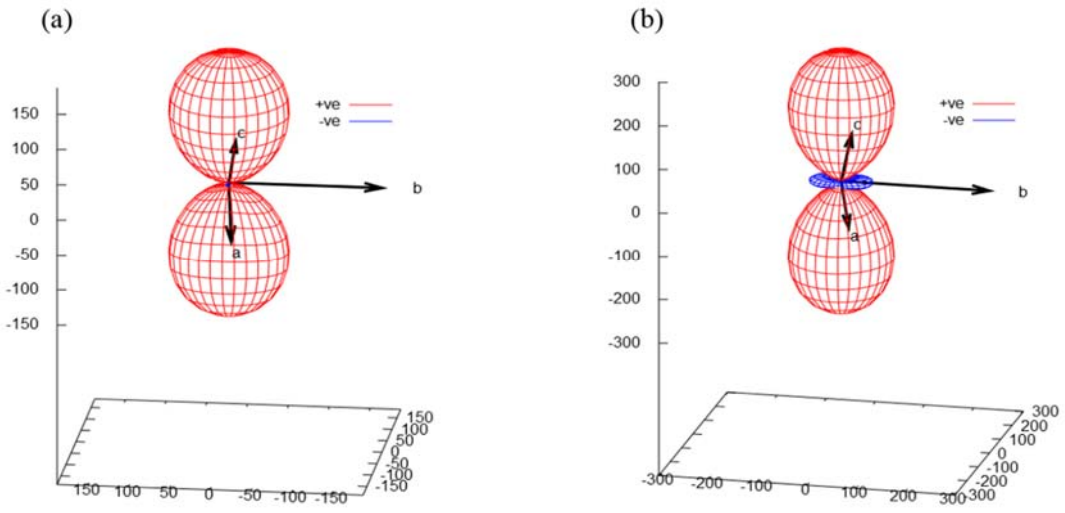


Figure S3. The thermal expansion indicatrices (red positive; blue negative) of (a) Edimim[Cl] and (b) Edimim[Br] related to the crystallographic axes (black).

The strong positive thermal expansion, the principle orthogonal axis $\mathbf{X}_3$,is inclined by 72.5º and 54.8º to crystallographic *c*-axis for Cl and Br, respectively. (see Supplementary Table 8), while the principle axis $\mathbf{X}_2$ of the negative thermal-expansion tensor is exactly parallel to the crystal **b** axis.

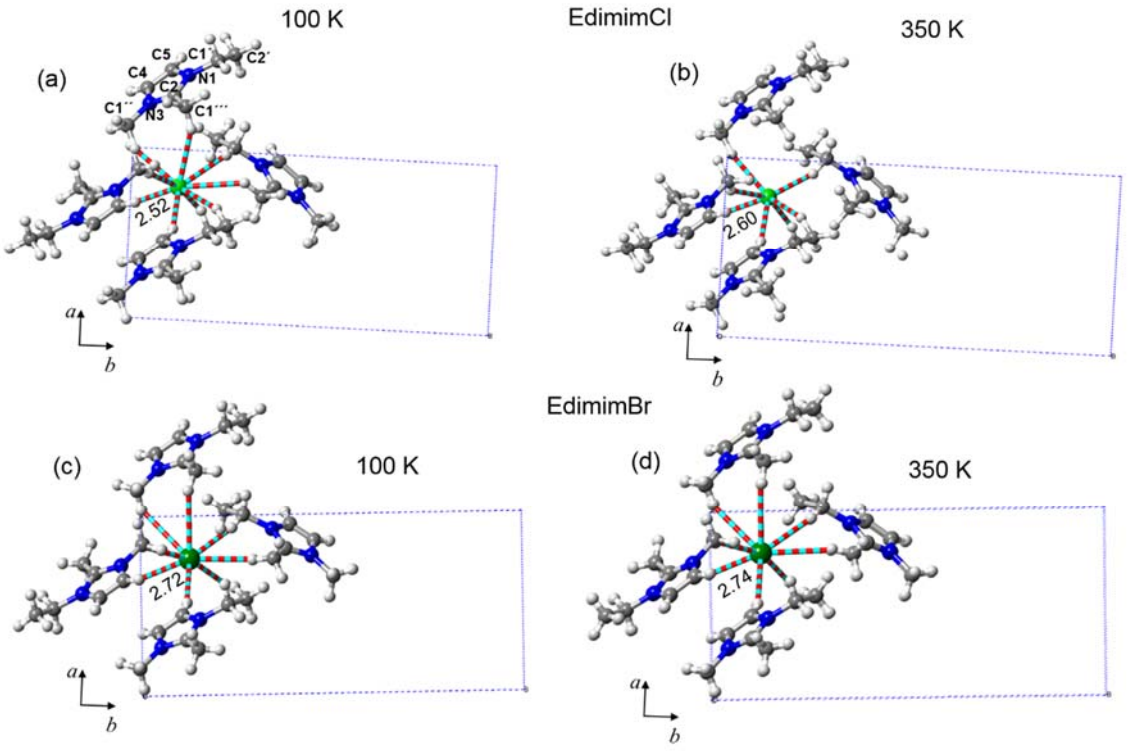


Figure S4. Hydrogen-bonding network in Edimim[Cl] at (a) 100 K and (b) 350 K and Edimim[Br] at (c) 100 K and (d) 350 K (H—Cl and H—Br contact up to 3.10 and 3.20 Å are marked with green and red stripes). The shorter hydrogen-bonding distance is displayed.

Color code: green (chloride or bromide), grey (carbon), blue (nitrogen) and white (hydrogen). Hydrogen-bonding network are marked with green and blank stripes. The blue dashed squares represent the unit cell.

