Influence of the Dimensionality and Organic Cation on Crystal and Electronic Structure of Organometallic Halide Perovskites

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ABSTRACT: Layered perovskites open a plethora of possibilities for tuning organometallic halide perovskite (OMHP) properties via the incorporation of larger organic cations. Promising applications of this increased structural freedom include enhanced chemical stability and tunable exciton binding. Owing to the larger cation, crystal and electronic structures vary with layer stacking, having layered bulk and a monolayer as limiting cases. Using ab initio calculations, here we study the atomic and electronic structures of such a layered material, \((\text{C}_6\text{H}_5\text{C}_2\text{H}_4\text{NH}_3)_2\text{PbI}_4\), which has recently attracted attention as a promising solar cell material. The reduction of layer thickness between the bulk and a monolayer is investigated and compared to that of the benchmark OMHP, \((\text{CH}_3\text{NH}_3)_2\text{PbI}_3\), showing that the bulkier \(\text{C}_6\text{H}_5\text{C}_2\text{H}_4\text{NH}_3\) cations largely preserve the two-dimensional nature of the electronic structure in the layered bulk OMHP.

INTRODUCTION

Organometallic (or hybrid) halide perovskites (OMHP) are intensively studied due to the drastic improvement of \(\text{CH}_3\text{NH}_3\text{PbI}_3\) (MAPbI\(_3\))-based photocells from initially 3.8%\(^1\) to the current record holder of 20.1%.\(^2,3\) However, current OMHPs are sensitive to humidity, oxygen, solvents and other chemicals, UV-light, and operating temperature.\(^4\)

The instability of OMHPs, in particular due to water degradation, can be suppressed by the small hydrophilic organic cations with cations that carry bulky, hydrophobic moieties. A plethora of molecules can be envisioned for this purpose, once one is no longer limited to small molecules. For example, it is possible to fabricate hydrophobic moieties with any desired size and hydrophobic character to shield hydrophilic end groups (such as \(\text{NH}_3^+\)). One possible scenario is to use 2-phenylethane-1-aminium (or 1-phenethylaminium) (PEA) cations as a coating layer of MAPbI\(_3\). Such a coating layer was reported recently to improve the stability toward water relative to pristine MAPbI\(_3\).\(^5,6\)

Herein, we study the atomic and electronic structure of \(\text{PEA}_2\text{PbI}_4\) using first-principles calculations. First, we study 2D monolayer (ML) and quasi-2D \(\text{PEA}_2\text{PbI}_4\) bulk. Next, we compare the obtained atomic and electronic structures of the PEA systems with those of the benchmark OMHP systems, MAPbI\(_3\), especially with regard to the effects of (i) cation exchange accompanied by phase and stoichiometry change and (ii) interlayer interaction change, that is, bulk versus ML structures. This three-way comparison between 3D (MAPbI\(_3\) bulk), quasi-2D with weak interlayer interactions (\(\text{PEA}_2\text{PbI}_4\) bulk), and 2D systems (\(\text{MA}_2\text{PbI}_4\) and \(\text{PEA}_2\text{PbI}_4\) MLs) reveals that, unlike the MA case (band gap increase by 0.74 eV), the electronic structure of \(\text{PEA}_2\text{PbI}_4\) is largely preserved during the (structural) dimensionality change (band gap increase by only 0.07 eV). In the case of PEA, electronic states of the organic cation are located closer to the conduction band edge (CBE), which dominate the conduction band at corner points of the Brillouin zone (BZ). Furthermore, the large effects of spin–orbit coupling (SOC) on the electronic structure that were reported earlier for MAPbI\(_3\) are also found in the related layered perovskite.

