Electronic Supporting Information

Structure and cation orientation in the perovskite photovoltaic methylammonium lead iodide between 100 and 352 K.

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S1-4. Structure Refinements and Results

Reference numbers refer to main text

S1 Orthorhombic Phase at 100 K.

Structure refinement.

The previous descriptions for the structures for methylammonium Group IV halides were investigated as possible models for that of $MAPbI_3$. Le Bail extractions on the raw diffraction data yielded similarly good fits in both Pnma and $Pna2_1$ space groups. Therefore, the Pnma model by Swainson[7] for $CH_3ND_3PbBr_3$ was used as the basis for the full structural model refinement. Atomic positions were taken from this work and soft constraints added for just the C-N (1.460(1) Å) and C-H and N-H bond lengths (1.10(5) and 1.00(5) respectively) – rather than the rigid body model employed by Swainson.[7] Initial cycles of refinement included the full profile parameters and atomic position and atomic displacement parameters (ADPs) for lead and iodine. Latter cycles of refinement included all atomic coordinates and ADPs including anisotropic ADPs for iodine and hydrogen atoms in order to model the expected significant anisotropy for these species. A model was also constructed and refined in the $Pna2_1$ space group but did not lead to significant improvement of the fits. Final cycles of the Pnma refinement converged smoothly to give the data summarized in Table S1.1 and the final fit to profile is shown in Figure S1.1.

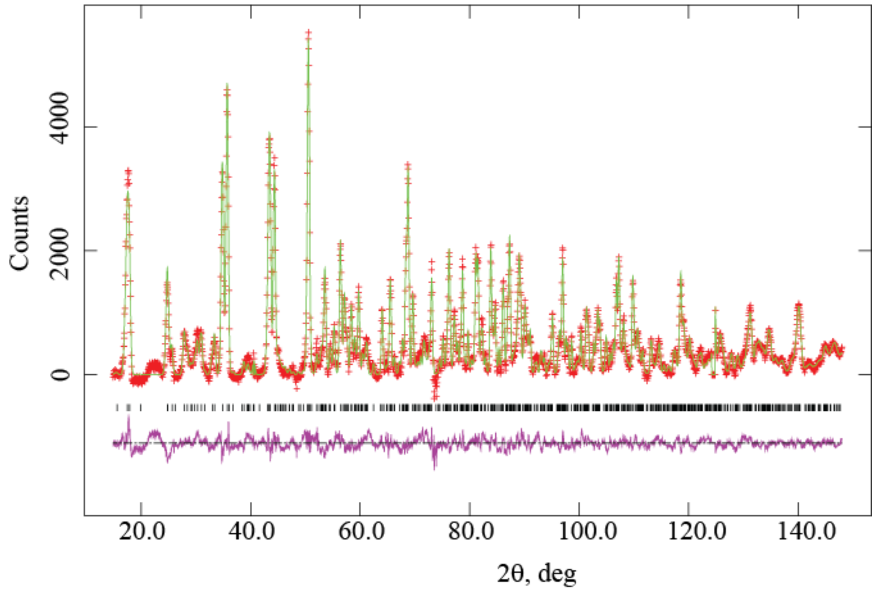

Figure S1.1 Profile fit achieved to the NPD data (background subtracted) from $MAPbI_3$ at 100K. Red crosses mark observed intensities, upper green line the calculated profile and lower purple line the difference. Tick marks show reflection positions.

Table S1.1 Refined structural model for $MAPbI_3$ in the orthorhombic phase, space group Pnma, at 100 K. a = 8.86574(30) Å, b = 12.6293(4) Å, c = 8.57689(31) Å.