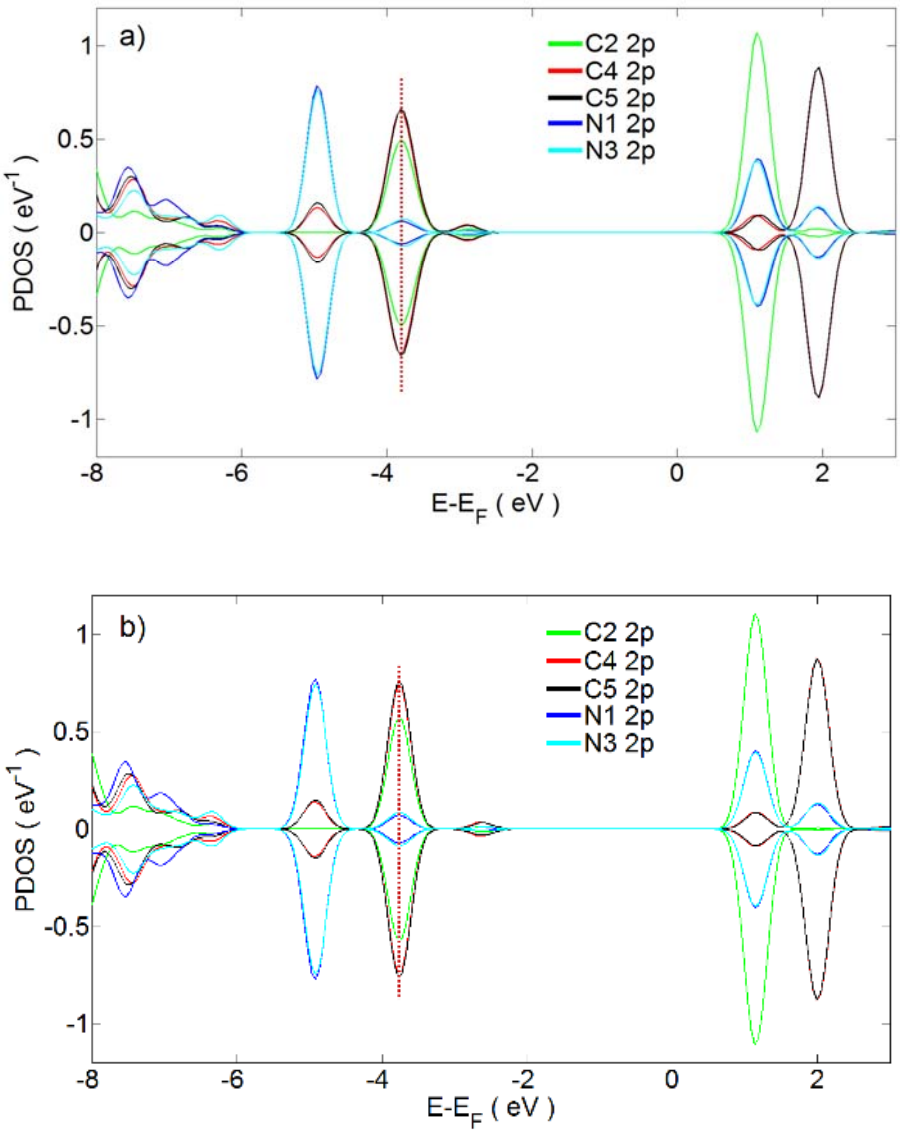


Figure S5 | PDOS of in the imidazolium ring for (a) Edimim[Cl] and (b) Edimim[Br] at 0 K. Dashed line shows the state with energy of −3.79 eV (a) and -3.81 eV (b) form below the Fermi energy, where the π^+–π^+ interactions are detected.

To check the existence of existence of π^+–π^+ interactions in the condensed phase of these salts, we studied the projected density of states (PDOS) of the imidazolium rings in the anti-parallel projection. We observed a wide range of energies between-3.5 and -4.5 eV below the Fermi energy, where the PDOS take a non-zero value, proving the existence of bonding between them. We have plotted a representative state at the Gamma point, with an energy of −3.79 eV and -3.81 eV for Cl and Br respectively, below the Fermi energy, for the representation of the π^+–π^+ interactions wave-function of Figure 3 (b).

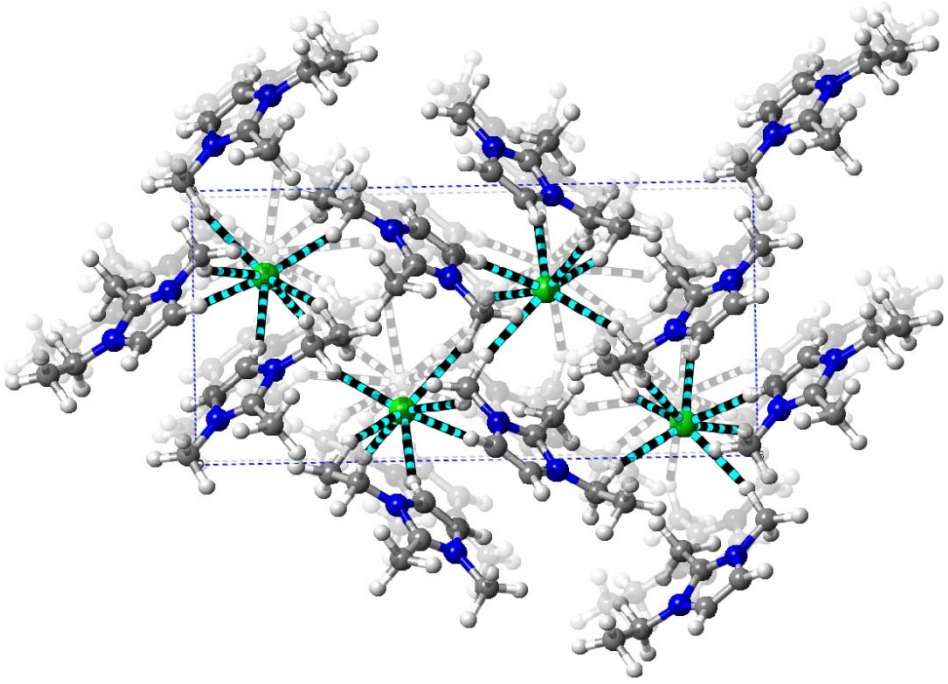


Figure S6. Crystal packing evolution in the *ab* plane of Edimim[Cl] from 100 K to 350 K (sharp figure). Hydrogen-bonding network contact up to 3.00 are marked with green and blank stripes. The blue dashed squares represent the unit cell.