COMPUTATIONAL DETAILS

The electronic structure of \(\text{PEA}_2\text{PbI}_4\) is obtained from first-principles calculations based on noncollinear density-functional theory (DFT). We use the Perdew–Burke–Ernzerhof (PBE) generalized gradient approximation\(^7\) as implemented in the QUANTUM ESPRESSO package\(^8\) supplemented by the D2 method\(^9\) in order to account for dispersive interactions. Core electrons are treated by norm-conserving, optimized, designed nonlocal, scalar-relativistic (SRL) pseudopotentials generated with OPIN\(^10,11\). Thus, relativistic effects including SOC are treated for core orbitals, whereas the splitting due to SOC is averaged in the valence region.\(^12\) Wave functions are expanded in a plane-wave basis with an energy cutoff of 680 eV. Total energies and atomic structures are fully relaxed to 3 \(\times 10^{-9}\) eV/cell and until forces acting on ions are below 0.005 eV/Å. For the \(\text{PEA}_2\text{PbI}_4\) bulk, the BZ is sampled by a \(4 \times 4 \times 4\) Monkhorst–Pack k-point grid.\(^13\) From the bulk, the 2D system

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is constructed by introducing 15 Å of vacuum in order to detach periodic images along z and by reducing the k-point grid to $4 \times 4 \times 1$. An analogous procedure was followed for MAPbI$_3$ bulk and ML systems. Alternative phases were computed with similar k-point density. For the evaluation of the projected density of states (PDOS), an increased k-point mesh of $12 \times 12 \times 4$ was used. For the computation of band structures, we also show results including the effect of SOC on the valence levels explicitly, using full-relativistic (FRL) pseudopotentials in noncolinear calculations. Charge-density differences (CDDs) are computed by subtracting the charge of either neutral or charged isolated systems A and B from a combined system, $\varrho_{\text{CDD}} = \varrho_{A+B} - \varrho_A - \varrho_B$.

### RESULTS AND DISCUSSION

#### Crystal Structure. Phase Stability. The structural phase of layered perovskites$^{14-17}$ can be related to the 3D parent material. Because of the large organic cation, horizontal, 2D $BX_2$ perovskite-like layers are separated by a double layer of the $A$-site cation as shown in Figure 1. This means the stacking sequence changes from $\cdots BX_2 - AX \cdots$ in the perovskite crystal to $\cdots AX - BX_2 - AX \cdots$. The coordination number of $A$-site cations is reduced from 12 to 9 in the layered material. In addition, the stoichiometry changes from $AX_B X$ to $AX_B^2$, joining the class of Ruddlesden–Popper phases.$^{18}$ The latter can be envisioned as members of the family of structures with formula unit $A_{n+1}B_nX_{3n+1}$, where $n$ is a positive integer. This structural change is accompanied by a change of the vertical bonding motifs. The ionic bonds of the backbone connecting $B$ and $X$ atoms are decoupled along the stacking direction, with the 2D sheets being connected by the interactions of the $AX$ double layer.

We first identify the thermodynamically most stable phase of PEA OMHPs. Diverse crystal structures have been experimentally reported for a variety of bulk phases of layered perovskites, including those with PEA cations for $X = Cl$.$^{19}$ Br$^-$, and I.$^{14}$ They all have a similar structure in triclinic P1 space group (No. 2), which is our primary concern in the present study. We tested other crystal structures in diverse space groups known from similar compounds including orthorhombic, monoclinic, and other triclinic phases. They all were found to be energetically unfavorable compared to the triclinic P1 phase (the energetic and geometric details of the alternative phases are discussed in detail in the Supporting Information (SI)).

#### Ion Arrangement. The ground-state triclinic structure is shown in Figure 1. The observed symmetry is low, preserving only an inversion symmetry, due to the distortion of the PbI$_6$ cages. We observe a buckling of the PbI$_2$ layers, caused by an off-center movement of Pb ions in the PbI$_6$ octahedrons (Figure 1a). This leads to a bond length alternation in each octahedron along the vertical (polar) axis (which is defined to be the stacking direction hereafter), with a long and a short Pb–I bond length $d_{\text{PbI}}(c)$ differing by 0.4 Å. The off-center movements along $c$ are arranged in a way that Pb atoms are displaced into the same direction along two lattice directions ($b$ and $c$) and in an alternating pattern along the third lattice direction ($a$), resulting in an antiferroelectric ordered structure analogous to an a-type ferromagnet.