Atom	x	y	z	U_i/U_e*100 [$Å^2$] $^{(a)}$	Site	Mult
Pb1	0.500000	0.000000	0.000000	0.77(9)	-1	4
I1	0.4842(7)	0.250000	-0.0562(5)	0.91(14)	M(010)	4
I2	0.1886(4)	0.0147(4)	0.1844(4)	1.41(12)	1	8
N	0.9421(4)	0.750000	0.0297(4)	2.36(12)	M(010)	4
C	0.9372(17)	0.250000	0.0575(5)	2.52(16)	M(010)	4
CH1	0.9372(17)	0.250000	0.1874(6)	5.14*	M(010)	4
CH2	0.8661(11)	0.1701(5)	0.0290(14)	7.50*	1	8
NH1	0.1275(11)	0.1891(6)	-0.0085(15)	8.61*	1	8
NH2	0.9543(20)	0.750000	0.1459(5)	6.36*	M(010)	4

* U_e values calculated from anisotropic values modelled for hydrogen atoms

Final profile fit parameters R_P=0.86%, R_{WP} = 0.69 %, χ^2 = 12.6 R_F2 = 7.49. (Note that R values for hydrogen containing samples are artificially low due to the low residuals in fitting high intensity background points)

Table S1.2 Derived bond lengths and angles of interest for $MAPbI_3$ in the orthorhombic phase, space group Pnma, at 100 K.

Bond / Å	Bond length (esd)	Bond Angle	Bond Angle / degrees (esd)
Pb-I1 x2	3.1970(7)	Pb-I1-Pb	161.94(16)
Pb-I2 x2	3.1874(33)	Pb-I2-Pb	150.75(12)
Pb-I2 x2	3.1868(32)		
C-N	1.460(3)*		
C-CH1	1.129(4) *		
C-CH2	1.131(3) *		
N-NH2	1.002(3) *		
N-NH2	1.002(3) *		
NH….I1	2.613(7)		
NH….I2	2.808(9)		

*** constrained – see text**

S2. Tetragonal phase at 180 K.

Structure refinement.

No full structural model, including hydrogen atom positions or detailed orientation information for the C-N axis, for a tetragonal phase of methylammonium Group IV halides has been published. Swainson[7] was unable to determine the position of the partially deuterated $[CH_3ND_3]^+$ cation in $CH_3ND_3PbBr_3$ from high quality neutron powder diffraction data – though this work reports a preference for the a structure description in I4/mcm and disordering of the MA in the <001> or <110> planes. (Such a disordered cation would be hard to model due to the close superposition of hydrogenous CH_3 and deuterated ND_3 with the opposing scattering lengths of H and D). Initially, both the I4/mcm and I4cm descriptions of Swainson[7] and Stoumpos[6] were investigated with just the reported / inferred carbon and nitrogen positions. Both models gave very poor fits to the experiment data with just Pb, I, C and N positions (see Figure S2.1), confirming the high sensitivity of the powder neutron diffraction data to the hydrogen positions. Difference Fourier maps were calculated for both space groups and hydrogen positions (negative peaks around 1 Å from C/N) were rapidly identified for I4/mcm but not for I4cm and only the former structure model was developed further. The C and N positions were assigned to (x,½-x, z) sites with x~0.45 and z~0.25 either side of, but close to, the centre of the distorted perovskite cube and the soft constraint C-N = 1.460(1) Å introduced. This model, with a ¼ site occupation, allows the C-N unit to adopt four positions directed near to the four cube faces in the *xy* plane. A new difference Fourier map was calculated with this model and hydrogen was assigned (with appropriate site fractional occupancies) to two negative peaks identified ~1 Å from C or N and soft constraints introduced with C/N-H at 1.05(1)Å. This model is a relatively simple representation of the $[CH_3NH_3]^+$ cation using just two hydrogen positions, note that it averages the CH_3 and NH_3 ends of the cation and thereby the C/N-H distances (hence the use of the C/N at 1.05 Å constraint) and formally produces an eclipsed conformation for the molecular cation. However, the simplicity of this model also allowed introduction of anisotropic ADPs for the hydrogen atoms which models the likely (near) free rotation of the ends of the molecular cation around the C-N bond. Full refinement of atom positions and ADPs for all atoms (anisotropic for iodine and hydrogen) rapidly converged to give a very good fit to the experimental diffraction profile (Figure S2.2). The final structural model developed is summarised in Table S2.1 and derived bond lengths and angles given in Table S2.2. Figure S2.3 represents possible orientations of the methylammonium cation in adjacent sites.

