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Role of hydrogen-bonding and its interplay with octahedral tilting in $\text{CH}_3\text{NH}_3\text{PbI}_3$

Jung-Hoon Lee,^a Nicholas C. Bristowe,^b Paul D. Bristowe*^a and Anthony K. Cheetham*^a

First principles calculations on the hybrid perovskite $\text{CH}_3\text{NH}_3\text{PbI}_3$ predict strong hydrogen-bonding which influences the structure and dynamics of the methylammonium cation and reveal its interaction with the tilting of the PbI_6 octahedra. The calculated atomic coordinates are in excellent agreement with neutron diffraction results.

$\text{CH}_3\text{NH}_3(\text{MA})\text{PbI}_3$ is one of the most extensively studied hybrid halide perovskites due to its impressive power conversion efficiency for solar cell applications.¹ In spite of numerous studies on its structural properties,^{2–8} relatively little progress has been made in our understanding on the role of hydrogen-bonding in the orthorhombic phase (*o*-MAPbI₃). In this study we have used density functional theory (DFT) calculations to examine the thermodynamic consequences of hydrogen-bonding and its interplay with the octahedral rotations that are ubiquitous in perovskites. The computed atomic positions, including those of the hydrogen atoms, are compared to a recent powder neutron diffraction study.⁹

The DFT calculations were performed using the generalized gradient approximation (GGA) and projector augmented wave (PAW)¹⁰ pseudopotentials as implemented in the Vienna ab initio Simulation Package (VASP).^{11–13} The effects of spin-orbit coupling and van der Waals (vdW) interactions¹⁴ were included during structural and electronic relaxation. We adopted (i) a $4 \times 3 \times 4$ Monkhorst–Pack *k*-point mesh centered at Γ ,¹⁵ (ii) a 500 eV plane-wave kinetic energy cutoff, and (iii) the tetrahedron method with the Blöchl corrections for the Brillouin zone integrations.¹⁶ We explicitly treated 14 valence electrons for Pb ($5d^{10}6s^26p^2$), 7 for I ($5s^25p^5$), 4 for C ($2s^22p^2$), 5 for N ($2s^22p^3$), and 1 for H ($1s^1$). The ions were relaxed until the forces on them were less than $0.01 \text{ eV } \text{Å}^{-1}$. The experimentally

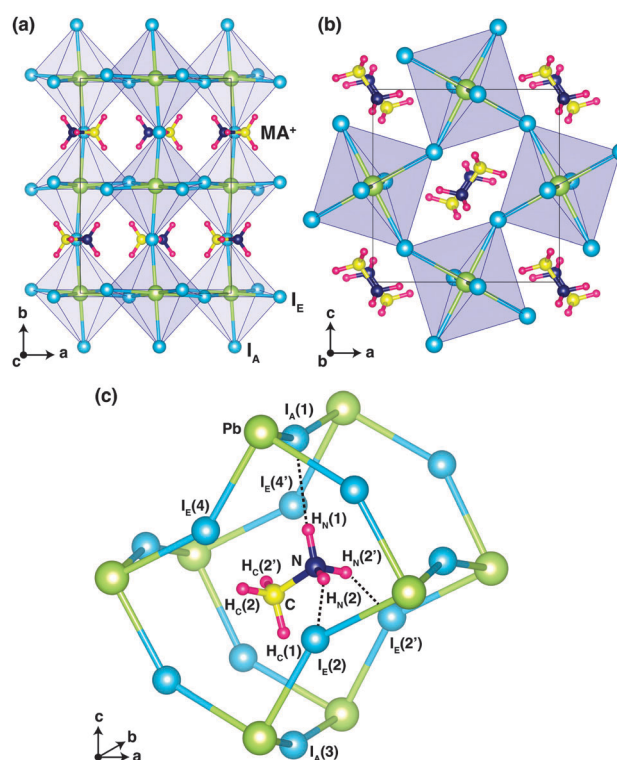


Fig. 1 (a) Optimized crystal structure of *o*-MAPbI₃, viewed in the *a*-*b* and (b) *a*-*c* planes. PbI_6 octahedra are highlighted in purple. (c) Local cage structure of *o*-MAPbI₃ is characterized by hydrogen-bonding between the three H atoms in the NH_3 group and one axial I [$I_A(1)$] atom and two equatorial I [$I_E(2)$ and $I_E(2')$] atoms. Hydrogen-bonding interactions are indicated by dotted lines.

observed ratio of the orthorhombic unit cell vectors² was imposed when we optimized the lattice parameters by calculating the Kohn–Sham (K–S) energy as a function of volume.¹⁷

Fig. 1 shows the optimized crystal structure of *o*-MAPbI₃ with space group *Pnma*. The computed lattice parameters are $a = 8.844 \text{ Å}$, $b = 12.592 \text{ Å}$, and $c = 8.563 \text{ Å}$, in good agreement with the experimental values at 100 K ($a = 8.8362 \text{ Å}$, $b = 12.5804 \text{ Å}$,