Besides this distortion of the PbI$_6$ cage, the main structural variation is introduced via the organic cation. On one hand, the NH$_3$ group can form different H–X bonding motifs: (i) bonds to iodines bridging two Pb ions and (ii) terminal iodines that are only attached to one Pb ion$^{21}$ (see Figure 1a). We find that bonding to two terminal and one bridging iodines is energetically favorable (Figure 1b), in agreement with experimental results.$^{19,20}$ On the other hand, different orientations of the phenyl units are also plausible, with competing effects of maximizing the phenyl–phenyl interactions (via $\pi-\pi$ stacking) and reducing the steric demands of being incorporated into the PbI$_6$ backbone. The phenyl units are intertwined, forming horizontal layers along one direction (b) that resemble parallel-displaced benzene dimers (Figure 1d). Along the other horizontal direction (a), these layers are arranged in an alternating pattern, without apparent interactions. Along the stacking direction, phenyl arrangements that are closest to the displaced T-shape (TT structure)$^{22}$ benzene dimer structure are observed between PEA layers, that is, perpendicular phenyl moieties, one pointing toward the plane of the other.
We also investigate the lateral packing of the PEA units and find that the PEA units would prefer a closer proximity and a more upright orientation toward each other than it is allowed by the PbI$_2$ backbone (Figure 2b). This demonstrates the flexibility of the organic cation double layer, which adjusts to the rigid PbI$_2$ backbone.

**Influence of Dimensionality and Organic Cation.** We also compare our results for the novel PEA$_2$PbI$_4$ phase with results for MAPbI$_3$ using the same computational setup. We consider the most stable “crossed” structure, in which MA units alternate their tilt angles along two different crystal axes (Figure 1g). With our setup this structure is 0.16 eV more stable than a bulk structure where all MA units are oriented into the same direction. The structure agrees well with experimental results, validating our computational setup. In this bulk MAPbI$_3$ structure, the bonding motif of the NH$_3$ units differs from the layered structure. Here, one hydrogen atom interacts equally with three iodine neighbors with almost identical bonding distances (Figure 1e).

We also discuss the atomic structures of MLs of PEA$_2$PbI$_4$ and MA$_2$PbI$_4$, which can be considered as the extreme thin film limit of these materials. A PEA$_2$PbI$_4$ ML is directly obtained from the layered perovskite bulk structure by introducing vacuum between two units. For a ML from the MAPbI$_3$ bulk it can be expected to be energetically favorable that the tilt direction is alternating for both sides of the PbI$_2$ plane, so that the NH$_3$ groups are pointing toward the PbI$_2$ plane on both sides. There are two different possibilities to fulfill this. One introduces a mirror symmetry between the MA units in the PbI$_2$ plane, whereas in the other structure, MA units are related to each other by inversion. We find that the latter structure (Figure 1h) is energetically favorable by 0.25 eV per MA unit. In this geometry, the NH$_3$ bonding motif changes compared to that of MAPbI$_3$ bulk and is identical to the arrangement found in layered perovskites, that is, bonding of hydrogen atoms to two terminal and one bridging iodine atom, with a single closest iodine neighbor for each H−I bond (see Figure 1f). This arrangement is also slightly more stable (by 0.03 eV per MA unit) than a “crossed” structure, that is, MA units that are rotated alternating along one axis by 90°, which is observed in the MAPbI$_3$ bulk (or analogously for PEA units in PEA$_2$PbI$_4$).

For the most stable structures, we can compare structural changes between ML and bulk structures, as well as changes due to a reduction of dimensionality from 3D over quasi-2D toward 2D. Comparing first the bulk systems with the MLs, the latter have expanded lattice parameters in the PbI$_2$ plane, whereas in the other structure, MA units are related to each other by inversion. We find that the latter structure (Figure 1h) is energetically favorable by 0.25 eV per MA unit. In this geometry, the NH$_3$ bonding motif changes compared to that of MAPbI$_3$ bulk and is identical to the arrangement found in layered perovskites, that is, bonding of hydrogen atoms to two terminal and one bridging iodine atom, with a single closest iodine neighbor for each H−I bond (see Figure 1f). This arrangement is also slightly more stable (by 0.03 eV per MA unit) than a “crossed” structure, that is, MA units that are rotated alternating along one axis by 90°, which is observed in the MAPbI$_3$ bulk (or analogously for PEA units in PEA$_2$PbI$_4$).