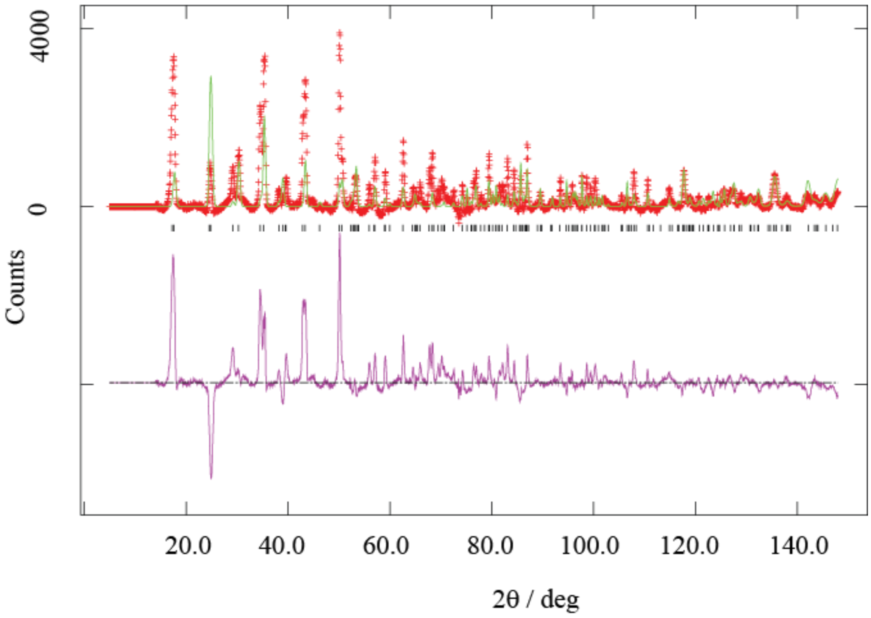

Figure S2.1. Profile fit achieved to the NPD data (background subtracted) from $MAPbI_3$ at 180K in the space group I4/mcm with just Pb, I, C and N positions. Red crosses mark observed intensities, upper green line the calculated profile and lower purple line the difference. Tick marks show reflection positions.