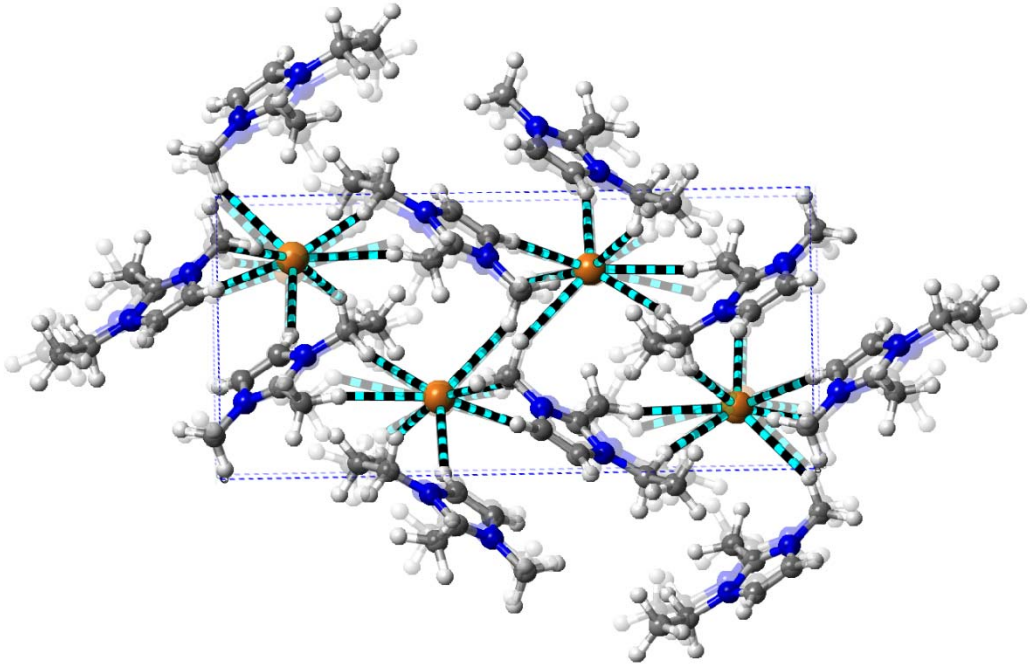


Figure S7. Crystal packing evolution in the *ab* plane of Edimim[Br] from 100 K to 350 K (sharp figure). Hydrogen-bonding network contact up to 3.12 are marked with green and blank stripes. The blue dashed squares represent the unit cell.

Table S1. Crystallographic data and structure refinement details for Edimim[Cl] and Edimim[Br] from synchrotron powder X Ray diffraction patterns (100 and 350 K).

	Edimim[Cl]		Edimim[Br]	
	100 K	350 K	100 K	350 K
Molecular formula	$C_7N_2H_{13,}Cl$	$C_7N_2H_{13,}Cl$	$C_7N_2H_{13,}Br$	$C_7N_2H_{13,}Br$
Formula weight	160.64	160.64	205.10	205.10
Crystal System	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	P 2_1/a	P 2_1/a	P 2_1/a	P 2_1/a
a (Å)	7.99133(7)	8.36354(6)	7.84687(6)	8.35614(5)
b (Å)	16.45673(15)	16.48736(12)	17.33455(12)	17.03647(11)
c (Å)	6.68451(7)	6.71642(6)	6.75091(5)	6.87656(5)
α (º)	90º	90º	90º	90º
β (º)	104.042(1)º	105.536(1)º	100.290(1)º	104.287(1)º
γ (º)	90º	90º	90º	90º
Volume (Å^3)	852.819(14)	892.306(13)	903.503(12)	948.664(12)
Z	4	4	4	4
Calculated density (g/cm^3)	1.251	1.196	1.508	1.436
Measurement Temperature (K)	100 K	350 K	100 K	350 K
Radiation (wavelengths in Å)	0.82621(3)	0.95336(3)	0.95336(3)	0.95336(3)
Measured 2θ range, stepsize (º)	2.00-64.00, 0.006	2.00-82.00, 0.006	2.00-82.00, 0.006	2.00-45.00, 0.006
Rietveld refinement details:				
Profile function	Pseudo-Voigt	Pseudo-Voigt	Pseudo-Voigt	Pseudo-Voigt
2θ range used	4.00-60.00	4.00-60.00	4.00-60.00	4.00-45.00
Num. of reflections	1575	1082	1090	520
Data points	7666	9334	9334	6849
Parameters[a]	41	41	41	41
Restraints[b]	26	26	26	26
R_{wp}	0.089	0.080	0.086	0.080
$\chi_{Rietveld}/\chi_{Pattern-Matching}$	8.499/5.561=1.79	6.073/3.361=1.80	7.753/4.075=1.90	5.384/2.936=1.83

[a] Parameters: 30 atomic coordinates (x,y,z), 3 pseudo-Voigt parameters, zero offset, scale factor, 4 cell parameters and 2 isotropic atomic displacement parameters (one for the halide and one for all the atoms of the imidazolium cation)
[b] Restraints: 9 bond distances, 12 bond angles and 5 for the imidazole plane.

Table S2. Final refined positional coordinates from synchrotron powder X Ray diffraction patterns of Edimim[Cl] at 100 and 350 K. Label of the atoms as in Figure 3.

	Edimim[Cl] at 100 K			Edimim[Cl] at 350 K		
Atom	*x/a*	*y/b*	*z/c*	*x/a*	*y/b*	*z/c*
Cl1	0.2193(4)	0.63160(10)	0.3716(3)	0.7170(4)	0.12910(10)	0.8735(3)
N1	0.9324(4)	1.1426(4)	-0.0058(9)	0.0642(4)	0.1404(3)	0.5087(9)
N3	0.7575(4)	1.0396(4)	-0.0766(9)	0.2358(4)	0.0400(3)	0.5726(9)
C1'	1.0289(4)	1.2189(4)	-0.0357(9)	-0.0257(4)	0.2133(4)	0.5476(9)
C1"	0.6222(4)	0.9819(3)	-0.1889(9)	0.3625(4)	-0.0139(3)	0.6958(9)
C1"'	0.7506(4)	1.1382(4)	-0.3761(10)	0.2514(4)	0.1374(3)	0.8694(9)
C2	0.8087(4)	1.1067(4)	-0.1563(10)	0.1867(4)	0.1024(4)	0.6553(9)
C2'	1.0704(4)	1.2679(4)	0.1715(9)	-0.0634(4)	0.2627(4)	0.3436(9)
C4	0.8436(4)	1.0333(4)	0.1339(10)	0.1508(4)	0.0352(3)	0.3648(10)
C5	0.9563(4)	1.0977(4)	0.1763(10)	0.0435(4)	0.0980(4)	0.3293(8)
H1A"	0.6606	0.9563	-0.2989	0.3280	-0.0307	0.8147
H1B"	0.5172	1.0111	-0.2447	0.4664	0.0144	0.7398
H1C"	0.6019	0.9412	-0.0946	0.3754	-0.0606	0.6164
H1A"'	0.8240	1.1821	-0.3959	0.1636	0.1653	0.9081
H1B"'	0.6338	1.1572	-0.4003	0.3406	0.1746	0.8729
H1C"'	0.7569	1.0951	-0.4708	0.2913	0.0938	0.9644
H2A'	1.1324	1.3164	0.1554	-0.1025	0.3152	0.3700
H2B'	0.9650	1.2785	0.2104	0.0366	0.2685	0.3004
H2C'	1.1389	1.2354	0.2802	-0.1464	0.2362	0.2367
H1A'	1.1354	1.2048	-0.0727	-0.1292	0.1971	0.5751
H1B'	0.9592	1.2516	-0.1457	0.0383	0.2445	0.6641
H4	0.8281	0.9935	0.2265	0.1630	-0.0037	0.2697
H5	1.0354	1.1090	0.3002	-0.0325	0.1100	0.2039