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**Electronic Structure.** Figure 2a shows the CDD of the bulk between neutral species of the PEA and PbI$_4$ backbone.

![Image](https://example.com/image.png)

**Table 1. Lattice Parameters, Averaged Volumes of the PbI$_6$ Octahedra ($V_{\text{PbI}_6}$), and Averaged Pb−I Bond Lengths ($d_{\text{PbI}_4}(\vec{x})$) Orientated Along Each Crystal Direction for Bulk and ML Structures of MAPbI$_3$ and PEA$_2$PbI$_4$, Respectively.** Lattice Dimensions and Angles Are Obtained from a (2 × 2 × 2) Supercell Whereas the Cell Volume Ω Is Given per Formula Unit.

<table>
<thead>
<tr>
<th></th>
<th>MAPbI$_3$</th>
<th>MA$_2$PbI$_4$</th>
<th>PEA$_2$PbI$_4$</th>
</tr>
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<tbody>
<tr>
<td>bulk</td>
<td>12.20</td>
<td>12.05</td>
<td>11.88</td>
</tr>
<tr>
<td>ML</td>
<td>12.37</td>
<td>11.75</td>
<td>11.94</td>
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<tr>
<td>$a/\text{Å}$</td>
<td>9.04</td>
<td>89.35</td>
<td>89.34</td>
</tr>
<tr>
<td>$b/\text{Å}$</td>
<td>88.80</td>
<td>88.61</td>
<td>100.25</td>
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<tr>
<td>$c/\text{Å}$</td>
<td>90.39</td>
<td>90.39</td>
<td>89.97</td>
</tr>
<tr>
<td>$\beta$</td>
<td>106.32</td>
<td>106.76</td>
<td>106.76</td>
</tr>
<tr>
<td>$\gamma$</td>
<td>90.47</td>
<td>90.39</td>
<td>89.97</td>
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<tr>
<td>$\Omega/\text{Å}^3$</td>
<td>237.81</td>
<td>542.62</td>
<td>43.46</td>
</tr>
<tr>
<td>$V_{\text{PbI}_6}/\text{Å}^3$</td>
<td>42.77</td>
<td>44.53</td>
<td>41.70</td>
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<tr>
<td>$d_{\text{PbI}_4}(a)/\text{Å}$</td>
<td>3.18</td>
<td>3.22</td>
<td>3.13</td>
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<tr>
<td>$d_{\text{PbI}_4}(b)/\text{Å}$</td>
<td>3.18</td>
<td>3.21</td>
<td>3.10</td>
</tr>
<tr>
<td>$d_{\text{PbI}_4}(c)/\text{Å}$</td>
<td>3.20</td>
<td>3.26</td>
<td>3.28</td>
</tr>
</tbody>
</table>

Figure 2. Neutral (a) and ionic (c) CDD (see Computational Details) between PEA groups and the PbI$_4$ backbone. Charge accumulation and depletion are shown in yellow and cyan for isodensity values of 0.9 and 0.75 (with 1(0) corresponding to perfect (de)localization of electron pairs), respectively. It shows charge redistribution from the organic molecules to the PbI$_4$ backbone, in line with the expected charge transfer and the nominal charge of +1 for each PEA cation. Interestingly, charge is mainly depleted from $p_z$ orbitals of the phenyl units. We also confirm the charge transfer by a
Bader analysis, which attributes approximately 0.7 electrons of each PEA cation to the PbI$_4$ backbone.

Figure 2c shows a similar CDD with respect to charged isolated species PEA$^+$ and PbI$_4$$. It shows that charge is accumulated on the H–I bonds to terminal iodides (indicated by green, dashed lines for one NH$_3$ group), whereas no such charge accumulation is found between the third hydrogen atom and the nearest bridging iodides, indicating a stronger interaction of hydrogen atoms with terminal iodides. Charge is depleted from the terminal iodides along the stacking direction, which is, in addition to the H–I bonds, also accumulated on the phenyl moieties.