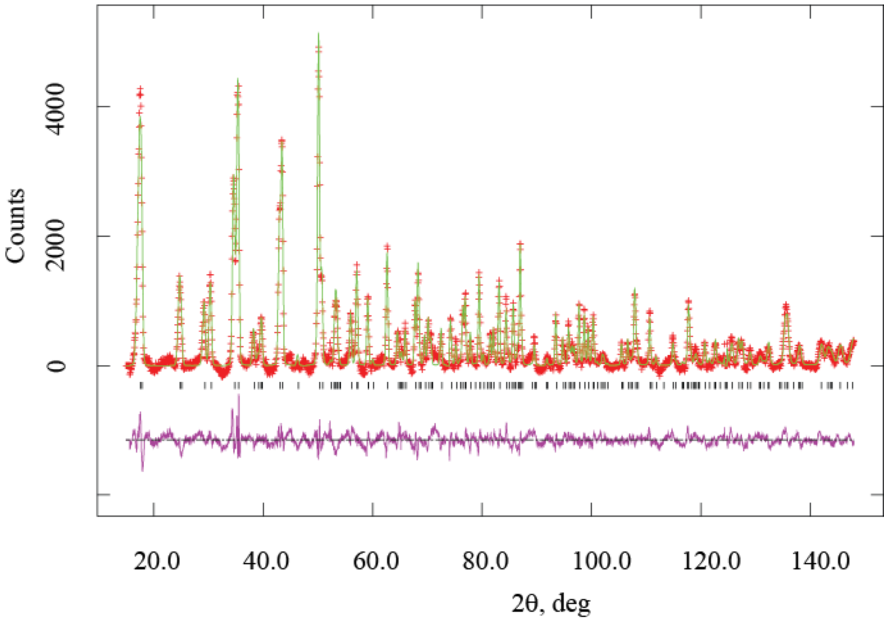

Figure S2.2. Final profile fit achieved to the NPD data (background subtracted) from $MAPbI_3$ at 180K. Red crosses mark observed intensities, upper green line the calculated profile and lower purple line the difference. Tick marks show reflection positions.

Final Crystallographic Model

Table S2.1. Refined structure model for $MAPbI_3$ in the tetragonal phase, space group I4/mcm, at 180K. a = 8.80625(28) Å, c = 12.7127(5) Å

Atom	x	y	z	Ui/Ue*100 [Å^2]$^{(a)}$	Site	Mult	Fractn
PB1	0.500000	0.500000	0.500000	2.16(13)	4/M(001)	4	1.0
I2	0.20122(34)	0.29878(34)	0.500000	4.68*	MM2(+-0)	8	1.0
I3	0.500000	0.500000	0.750000	4.03*	422(001)	4	1.0
N4	0.4128(8)	0.0872(8)	0.2833(10)	5.3(4)	M(110)	16	0.25
H5	-0.0381(41)	0.3531(14)	0.2203(18)	25.79*	1	32	0.50
C6	0.5273(7)	-0.0273(7)	0.2588(13)	7.2(4)	M(110)	16	0.25
H7	0.4297(14)	0.0703(14)	0.3336(16)	15.54*	M(110)	16	0.50

*U_e values calculated from anisotropic values modelled for hydrogen and iodine atoms
Final profile fit parameters R_P=0.90%, R_{wP} = 0.69 %, χ^2 = 13.5 R_F2 = 9.83

Table S2.2 Derived bond lengths and angles of interest for $MAPbI_3$ in the tetragonal phase, space group I4/mcm at 180 K.

Bond	**Bond length (esd) / Å**	**Bond Angle**	**Bond Angle / degrees**
Pb-I2 x4	3.1722(8)	Pb-I2-Pb x 2	157.92(15)
Pb-I3 x2	3.174(33)	Pb-I3-Pb	180
Pb-I2 x2	3.17818(13)		
C6-N4	1.459(3)*		
N4-H5	1.05(4) *		
N4-H7	0.67(3) *		
C6-H5	1.16(2) *		
C6-H7	1.09(3) *		
(C/N)H5….I2	3.184(12)		
(C/N)H7….I2	3.394(16)		

