The synthesis of dimethylzinc (Me₂Zn) and diethylzinc (Et₂Zn) by Frankland in the mid-nineteenth century marks a cornerstone in the history of chemistry. Not only were they among the first organometallic compounds, but studies on their chemical reactions and vapor densities led to the first clear exposition of valency theory. Since then both compounds have found widespread applications: They are important reagents in organic synthesis, for example in the enantioselective alkylation of carbonyls and imines, and in cyclopropanation reactions. Their high vapor pressures have led to extensive uses in metalorganic chemical vapor deposition (MOCVD) for the preparation of wide band gap II–VI semiconducting films (e.g. ZnS, ZnSe, ZnTe), ZnO nanostructures, and as p-dopant precursors for III–V semiconductors (e.g. GaAs, InP, AlₓGa₁₋ₓAs), which have numerous electronic and photonic applications.

Despite their prominence in chemical and materials synthesis, the solid-state structures of these prototypical organometallic systems remained elusive. Me₂Zn and Et₂Zn feature the smallest and lightest molecules containing metal atoms in the condensed phase. At standard conditions they exist as volatile, pyrophoric liquids (Me₂Zn: m.p. −42 °C, b.p. 46 °C; Et₂Zn: m.p. −28 °C, b.p. 118 °C), which are moderately soft Lewis acids that form adducts with a variety of ligands. Structural studies of the gas phase have revealed a linear coordination mode. Solid-state structures of diaryl and bulky dialkyazine derivatives exhibit monomeric structures with the exception of Ph₂Zn, which forms a loosely bonded dimer. Here we present a combined crystallographic and computational study, which shows that Me₂Zn and Et₂Zn exhibit a rich solid-phase behavior. We have used density functional theory with dispersion corrections including an uncertainty analysis for the van der Waals forces to elucidate the detailed structure of the crystals.

Single crystals were grown from samples sealed in quartz capillaries. Me₂Zn was found to exist in two polymorphic forms, which are enantiotropic undergoing a reversible transition at 180 K (Figure 1). We were able to determine X-ray crystal structures of both the high-temperature phase, α-Me₂Zn, and the low-temperature phase, β-Me₂Zn. A single crystal of α-Me₂Zn was grown by gradually cooling the sample to 200 K. X-ray data indicate a tetragonal unit cell with Laue symmetry 4/mmm. Refinement in space group P4₁/mmm exhibits two molecules per unit cell aligned orthogonally to each other and parallel to the ab plane occupying D₄h sites. This setting, however, is incompatible with the molecular three-fold symmetry. Also, the C atom exhibits a high anisotropic displacement in the z direction. Refinement in the monoclinic space group P2₁/n as a pseudo-merohedral twin decreases the site symmetry to C, and tilts the molecule by 5.6° with respect to the ab plane (Figure 1). As a result, the two methyl groups adopt a staggered conformation. The C–Zn–C unit is strictly linear and the Zn–C bond measures 1.927(6) Å in good agreement with the gas-phase structure. Each zinc atom is surrounded by four methyl groups of neighboring molecules with two shorter and two longer CH₃–Zn distances (C–Zn 3.491(7) and 3.708(7) Å, respectively). The twinning can be attributed to a two-dimensional disorder as stacks of molecules along the c axis can adopt two tilt orientations (see the Supporting Information). The disorder leads to an entropic free-energy term of kₐTln₂ per stack, contributing to the stabilization of the α phase at higher temperature.
Our calculated structure is in good general agreement with the X-ray structure\cite{15} and we obtain a cohesive energy of 0.61(4) eV per molecule, of which 94 % is due to van der Waals forces. A molecular tilt with respect to the \( ab \) plane is also favored, albeit by a larger angle of 9.8\(^\circ\). The molecules have strictly linear C-Zn-C units and the Zn-C bonds compare favorably (1.933 Å), as do the intermolecular Zn-C distances of 3.357 and 3.718 Å.