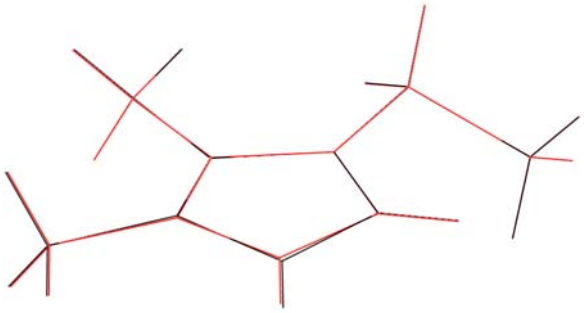
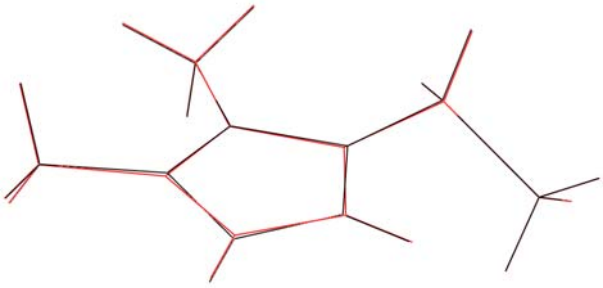
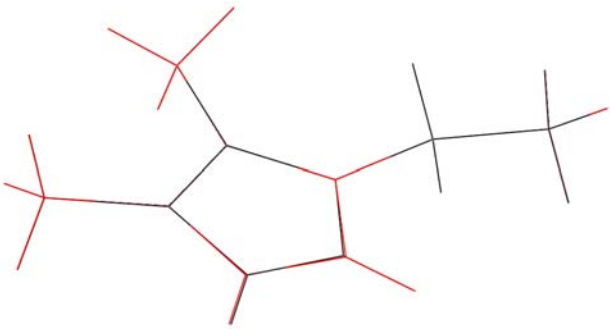
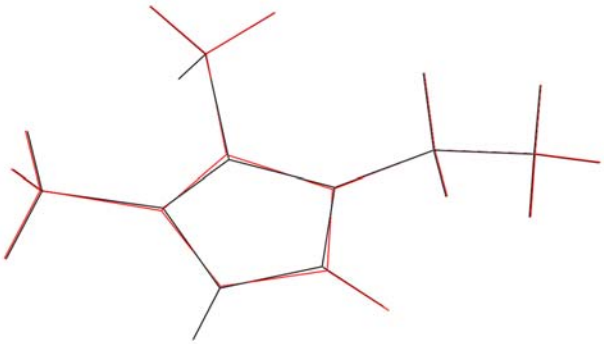
Full occupancies for all atoms.
(100 K) a =7.99133(7)Å, b = 16.45673(15)Å, c = 6.68451(7)Å, $\alpha = \gamma = 90º$, β = 104.042(1)º, s.g. $P2_1/a$. B_{Cl} = 0.019(2)Å^2, $B_{C,N,H}$ = 0.025(1)Å^2
(350 K) a =8.36354(6)Å, b = 16.48736(12)Å, c = 6.71642(6)Å, $\alpha = \gamma = 90º$, β = 105.536(1)º, s.g. $P2_1/a$. B_{Cl} = 0.049(2)Å^2, $B_{C,N,H}$ = 0.066(1)Å^2

Table S3. Final refined positional coordinates from synchrotron powder X Ray diffraction patterns of Edimim[Br] at 100 and 350 K. Label of the atoms as in Figure 3.

	Edimim[Br] at 100 K			Edimim[Br] at 350 K		
Atom	*x/a*	*y/b*	*z/c*	*x/a*	*y/b*	*z/c*
Br1	0.73898(5)	0.62816(7)	0.36726(18)	0.72201(5)	0.62885(8)	0.3713(2)
N1	0.92224(5)	0.3465(3)	-0.0081(9)	0.92945(5)	0.3561(4)	-0.0167(10)
N3	0.77007(5)	0.4486(4)	-0.0718(9)	0.77312(5)	0.4561(4)	-0.0760(11)
C1'	1.00380(5)	0.2712(4)	-0.0171(9)	1.01815(5)	0.2845(4)	-0.0389(11)
C1"	0.65521(5)	0.5056(3)	-0.1816(10)	0.64938(5)	0.5108(4)	-0.1847(11)
C1"'	0.75794(5)	0.3507(3)	-0.3587(10)	0.76548(5)	0.3616(4)	-0.3587(10)
C2	0.81050(5)	0.3807(5)	-0.1482(9)	0.82275(5)	0.3966(4)	-0.1559(9)
C2'	1.03289(5)	0.2247(3)	0.1741(9)	1.04771(5)	0.2336(5)	0.1369(12)
C4	0.85397(5)	0.4553(4)	0.1242(11)	0.84475(5)	0.4593(4)	0.1235(12)
C5	0.94490(5)	0.3925(4)	0.1584(10)	0.94130(5)	0.3959(4)	0.1559(9)
H1A"	0.6646	0.5042	-0.3214	0.6614	0.5166	-0.3192
H1B"	0.5379	0.4948	-0.1678	0.5404	0.4920	-0.1882
H1C"	0.6875	0.5559	-0.1278	0.6661	0.5607	-0.1179
H1A"'	0.7519	0.2955	-0.3554	0.7894	0.3064	-0.3536
H1B"'	0.6465	0.3712	-0.4165	0.6488	0.3694	-0.4087
H1C"'	0.8416	0.3662	-0.4387	0.8228	0.3870	-0.4462
H2A'	1.0952	0.1784	0.1548	1.1447	0.2029	0.1409
H2B'	0.9233	0.2114	0.2091	0.9548	0.1994	0.1272
H2C'	1.0989	0.2546	0.2806	1.0642	0.2645	0.2570
H1A'	1.1146	0.2788	-0.0589	1.1229	0.2985	-0.0665
H1B'	0.9317	0.2411	-0.1207	0.9557	0.2551	-0.1535
H4	0.8482	0.4962	0.2120	0.8322	0.4971	0.2162
H5	1.0147	0.3803	0.2807	1.0077	0.3815	0.2803

Full occupancies for all atoms.
(100 K) a=7.84687(6)Å, b=17.33455(12)Å, c =6.75091(5)Å, $\alpha = \gamma = 90^{o}$, β=100.290(1)º, s.g. P 2_1/a. B_{Br} = 0.034(1)Å^2, $B_{C,N,H}$ = 0.007(1)Å^2
(350 K) a=8.35614(5)Å, b=17.03647(11)Å, c=6.87656(5) Å, $\alpha = \gamma = 90^{o}$, β=104.287(1)º, s.g. P 2_1/a. B_{Br} = 0.080(2)Å^2, $B_{C,N,H}$ = 0.040(1)Å^2

Table S4. Overlay of refined crystal structures using bond/angle/plane restraints (red) and without using any restraints (black). Figures of merit for both refinements are shown.