* Constrained – see text

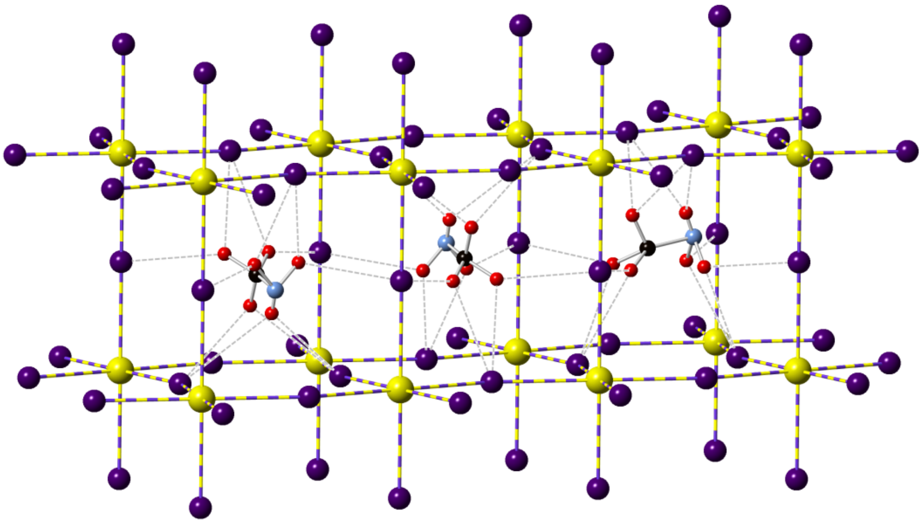

Figure S2.3. Representation of the structures of $MAPbI_3$ in the tetragonal phase showing three adjacent cells. Pb-yellow, I-purple, N-blue, C-black and H-red. The orientation of the methylammonium cation in neighbouring unit cells is shown in three of the four possible orientations. *c*-Axis vertical and *a* or *b* horizontal.

S3 Cubic Phase at 352 K.

Structure refinement

The structure refinement was undertaken in Pm-3m with Pb on (0 0 0) and I on (0.5 0 0). Based on the orientation of the methylammonium cation in both the orthorhombic and tetragonal phases, a model was developed with the C-N bond directed at the square window of the perovskite cube with an atom representing fully disordered C and N situated at (x, 0.5, 0.5), site multiplicity 6, site occupancy 1/3, with x~0.4 producing a C-N distance of ~1.4Å. Refinement of this structural model, employing an anisotropic ADP for iodine, yielded a χ^2 of ~130. Difference Fourier maps were calculated using this model and a hydrogen atom position identified ~1 Å from C/N near (0.3, 0.45, 0.38), site multiplicity 48. Hydrogen was assigned to this site with an occupancy of 1/8 (yielding 6 hydrogen atoms in the unit cell). A full structure refinement using this model and including all coordinates and ADPs (anisotropic for I and H) but no bond length constraints converged to the structure description and refinement parameters given in Table S3.1. Note that because of the high thermal motion in this phase an alternative structural model in which the C-N direction was orientated along <111> was also investigated – refinement of this model using similar hydrogen positions gave a slightly worse χ^2 value (10% higher) and shorter C/N-N/C bond length at 1.31Å – such a structural model, which would also reflect a very freely re-orientating MA cation, cannot be fully ruled out - but seems a poorer description of the structure.

The final profile fit achieved is shown in Figure S3.1. Figure 2 (main text) shows a summary of all possible orientations of the methylammonium cation indicating effectively free rotation of the cation around the cube centre and Figure S3.2 shows one possible orientation of the molecular cation.

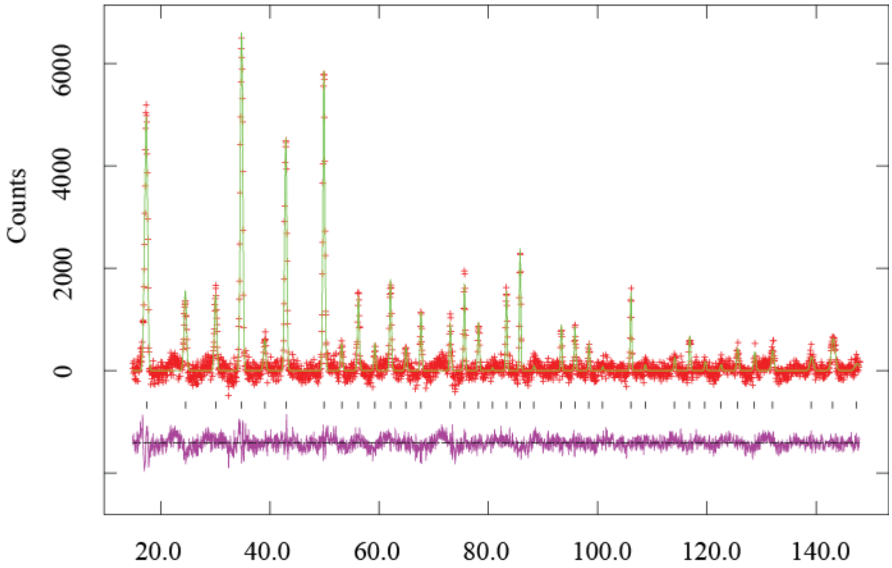

Figure S3.1. Final profile fit achieved to the NPD data (background subtracted) from $MAPbI_3$ at 352K. Red crosses mark observed intensities, upper green line the calculated profile and lower purple line the difference. Tick marks show reflection positions.