^a Department of Materials Science and Metallurgy, University of Cambridge, 27 Charles Babbage Road, Cambridge, CB3 0FS, UK. E-mail: akc30@cam.ac.uk, pdb1000@cam.ac.uk

^b Department of Materials, Imperial College London, Exhibition Road, London, SW7 2AZ, UK



Table 1 Calculated fractional coordinates for *o*-MAPbI₃ compared with experimental values. The H_C(1) and H_C(2) atoms are connected to C while the H_N(1) and H_N(2) atoms are connected to N in the MA cation. ND and XD denote neutron powder diffraction data⁹ and X-ray diffraction data,² respectively

Wyckoff site	This work			Experiment				
	<i>x</i>	<i>y</i>	<i>z</i>	<i>x</i>	<i>y</i>	<i>z</i>		
Pb	4b	0.500	0.000	0.000	ND	0.500	0.000	0.000
I _A (1)	4c	0.476	0.250	0.938	ND	0.484	0.250	0.944
I _E (2)	8d	0.176	0.017	0.172	ND	0.189	0.015	0.184
N	4c	0.953	0.750	0.023	ND	0.942	0.750	0.030
C	4c	0.908	0.250	0.075	ND	0.937	0.250	0.058
H _C (1)	4c	0.941	0.250	0.198	ND	0.937	0.250	0.187
H _C (2)	8d	0.842	0.178	0.048	ND	0.866	0.170	0.029
H _N (1)	8d	0.111	0.183	0.003	ND	0.128	0.189	-0.009
H _N (2)	4c	0.978	0.750	0.142	ND	0.954	0.750	0.146

and $c = 8.5551 \text{ \AA}$ for the X-ray study² and $a = 8.8657 \text{ \AA}$, $b = 12.6293 \text{ \AA}$, and $c = 8.5769 \text{ \AA}$ for the neutron study⁹). Note that the calculated values lie between the experimental ones. The perovskite structure exhibits corner-linked PbI₆ octahedra forming a three-dimensional network. The *Pnma* phase displays a particular pattern of rotations of the octahedra involving either in-phase or out-of-phase rotations around the three I–Pb–I octahedral axes, denoted by $a^-b^+a^-$ in Glazer's notation.¹⁸ Regarding the organic MA ion, the C–N bonds are aligned approximately along the [101] and [10 $\bar{1}$] directions with a head-to-tail configuration as shown in Fig. 1. Our optimized atomic positions for this structure are listed in Table 1, where H atoms that are connected to N atoms are denoted by H_N, and H atoms that are connected to C atoms are denoted by H_C. The subscripts A and E on the iodine atoms refer to axial and equatorial configurations, respectively, as shown in Fig. 1(c). Our optimized atomic positions agree very well with the previous experimental values. In particular, the coordinates of the H atoms are in very good agreement with the recent powder neutron diffraction study.⁹

Fig. 1(c) shows the ground-state configuration of the H atoms in the surrounding inorganic Pb–I cage. The positions of the H atoms conform with the *Pnma* space group. If we assume that hydrogen-bonding is important when $\text{H} \cdots \text{I} < 3 \text{ \AA}$, there are three hydrogen-bonds in the Pb–I cage between H_N(1), H_N(2), and H_N(2') and I_A(1), I_E(2), and I_E(2'), respectively.

These three $\text{H} \cdots \text{I}$ bonds per MA ion are controlled by both the particular inorganic $a^-b^+a^-$ tilt pattern and the organic MA conformation. Among these, the H_N(1) \cdots I_A(1) hydrogen bond is the shortest (2.565 Å) and presumably the strongest. Accordingly, the N–H_N(1) \cdots I_A(1) angle is almost 180° (Table 2). These results are in good agreement with the recent powder neutron diffraction study, as well as the structure of ammonium iodide (NH₄I)¹⁹ where hydrogen-bonding is known to play a key role in structural stabilization.²⁰ Details of the computed bond lengths and bond angles for the principal interactions are given in Table 2 and compared with the experimental neutron diffraction values. The N \cdots I distances are much shorter than those of C \cdots I and also the angle of C–H_C(1) \cdots I_A(3) is smaller than that

Table 2 Calculated H \cdots I, N \cdots I, and C \cdots I bond lengths and N–H \cdots I, C–H \cdots I and Pb–I–Pb bond angles compared with NH₄I and ND data for MAPbI₃