EdimimCl 100K	**EdimimCl 350K**
	
r.m.s.d between atomic positions = 0.0267Å Rietveld R_{wp} with restraints = 0.089 Rietveld R_{wp} without restraints =0.088 Imidazole ring plane σ (with restraints)[a] = 0.018 Imidazole ring plane σ (without restraints)[a] = 0.024	r.m.s.d between atomic positions = 0.0322Å Rietveld R_{wp} with restraints = 0.080 Rietveld R_{wp} without restraints = 0.079 Imidazole ring plane σ (with restraints)[a] = 0.010 Imidazole ring plane σ (without restraints)[a] = 0.014
EdimimBr 100K	**EdimimBr 350K**
	
r.m.s.d between atomic positions = 0.0160Å Rietveld R_{wp} with restraints = 0.086 Rietveld R_{wp} without restraints = 0.086 Imidazole ring plane σ (with restraints)[a] = 0.015 Imidazole ring plane σ (without restraints)[a] =0.024	r.m.s.d between atomic positions = 0.0511Å Rietveld R_{wp} with restraints = 0.080 Rietveld R_{wp} without restraints = 0.078 Imidazole ring plane σ (with restraints)[a] = 0.003 Imidazole ring plane σ (without restraints)[a] = 0.007

[a] ring plane *σ = Sqrt(Sum(j=1:N)(D(j)**2/(N-3))* where *D* is the deviation of each atom *j* from the least-squares plane (calculated from N atoms, in this case N=5 for the imidazol ring)

Table S5. Imidazolium bond distances of Edimim[Cl] and Edimim[Br] at 100 and 350 K obtained from Rietveld refinements of synchrotron powder X-ray diffraction.

	Edimim[Cl] 100 K		Edimim[Br]	
	100 K	350 K	100 K	350 K
Imidazolium bond distance ()				
C1'''-C2	1.521(9)	1.509(8)	1.500(9)	1.483(9)
C2-N3	1.333(9)	1.288(8)	1.346(10)	1.270(9)
N3-C1''	1.497(7)	1.459(7)	1.449(7)	1.454(8)
N3-C4	1.412(9)	1.389(9)	1.374(9)	1.356(11)
C4-C5	1.375(8)	1.349(7)	1.300(8)	1.334(8)
C5-N1	1.397(9)	1.363(8)	1.364(9)	1.349(9)
N1-C2	1.362(8)	1.368(7)	1.311(8)	1.329(8)
N1-C1'	1.512(8)	1.478(7)	1.460(8)	1.455(8)
C1'-C2'	1.567(9)	1.552(9)	1.504(9)	1.458(11)
N1···C1'··· C2' Angle (º)	108.4(4)	105.3(4)	116.4(5)	113.5(6)

Table S6. Variable-temperature lattice parameter data as determined using synchrotron powder X-ray diffraction upon warming from 100 K to 350 K for Edimim[Cl].

Edimim[Cl]					
T (K)	*a* (Å)	*b* (Å)	*c* (Å)	*β* (°)	*V* (Å)^3
100.00	7.9913(1)	16.457(1)	6.6845(1)	104.04(1)	852.82
107.00	7.9970(2)	16.454(1)	6.6851(1)	104.09(1)	853.21
111.00	8.0016(1)	16.453(1)	6.6858(1)	104.13(1)	853.56
116.00	8.0065(1)	16.452(2)	6.6866(2)	104.16(1)	853.99
120.00	8.0117(2)	16.452(2)	6.6875(1)	104.20(1)	854.54
125.00	8.0168(1)	16.452(1)	6.6883(2)	104.24(1)	855.02
129.00	8.0221(1)	16.451(3)	6.6891(1)	104.28(1)	855.50
134.00	8.0272(3)	16.450(1)	6.6898(1)	104.32(1)	855.94
138.00	8.0331(1)	16.451(1)	6.6906(1)	104.35(1)	856.59
143.00	8.0383(1)	16.451(1)	6.6912(2)	104.38(1)	857.09
147.00	8.0438(3)	16.450(3)	6.6921(1)	104.42(1)	857.61
152.00	8.0489(1)	16.450(1)	6.6929(1)	104.45(1)	858.11
156.00	8.0545(3)	16.450(1)	6.6934(2)	104.49(1)	858.67
161.00	8.0605(1)	16.450(1)	6.6941(1)	104.52(1)	859.26
165.00	8.0665(1)	16.450(1)	6.6949(1)	104.55(1)	859.86
170.00	8.0714(2)	16.450(1)	6.6954(1)	104.58(1)	860.37
174.00	8.0774(1)	16.451(1)	6.6964(1)	104.61(1)	861.06
179.00	8.0833(1)	16.452(2)	6.6971(2)	104.64(1)	861.70
183.00	8.0890(2)	16.452(1)	6.6977(2)	104.67(1)	862.25
188.00	8.0947(1)	16.452(2)	6.6986(1)	104.70(1)	862.88
192.00	8.1009(1)	16.453(1)	6.6991(1)	104.73(1)	863.53
197.00	8.1073(2)	16.453(1)	6.6994(2)	104.76(1)	864.13
201.00	8.1133(1)	16.454(2)	6.7000(1)	104.79(1)	864.80
206.00	8.1188(1)	16.454(1)	6.7003(1)	104.81(1)	865.33
210.00	8.1259(1)	16.455(1)	6.7012(2)	104.84(1)	866.15
215.00	8.1322(3)	16.456(1)	6.7017(1)	104.86(1)	866.84
219.00	8.1383(1)	16.456(1)	6.7021(1)	104.88(1)	867.46
224.00	8.1448(2)	16.457(2)	6.7027(2)	104.91(1)	868.20
228.00	8.1513(2)	16.458(1)	6.7033(1)	104.94(1)	868.91
232.00	8.1575(1)	16.459(1)	6.7038(3)	104.96(1)	869.58
237.00	8.1635(1)	16.460(1)	6.7042(2)	104.98(1)	870.20
241.00	8.1703(1)	16.460(2)	6.7049(1)	105.01(1)	870.95
246.00	8.1772(1)	16.461(1)	6.7054(1)	105.03(1)	871.70
250.00	8.1838(1)	16.462(1)	6.7059(1)	105.05(1)	872.43
255.00	8.1911(2)	16.463(1)	6.7065(1)	105.08(1)	873.24
259.00	8.1979(1)	16.463(1)	6.7069(1)	105.10(1)	873.95
264.00	8.2046(2)	16.464(1)	6.7074(1)	105.12(1)	874.69
268.00	8.2117(1)	16.465(1)	6.7079(1)	105.14(1)	875.46
273.00	8.2190(1)	16.466(1)	6.7085(1)	105.17(1)	876.25
277.00	8.2264(2)	16.466(2)	6.7089(2)	105.19(1)	877.03
282.00	8.2337(1)	16.467(1)	6.7094(2)	105.21(1)	877.80

Table S6. (continue).