Final Crystallographic Model

Table S3.1 (Refined structure of $MAPbI_3$ in the cubic phase, space group Pm-3m, at 352 K, a = 6.31728(27) Å)

Atom	x	y	z	Ui/Ue*100 [$Å^2$]	Site	Mult	Fractn
PB1	0.000000	0.000000	0.000000	4.20	M3M	1	1.0000
I2	0.500000	0.000000	0.000000	12.30*	4/MMM100	3	1.0000
C3	0.393308	0.500000	0.500000	17.75	4MM(100)	6	0.3333
H4	0.305848	0.448981	0.379518	14.74*	1	48	0.1250

*U_e values calculated for anisotropic values modelled for hydrogen and iodine atoms

Final profile fit parameters R_P=1.34%, R_{wP} = 1.06 %, χ^2 = 1.61 R_F2 =13.6%

Table S3.2. Derived bond lengths and angles of interest for $MAPbI_3$ in the cubic phase, space group Pm-3m at 352 K.

Bond	**Bond length (esd) / Å**	**Bond Angle**	**Bond Angle / degrees**
Pb1-I2 x6	3.1586(2)		
		Pb-I2-Pb	180
C/N – C/N	1.348(1)		
(C/N) – H4	0.994(1)		

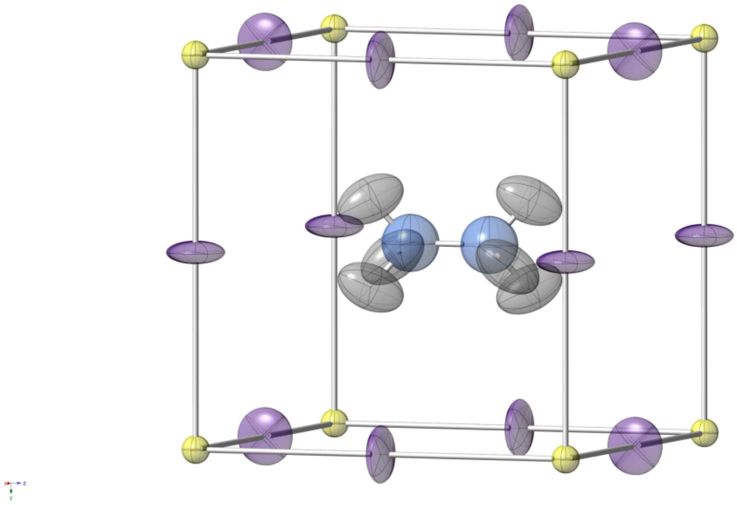

Figure S3.2. Representation of the structures of $MAPbI_3$ in the cubic phase showing one of the possible methylammonium cation orientations. Pb-yellow, I-purple, N-blue, C-black and H-red.