	This work	NH ₄ I ¹⁹	Experiment ⁹
Bond type (Å)			
H _N (1) \cdots I _A (1)	2.565	2.454	2.613
H _N (2) \cdots I _E (2)	2.611		2.808
H _C (1) \cdots I _A (3)	3.137		3.190
H _C (2) \cdots I _E (4)	3.094		3.006
N \cdots I _A (1)	3.606	3.473	3.611
N \cdots I _E (2)	3.566		3.681
C \cdots I _A (3)	4.221		4.298
C \cdots I _E (4)	4.032		4.090
Angle type (°)			
N–H _N (1) \cdots I _A (1)	177	178	174
N–H _N (2) \cdots I _E (2)	152		146
C–H _C (1) \cdots I _A (3)	170		172
C–H _C (2) \cdots I _E (4)	144		148
Pb–I _A (1)–Pb	159		162
Pb–I _E (2)–Pb	145		151

of N–H_N(1) \cdots I_A(1). Accordingly, the hydrogen-bond interactions mainly originate from H atoms on nitrogen.

To understand the strength of the hydrogen-bonding in *o*-MAPbI₃, we have examined the energetics as a function of the H positions. The most stable structure shows that the MA cation adopts a staggered conformation [Fig. 2(b) inset], as expected and in agreement with the neutron results; this is denoted by $\theta = 0^\circ$ in the following calculations in which we rotate the NH₃ and CH₃ groups around the C–N axis for all four MA-ions in the unit cell. We have calculated the Kohn–Sham (K–S) energies as a function of the torsion angle θ , fixing all

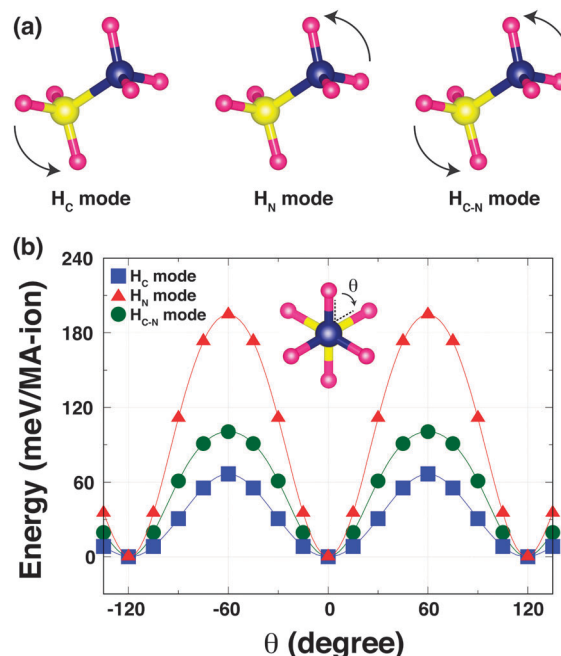


Fig. 2 (a) Schematic view of three MA rotational modes (see text). (b) The computed Kohn–Sham (K–S) energies as a function of the torsion angle θ for the three rotational modes and a staggered conformation (inset) with the torsion angle $\theta = 0^\circ$.



As a way of visualising the hydrogen-bonding in *o*-MAPbI₃, we present in Fig. 4 the non-covalent interaction isosurfaces calculated using the Critic2 code^{26,27} for the ground-state and high-symmetry structures at $\theta = 0^\circ$. The ground-state case in Fig. 4(a) shows non-covalent interaction density located between three H atoms [$H_N(1)$, $H_N(2)$, and $H_N(2')$] and three I atoms [$I_A(1)$, $I_E(2)$, and $I_E(2')$], which is consistent with hydrogen bonding in the energy minimised structure. On the other hand, there is only one non-covalent interaction density contour between $H_N(1)$ and $I_A(1)$ in the high-symmetry structure. The octahedron tilting is clearly coupled to the strength of the hydrogen-bonding. To further quantify this strength we have calculated the hydrogen bond strength index²⁸ from the N–H stretching frequencies of the MA molecule in isolation and in the perovskite. For the $H_N(1) \cdots I_A(1)$ bond, for example, this index is 0.11 in the ground-state structure but only 0.03 in the high-symmetry structure. For the $H_N(2) \cdots I_E(2)$ bond the values are 0.05 and 0.02 respectively. The 11% softening of the N–H stretching frequency in *o*-MAPbI₃ is comparable to the softening of the O–H stretching frequency in ice,²⁹ suggesting similar strengths of hydrogen bonding in both cases.

We have calculated precise positions for the H atoms in *o*-MAPbI₃ and found excellent agreement with a recent powder neutron diffraction study.⁹ We have also explored the role of hydrogen bonding in relation to the behaviour of the MA cations and the tilting of the PbI₆ octahedra. The MA cation adopts a staggered conformation in the optimised structure. It is shown that rotation of the staggered MA cation around its C–N bond is quite hindered, with an activation energy of ~ 102 meV per MA-ion, due to the strong hydrogen-bonding. The strength of the hydrogen-bonding is found to be highly correlated with the octahedral rotations in MAPbI₃, providing an explanation for why the MA-ordering transition is coincident with the tilting phase transition temperature.

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