Figure 2 panels b and d show the electron-localization function (ELF) for the same structure. As expected, a high degree of electron localization is observed on covalent bonds between carbon atoms in the phenyl units and on C–H and N–H bonds. In contrast, such features are absent in the PbI$_4$ backbone, showing typical features of metal organic bonds with strong ionic bonding character for Pb–I bonds. Despite the charge rearrangements on the H–I bonds for terminal iodides, no ELF is observed between PbI and PEA, exhibiting weak ionic character. The discussed noncovalent interactions (NCI) between the fragments can also be visualized by NCI-plots (see Figure S3).

To quantify the bonding strength between PbI$_4$ layers along the stacking direction in PEA$_2$PbI$_4$, we calculate the cleavage energy of a layer from the PEA$_2$PbI$_4$ bulk as $E_{	ext{cl}} = |E_0(\text{ML}) - E_0(\text{bulk})|/2 = 0.91$ meV/Å$^2$ from the energies of the isolated ML ($E_0(\text{ML})$) and the bulk system ($E_0(\text{bulk})$), respectively. For reference, this is roughly 19 times less than the cleavage energy in graphite for the same computational method (estimated from the PBE-D2 cleavage energy of 17.01 meV/Å$^2$ that agrees well with experimental values).

We now investigate the PDOS of the PEA$_2$PbI$_4$ bulk and ML, respectively (Figure 3e,f). The states around the Fermi level in Figure 3e,f). The states around the Fermi level are of mainly iodine $p$ character, whereas bands with PEA character appear flat (Figure 3e,f), indicating the weak interaction between PEA units among each other and with the PbI$_4$ backbone. A comparison of the bulk and ML shows that the band structure is mostly retained, with a small band gap increase of 0.07 eV in the ML. This justifies the classification of layered hybrid perovskites as quasi-2D systems, since the multilayer systems are, to a large extent, electronically identical to a single ML.

Table 2. Scalar- and Full-Relativistic Band Gaps ($E_g$) for Quasi- and Truly 2D PEA$_2$PbI$_4$ Compared to Band Gaps for MAPbI$_3$ Bulk and MAPbI$_4$ ML, Respectively

<table>
<thead>
<tr>
<th>Structure</th>
<th>$E_g$(SRL)/eV</th>
<th>$E_g$(FRL)/eV</th>
<th>$E_g$(expt)/eV</th>
</tr>
</thead>
<tbody>
<tr>
<td>MAPbI$_3$ (bulk)</td>
<td>1.52</td>
<td>0.73</td>
<td>1.3–1.8</td>
</tr>
<tr>
<td>MAPbI$_4$ (ML)</td>
<td>2.26</td>
<td>1.52</td>
<td></td>
</tr>
<tr>
<td>PEA$_2$PbI$_4$ (bulk)</td>
<td>2.17</td>
<td>1.40</td>
<td>2.4–3.14</td>
</tr>
<tr>
<td>PEA$_2$PbI$_4$ (ML)</td>
<td>2.24</td>
<td>1.43</td>
<td></td>
</tr>
</tbody>
</table>

The related MAPbI$_3$ system is known to show a very strong influence of SOC in the electronic structure. Predicted band gap energies ($E_g$) of SRL DFT calculations are in very good agreement with experiments and high level many-body calculations, whereas FRL DFT and SRL many-body calculations lead to under- and overestimated band gaps, respectively. Thus, we also investigate the effect of SOC in our system (Figure S4). The band structures and PDOS including SOC reveals that both VBE and CBE are considerably broadened. The broadening is mainly observed around the $\Gamma$ point, affecting both Pb$_5$ and I$_{5}$ bands. Overall, SOC reduces the band gap by ≈0.8 eV for the studied layered hybrid perovskite as well as the traditional OMHP, independent of organic cation or dimensionality (Table 2).
Despite the spread in the reported experimental band gaps (see Table 2), the SRL DFT gap for PEA\(_2\)PbI\(_4\) is similar to the lowest reported value of optical band gaps. This indicates that similar error cancellation as for MAPbI\(_3\) occurs and that SRL DFT underestimated the true band gap only by a small margin. In any case, this shows that any future high-level many-body calculations for these systems must be carried out fully relativistic or are otherwise likely to systematically underestimate \(E_g\).