S4 Variable temperature data analysis

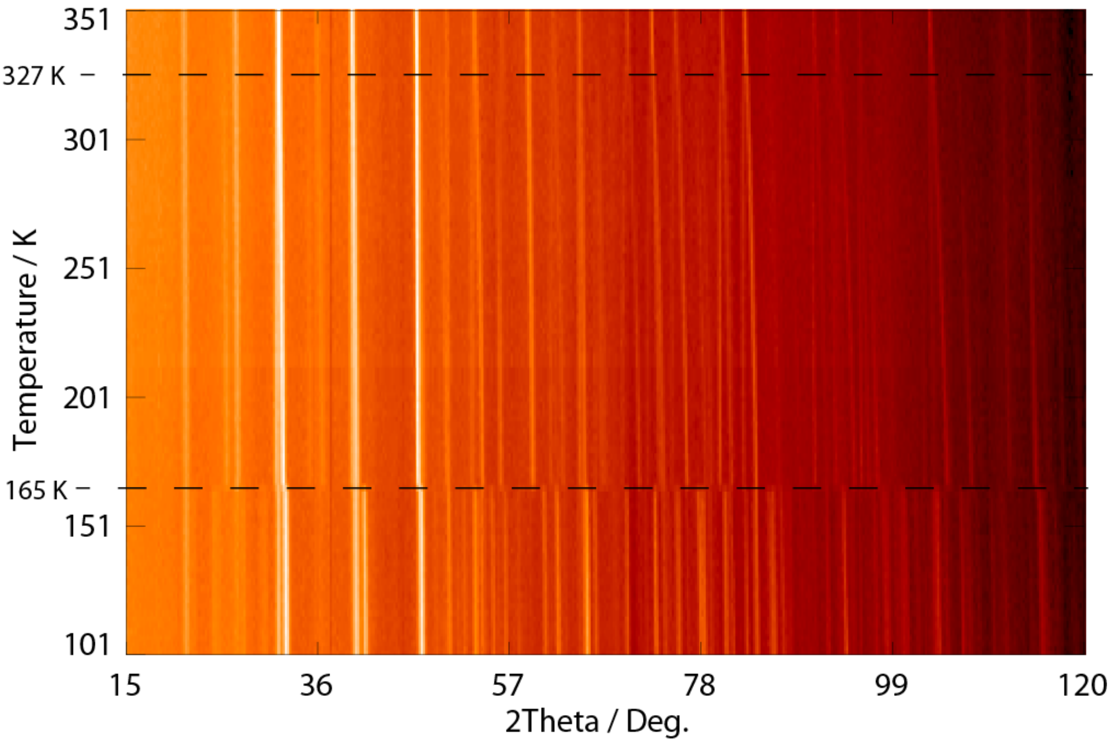

Figure S4.1. Stacked plot of the NPD patterns viewed vertically for the full temperature and diffraction angle range. The transition temperatures at 165 and 327 K are marked. Intensities on the out of page axis are shown on a scale from white (high intensity) to dark red.

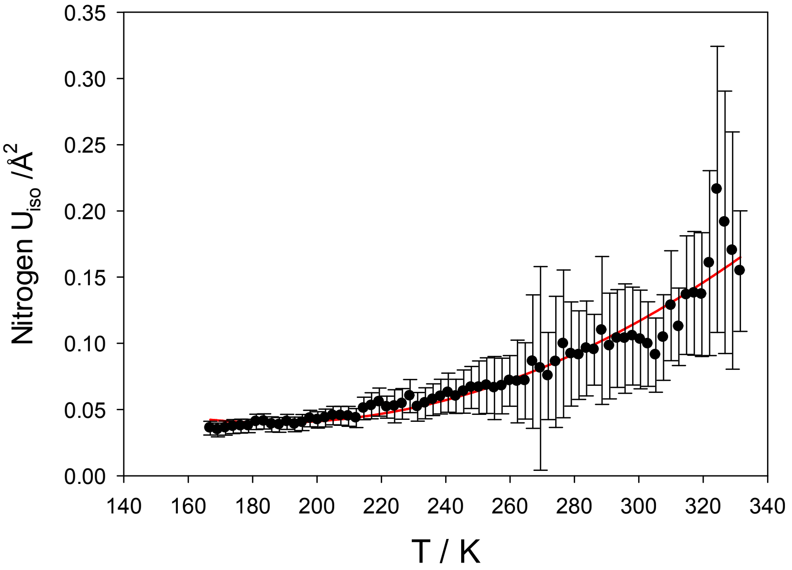

Figure S4.3. Variation of the nitrogen atom U_{iso} over the range of stability of the tetragonal phase showing an increase due to greater thermal motion of the methylammonium cation.