Edimim[Cl]					
T (K)	*a* (Å)	*b* (Å)	*c* (Å)	*β* (º)	*V* (Å)^3
286.00	8.2411(1)	16.467(1)	6.7098(1)	105.23(1)	878.58
291.00	8.2485(2)	16.468(1)	6.7101(2)	105.25(1)	879.37
295.00	8.2566(1)	16.469(2)	6.7106(1)	105.28(1)	880.26
300.00	8.2643(1)	16.470(1)	6.7109(1)	105.30(1)	881.07
304.00	8.2722(1)	16.471(2)	6.7114(1)	105.32(1)	881.93
309.00	8.2802(3)	16.471(1)	6.7120(1)	105.34(1)	882.78
313.00	8.2887(1)	16.472(1)	6.7126(2)	105.36(1)	883.72
317.00	8.2967(1)	16.472(1)	6.7132(2)	105.38(1)	884.61
322.00	8.3051(2)	16.473(2)	6.7136(1)	105.41(1)	885.48
326.00	8.3141(1)	16.474(1)	6.7141(1)	105.43(1)	886.44
331.00	8.3231(2)	16.475(1)	6.7146(1)	105.46(1)	887.40
335.00	8.3320(1)	16.476(1)	6.7148(1)	105.48(1)	888.34
340.00	8.3413(1)	16.476(1)	6.7151(1)	105.50(1)	889.27
344.00	8.3507(1)	16.477(2)	6.7155(1)	105.53(1)	890.27
350.00	8.3635(2)	16.479(1)	6.7164(1)	105.54(1)	891.85

Table S7. Variable-temperature lattice parameter data as determined using synchrotron powder X-ray diffraction upon warming from 100 K to 350 K for Edimim[Br].

Edimim[Br]					
T (K)	*a* (Å)	*b* (Å)	*c* (Å)	*β* (°)	*V* (Å)^3
100.00	7.8460(1)	17.335(1)	6.7508(1)	100.29(1)	903.39
109.00	7.8588(2)	17.317(1)	6.7571(1)	100.44(1)	904.34
114.00	7.8669(1)	17.305(1)	6.7609(1)	100.54(1)	904.86
119.00	7.8751(1)	17.293(1)	6.7646(1)	100.65(1)	905.37
123.00	7.8835(2)	17.281(2)	6.7682(2)	100.75(1)	905.87
128.00	7.8921(1)	17.269(1)	6.7720(1)	100.86(1)	906.43
132.00	7.9014(1)	17.257(1)	6.7763(1)	100.97(1)	907.08
137.00	7.9103(1)	17.245(2)	6.7802(2)	101.08(1)	907.66
141.00	7.9193(1)	17.234(1)	6.7837(1)	101.18(1)	908.25
146.00	7.9287(2)	17.222(1)	6.7876(1)	101.29(1)	908.87
150.00	7.9378(1)	17.210(1)	6.7913(1)	101.40(1)	909.49
155.00	7.9471(1)	17.199(1)	6.7949(2)	101.50(1)	910.12
159.00	7.9559(1)	17.190(1)	6.7984(1)	101.60(1)	910.80
164.00	7.9643(2)	17.181(1)	6.8015(1)	101.69(1)	911.38
168.00	7.9731(1)	17.172(2)	6.8048(1)	101.79(1)	912.03
173.00	7.9819(1)	17.164(3)	6.8078(2)	101.89(1)	912.65
177.00	7.9907(3)	17.155(1)	6.8107(1)	101.98(1)	913.28
182.00	7.9999(1)	17.147(1)	6.8137(1)	102.07(1)	914.00
186.00	8.0090(1)	17.138(1)	6.8166(1)	102.17(1)	914.61
190.00	8.0179(1)	17.131(2)	6.8201(2)	102.26(1)	915.42
195.00	8.0268(1)	17.125(1)	6.8239(1)	102.34(1)	916.35
199.00	8.0362(1)	17.119(1)	6.8268(1)	102.42(1)	917.19
204.00	8.0449(1)	17.113(1)	6.8293(1)	102.50(1)	917.91
209.00	8.0535(2)	17.107(1)	6.8315(1)	102.58(1)	918.56
213.00	8.0621(2)	17.101(1)	6.8335(1)	102.66(1)	919.24
217.00	8.0709(1)	17.096(1)	6.8356(2)	102.73(1)	920.00
222.00	8.0794(1)	17.091(1)	6.8378(1)	102.80(1)	920.75
227.00	8.0881(1)	17.087(1)	6.8401(1)	102.87(1)	921.56
231.00	8.0957(1)	17.083(21)	6.8417(1)	102.94(1)	922.20
235.00	8.1042(1)	17.080(1)	6.8437(2)	103.00(1)	923.02
240.00	8.1128(1)	17.077(1)	6.8457(1)	103.06(1)	923.89
244.00	8.1216(2)	17.074(1)	6.8476(1)	103.12(1)	924.74
249.00	8.1300(1)	17.070(1)	6.8492(1)	103.18(1)	925.49
253.00	8.1382(1)	17.067(1)	6.8507(3)	103.24(1)	926.22
258.00	8.1468(1)	17.065(1)	6.8526(2)	103.30(1)	927.14
262.00	8.1556(1)	17.063(2)	6.8542(1)	103.35(1)	928.01
267.00	8.1644(2)	17.060(1)	6.8557(1)	103.40(1)	928.91
271.00	8.1731(1)	17.058(1)	6.8571(1)	103.45(1)	929.76
276.00	8.1818(1)	17.055(1)	6.8584(1)	103.51(1)	930.58
280.00	8.1906(1)	17.053(2)	6.8597(1)	103.56(1)	931.42
285.00	8.1996(2)	17.051(1)	6.8612(1)	103.61(1)	932.34
289.00	8.2089(1)	17.050(1)	6.8626(2)	103.66(1)	933.34

Table S7. (continue)

Edimim[Br]					
T (K)	*a* (Å)	*b* (Å)	*c* (Å)	*β* (°)	*V* (Å)^3
294.00	8.2180(1)	17.048(1)	6.8636(1)	103.70(1)	934.23
298.00	8.2269(1)	17.047(1)	6.8647(1)	103.75(1)	935.12
303.00	8.2361(1)	17.045(2)	6.8657(1)	103.80(1)	936.04
321.00	8.2746(1)	17.040(1)	6.8709(1)	103.97(1)	940.12
325.00	8.2845(1)	17.039(1)	6.8717(1)	104.02(1)	941.15
329.00	8.2944(1)	17.039(2)	6.8724(1)	104.06(1)	942.17
334.00	8.3042(2)	17.037(1)	6.8729(2)	104.10(1)	943.11
338.00	8.3140(2)	17.036(1)	6.8737(1)	104.14(1)	944.10
343.00	8.3237(1)	17.035(1)	6.8743(2)	104.17(1)	945.07
347.00	8.3341(1)	17.036(1)	6.8752(1)	104.21(1)	946.25
350.00	8.3565(1)	17.036(1)	6.8766(1)	104.29(1)	948.70

Table S8. The thermal expansion coefficients (α) and the directions of the thermal expansion tensors of Edimim[Cl] and Edimim[Br]. These values were derived from a linear fitting (continuous lines of Fig. 2) using orthogonal lattice parameter evolution of synchrotron powder X-ray diffraction data.