We now investigate the influence of dimensionality on the band gaps. First we compare MAPbI\(_3\), bulk and MA\(_2\)PbI\(_4\) ML at the SRL DFT level. The band gap of MAPbI\(_3\) is 1.52 eV, in agreement with literature.\(^{28,35}\) It increases by roughly 0.7 eV in MAPbI\(_3\). To analyze the band gap increase, we compare the PDOSs and band structures of both systems in Figure 3gh. The PDOS has many common features. On closer inspection, however, the CBE changes in agreement with structural differences between bulk and ML. Because of the lack of long-range bond delocalization along \(z\) in the ML, the Pb-xz bands are more confined and shifted away from the Fermi edge. Pb-x and Pb-y remain mostly unchanged, despite the small difference between both species that is only noticeable in the bulk (see phase transition in Figure 1). Similar changes are also observed in the \(I_p\) contributions to the VBE. \(I_{px}\) and \(I_{py}\) show again small differences in the ML structure while being identical in the bulk. Bands with \(I_{pz}\) contribution are destabilized in the ML due to the broken Pb–I bonds along \(z\). Overall, these changes lead to the observed band gap increase in the 2D system. Since this effect is caused by the lack of long-range bond delocalization along \(z\), it is also observed in the PEA\(_2\)PbI\(_4\) bulk, due to the structural changes induced by the larger PEA cation. Since some of the vertical Pb–I bonds are already broken along the stacking direction, the band structure and gap are similar to the 2D cases (MA\(_2\)PbI\(_4\) and PEA\(_2\)PbI\(_4\) MLs), with only small modifications between PEA\(_2\)PbI\(_4\) bulk and ML due to the weak interlayer PEA interactions.

The band gap opening of PEA\(_2\)PbI\(_4\) compared to that of MAPbI\(_3\) bulk by \(\approx 0.7\) eV opens the possibility of adjusting the band gap in this range by controlling the number of MAPbI\(_3\) layers in the family of MA\(_{n+1}\)PEA\(_2\)PbI\(_{n+1}\) Ruddlesden–Popper phases, which might be interesting for light harvesting or sensors.

Comparing PEA\(_2\)PbI\(_4\) and MAPbI\(_3\) bulk, we also observe that the flat bands of the organic cation are even further away from the band edges in the case of MA cations. For PEA\(_2\)PbI\(_4\), the CBE is located at the organic cation around the BZ corners S. This opens possibilities for band gap engineering by shifting these bands via chemical modification of the PEA cations. These states could also be related to the electron–phonon coupling that is observed in this material with phonons that are located at the PEA units.\(^{36}\)

**CONCLUSION**

We investigated the effects of exchanging small MA with PEA cations in the OMHP benchmark case MAPbI\(_3\). We identify and discuss the resulting most stable Ruddlesden–Popper phase, which is in agreement with experiments and shows off-center displacement of Pb cations leading to antiparallel Pb–I distortions. By analyzing the bonding of the organic cation with the PbI\(_3\) backbone and the interactions within the hydrophobic moieties, we show that the vertical interaction along the stacking direction is weak. This is also consistent with the electronic structure of the layered bulk phase, which is rather unaffacted by reducing the dimensionality to a ML. In contrast, the electronic structure changes significantly when comparing 3D bulk with 2D ML for MAPbI\(_3\). Thus, interlayer bonding in layered perovskites is weaker compared to that in 3D OMHPs, opening the possibility toward thin film growth down to MLs for the layered material. There, the empty bands of the organic cation are significantly lowered in energy and contribute to the conduction band edge, which opens the possibility of band gap engineering. Besides these changes, the electronic structures of layered and traditional OMHPs are similar, even with the previously reported huge influence of SOC on the electronic structure.

**ASSOCIATED CONTENT**

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpcc.7b00890.

Details on structural variants and further discussion of the thermodinamical minimum of PEA\(_2\)I\(_3\); analysis of the noncovalent interactions in PEA\(_2\)PbI\(_4\); influence of RFL treatment on electronic structure (PDF)

Optimized crystal structures (ZIP)

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**Notes**

The authors declare no competing financial interest.

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