Compound	Edimim[Cl]	Edimim[Br]
α X1/MK^{-1}	-12.8(6)	-40(2)
direction	(0.37, 0, 0.92)	(0.52, 0, 0.85)
α X2/MK^{-1}	7.0(5)	-64(4)
direction	(0, 1, 0)	(0, 1, 0)
α X3/MK^{-1}	187(2)	301(3)
direction	(-0.95, 0, 0.30)	(-0.81, 0, 0.57)
α V/MK^{-1}	184(3)	197(3)

Table S9. Most Relevant Interatomic Distances in the crystal structure of (a) Edimim[Cl] and (b) Edimim[Br] at 100 and 350 K obtained from Rietveld refinements of synchrotron powder X-ray diffraction.

(a)

	Edimim[Cl] 100 K			Edimim[Cl] 350 K		
	length (Å)		angle (º)	length (Å)		angle (º)
C-H···Cl (probable hydrogen bonds)						
	C···Cl	*H···Cl*	*C-H···Cl*	*C···Cl*	*H···Cl*	*C-H···Cl*
C4-H4···Cl	3.412(7)	2.52	161	3.474(6)	2.59	158
C5-H5···Cl	3.516(6)	2.59	174	3.552(5)	2.63	170
C1'-H1A'···Cl	3.653(6)	2.81	145	3.725(6)	2.88	159
C1'-H1B'···Cl	3.587(6)	2.64	166	3.645(6)	2.73	159
C2'-H2C'···Cl	3.833(6)	2.89	169	3.884(6)	2.98	158
C1''-H1A''···Cl	3.719(6)	2.77	170	3.667(6)	2.75	159
C1''-H1B''···Cl	3.659(5)	2.73	163	3.725(5)	2.79	166
C1'''-H1A'''···Cl	3.796(7)	3.09	131			
C1'''-H1B'''···Cl	3.764(5)	2.91	150			
[Edimim]$^{+}$··· [Edimim]$^{+}$ (probable)						
Atom···Atom	3.394(7)			3.449(7)		
Centroid···Centroid	3.594(4)			3.603(3)		
[Cl]$^{-}$··· [Cl]$^{-}$						
a	7.991(5)			8.364(5)		
b	8.396(2)			8.405(2)		
c	6.685(3)			6.716(3)		

(b)

	Edimim[Br] 100 K			Edimim[Br] 350 K		
	length (Å)		angle (º)	length (Å)		angle (º)
C-H···Cl (probable hydrogen bonds)						
	C···Cl	*H···Cl*	*C-H···Cl*	*C···Cl*	*H···Cl*	*C-H···Cl*
C4-H4···Br	3.608(7)	2.72	160	3.628(7)	2.74	160
C5-H5···Br	3.701(6)	2.79	168	3.762(5)	2.86	162
C1'-H1A'···Br	3.796(6)	3.02	138	3.817(6)	2.99	144
C1'-H1B'···Br	3.709(6)	2.76	167	3.744(7)	2.82	159
C1''-H1A''···Br	3.865(6)	3.13	134	3.827(7)	3.00	146
C1''-H1B''···Br	3.890(3)	3.17	133	3.869(4)	3.04	145
C1'''-H1A'''···Br	3.858(5)	2.90	174	3.968(7)	3.03	167
C1'''-H1B'''···Br	3.907(1)	3.10	142	4.056(2)	3.17	154
[Edimim]$^{+}$··· [Edimim]$^{+}$ (probable)						
Atom···Atom	3.441(7)			3.591(5)		
Centroid···Centroid	3.981(4)			3.772(3)		
[Br]$^{-}$··· [Br]$^{-}$						
a	7.847(1)			8.356(1)		
b	8.846(2)			8.689(2)		
c	6.751(1)			6.877(2)		

Table S10. (a) Crystallographic data and (b) final refined positional coordinates from DFT calculations (0 K).

(a)

	Edimim[Cl] by DFT (0K)	**Edimim[Br] by DFT (0K)**
Molecular formula	C7N2H13Cl	C7N2H13Br
Formula weight	160.64	205.10
Crystal System	Monoclinic	Monoclinic
Space group	P 2_1/a	P 2_1/a
a (Å)	8.217092	8.096684
b (Å)	16.979815	17.877811
c (Å)	6.840729	6.977326
α (º)	90º	90º
β (º)	104.4162 º	102.2165º
γ (º)	90º	90º
Volume (Å^3)	924.3977	987.1042
Z	4	4

(b)

	Edimim[Cl] by DFT (0K)			**Edimim[Br] by DFT (0K)**		
Atom	*x/a*	*y/b*	*z/c*	*x/a*	*y/b*	*z/c*
Cl or Br	0.2171525	0.6324808	0.3654491	0.7336750	0.6250163	0.3626400
N1	0.9300814	0.1430006	0.9981625	0.9236730	0.3466140	0.9909120
N3	0.7654597	0.0390563	0.9308890	0.7742629	0.4498171	0.9235298
C1''	0.6394488	0.9814162	0.8218146	0.6591747	0.5077674	0.8168446
H1A''	0.6813189	0.9549095	0.6953069	0.7056130	0.5275270	0.6880953
H1B''	0.5181793	1.0116834	0.7636092	0.6578687	0.5546738	0.9186993
H1C''	0.6275896	0.9353106	0.9304971	0.5311977	0.4840713	0.7689621
C2	0.8163778	0.1049187	0.8476313	0.8182322	0.3847751	0.8438777
C1'''	0.7561418	0.1283005	0.6308824	0.7586436	0.3625705	0.6339232
H1A'''	0.8338940	0.1757645	0.5929442	0.8180548	0.3101162	0.6015659
H1B'''	0.6237101	0.1481325	0.5982148	0.7907370	0.4068655	0.5373408
H1C'''	0.7620824	0.0769756	0.5334353	0.6196290	0.3555526	0.5996783
C1'	0.0205732	0.2175744	0.9740907	0.0088669	0.2736432	0.9706266
H1A'	0.9398477	0.2506002	0.8480723	0.1299651	0.2869307	0.9292770
H1B'	0.1361216	0.2007107	0.9292677	0.9296979	0.2431448	0.8477001
C2'	0.0584865	0.2679960	0.1658232	0.0340156	0.2261167	0.1574770
H2A'	0.1133846	0.3241510	0.1319046	0.0879277	0.1717454	0.1271728
H2B'	0.1488131	0.2397416	0.2930609	0.9133820	0.2149513	0.2023733
H2C'	0.9432431	0.2818611	0.2147505	0.1217833	0.2521349	0.2823087
C4	0.8492177	0.0349368	0.1353462	0.8541858	0.4532253	0.1216208
H4	0.8277521	0.9857968	0.2296901	0.8371683	0.5012152	0.2129032
C5	0.9521378	0.0998709	0.1775385	0.9478006	0.3888835	0.1635711
H5	0.0398058	0.1178943	0.3184014	0.0305219	0.3709431	0.3003376

Table S11. Reference configuration and cut-off radii of the pseudopotentials used in our study. NLCC for non-linear corrections. Units in Bohr.

Reference		H $1s^1, 2p^0_0, 3d^0, 4f$	C $2s^2, 2p^2_0, 3d^0, 4f$	N $2s^2, 2p^3_0, 3d^0, 4f$	Cl $4s^2, 4p^0_0, 3d^6, 4f$	Br $4s^2, 4p^5_0, 4d^0, 4f$
Core radius	*s*	1.00	1.30	1.35	1.40	1.50
	p	1.25	1.30	1.35	1.40	1.80
	d	1.25	1.30	1.35	1.50	2.50
	f	1.25	1.30	1.35	1.50	1.50
Scalar relativistic		no	no	no	yes	yes
Core corrections		no	yes	yes	yes	yes
Cut-off radii for core corrections		no	1.40	1.30	1.30	1.00

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CIF validation and CCDC deposition numbers

EdimimCl 100K:

```
080_ALERT_2_C Maximum Shift/Error ..........................       0.10
340_ALERT_3_C Low Bond Precision on  C-C Bonds .............     0.0087 Ang.
790_ALERT_4_C Centre of Gravity not Within Unit Cell: Resd.  #          1 Note
              C7 H13 N2
#===============================================================================
128_ALERT_4_G Alternate Setting for Input Space Group  P21/a      P21/c   Note
142_ALERT_4_G su on b - Axis Small or Missing ..............    0.00015 Ang.
201_ALERT_2_G Isotropic non-H Atoms in Main Residue(s) .....         10 Report
210_ALERT_3_G No Anisotropic ADP's Found in CIF ............     Please Check
720_ALERT_4_G Number of Unusual/Non-Standard Labels ........         13 Note
860_ALERT_3_G Number of Least-Squares Restraints ...........         26 Note
#===============================================================================
```

EdimimCl 350K:

```
080_ALERT_2_B Maximum Shift/Error ..........................       0.11
#===============================================================================
340_ALERT_3_C Low Bond Precision on  C-C Bonds .............     0.0080 Ang.
#===============================================================================
128_ALERT_4_G Alternate Setting for Input Space Group  P21/a      P21/c   Note
142_ALERT_4_G su on b - Axis Small or Missing ..............    0.00012 Ang.
143_ALERT_4_G su on c - Axis Small or Missing ..............    0.00006 Ang.
201_ALERT_2_G Isotropic non-H Atoms in Main Residue(s) .....         10 Report
210_ALERT_3_G No Anisotropic ADP's Found in CIF ............     Please Check
720_ALERT_4_G Number of Unusual/Non-Standard Labels ........         13 Note
860_ALERT_3_G Number of Least-Squares Restraints ...........         26 Note
#===============================================================================
```

EdimimBr 100K:

```
080_ALERT_2_C Maximum Shift/Error ..........................       0.10
341_ALERT_3_C Low Bond Precision on  C-C Bonds .............     0.0087 Ang.
#===============================================================================
128_ALERT_4_G Alternate Setting for Input Space Group  P21/a      P21/c   Note
142_ALERT_4_G su on b - Axis Small or Missing ..............    0.00012 Ang.
143_ALERT_4_G su on c - Axis Small or Missing ..............    0.00005 Ang.
201_ALERT_2_G Isotropic non-H Atoms in Main Residue(s) .....         10 Report
210_ALERT_3_G No Anisotropic ADP's Found in CIF ............     Please Check
720_ALERT_4_G Number of Unusual/Non-Standard Labels ........         13 Note
860_ALERT_3_G Number of Least-Squares Restraints ...........         26 Note
#===============================================================================
```

EdimimBr 350K:

```
080_ALERT_2_B Maximum Shift/Error ..........................       0.14
#===============================================================================
341_ALERT_3_C Low Bond Precision on  C-C Bonds .............     0.0093 Ang.
#===============================================================================
128_ALERT_4_G Alternate Setting for Input Space Group  P21/a      P21/c   Note
142_ALERT_4_G su on b - Axis Small or Missing ..............    0.00011 Ang.
143_ALERT_4_G su on c - Axis Small or Missing ..............    0.00005 Ang.
201_ALERT_2_G Isotropic non-H Atoms in Main Residue(s) .....         10 Report
210_ALERT_3_G No Anisotropic ADP's Found in CIF ............     Please Check
720_ALERT_4_G Number of Unusual/Non-Standard Labels ........         13 Note
860_ALERT_3_G Number of Least-Squares Restraints ...........         26 Note
#===============================================================================
```

General comments about the alerts:
There are no level A alerts for any of the compounds. About the Maximum Shift/Error that appears as alert B or C type, it may be slightly high but not much considering a powder diffraction refinement.

The data have been assigned to the following deposition numbers.

CCDC 1053981-1053984

Summary of Data CCDC 1053981

Compound Name:
Formula: C7 H13 N2 1+,Br1 1-
Unit Cell Parameters: a 7.84646(8) b 17.33453(17) c 6.75078(7) P21/a
---

Summary of Data CCDC 1053982

Compound Name:
Formula: C7 H13 N2 1+,Br1 1-
Unit Cell Parameters: a 8.35615(5) b 17.03644(11) c 6.87656(5) P21/a
---

Summary of Data CCDC 1053983

Compound Name:
Formula: C7 H13 N2 1+,Cl1 1-
Unit Cell Parameters: a 7.99132(6) b 16.45676(13) c 6.68451(6) P21/a
---

Summary of Data CCDC 1053984

Compound Name:
Formula: C7 H13 N2 1+,Cl1 1-
Unit Cell Parameters: a 8.36352(5) b 16.48723(11) c 6.71641(5) P21/a
---