Cooling Me\(_2\)Zn below 180 K leads to the formation of polycrystalline \( \beta \)-Me\(_2\)Zn. A single crystal of this phase was obtained by annealing the sample at 150 K. The \( \beta \) phase is more compact than the \( \alpha \) phase and features a more complex but ordered structure (see the Supporting Information for a detailed structural comparison of \( \alpha \) and \( \beta \) phases). \( \beta \)-Me\(_2\)Zn exhibits a monoclinic unit cell of space group symmetry \( P2_1/n \) containing four molecules. These are arranged in square grid-type layers parallel to the \( ab \) plane, with each Zn atom forming two T-shaped interactions with methyl groups of neighboring molecules showing Zn-C distances of 3.327(14) Å and 3.424(14) Å (Figure 1). These layers are stacked upon each other such that Me\(_2\)Zn molecules of adjacent layers align in parallel fashion with a Zn-C distance of 3.455(15) Å. The molecules are virtually linear (C-Zn-C 178.2(6)\(^\circ\)) with Zn-C bond lengths of 1.911(14) Å (Zn1-C1) and 1.920(13) Å (Zn1-C2). The low quality of the data, which were obtained from a sample containing several single-crystal domains, did not allow us to locate H positions accurately. However, careful analysis of the various conformers shows that one particular conformation exhibits appropriate intermolecular distances with the methyl groups arranged eclipsed to each other (see the Supporting Information).

Computationally, we find several distinct local minima for this phase that are broadly consistent with the Zn-C distances, but all have slightly higher cohesive energies than \( \alpha \)-Me\(_2\)Zn. A sensitivity analysis\cite{14d} shows that these energies depend strongly on the radius of the Zn atoms and the ad hoc damping function in the dispersion correction.\cite{14c} This slightly unphysical dependence of the binding energies and geometries on fitted parameters in the description of the van der Waals forces is responsible for the inability to describe this particular phase theoretically. Note, however, that we do very well in determining the structures of \( \alpha \)-Me\(_2\)Zn and Et\(_2\)Zn, which could not be achieved with a selection of alternative methods.

Diethylzinc formed sufficiently large single crystals when the capillary was gradually cooled to 100 K. It exhibits a tetragonal body-centered unit cell of space group symmetry \( I4_1/mmd \) containing four molecules.\cite{21} These display \( C_\beta \) symmetry, the zinc atom and the four carbon atoms are co-planar, the C-Zn-C angle is very slightly bent (176.2(4)\(^\circ\)), while both ethyl groups (Zn-C-C 115.9(4)\(^\circ\)) are in mutual cis position. The Zn-C bonds, measuring 1.948(5) Å, are marginally longer than in Me\(_2\)Zn, as observed for the gas-phase structures.\cite{11} The molecules pack in a polar arrangement such that ethyl groups all face in one direction along \( z \). Each molecule has eight neighbors to which it is aligned orthogonally (Figure 2). The immediate intermolecular environment of the Zn atom is occupied by two CH\(_3\) (Zn–C 3.254(6) Å) and two CH\(_2\)\( \rangle \) groups of neighboring molecules (Zn–C 3.504(6) Å). Our calculations predict that the cohesion of 0.88(6) eV per molecule is 99 % due to dispersion forces, and the calculated structure agrees well with the experimental data.\cite{15}

A qualitative way to map the intermolecular interactions are Hirshfeld surfaces\cite{16} as presented in Figure 3a for \( \alpha \)-Me\(_2\)Zn and Et\(_2\)Zn (see also the Supporting Information). The red patches demonstrate relatively close contacts between the alkyl groups and the Zn atoms of neighboring molecules. To quantify the electronic contributions, we obtained the density

\begin{figure}
\centering
\includegraphics[width=\textwidth]{Figure2}
\caption{X-ray crystal structure of Et\(_2\)Zn. The ball-and-stick model is viewed along and the space-filling model perpendicular to the \( ab \) plane. Zinc atoms are shown in red.}
\end{figure}

\begin{figure}
\centering
\includegraphics[width=\textwidth]{Figure3}
\caption{a) Left: Density of states for \( \alpha \)-Me\(_2\)Zn (top) and Et\(_2\)Zn (bottom). The Fermi levels were aligned in the middle of each band gap for better comparison between the structures. The vertical dashed lines correspond to the free molecule energy eigenvalues. Right: Structure and Hirshfeld surfaces. The color denotes the distance from the nearest atom outside the surface. b) Four highest occupied Kohn–Sham orbitals of the free molecule and their energy difference to the HOMO.}
\end{figure}
of states (DOS, Figure 3a). In the occupied states, we find a
sharp peak because of the highest occupied molecular orbital
(HOMO) of α-Me₂Zn and Et₂Zn, respectively. The HOMO of
α-Me₂Zn has three nodal planes along the molecular axis
(Figure 3b), such that the overlap between the terminal lobe
of one molecule and the center of its neighbor is exactly zero
and gives rise to the sharp feature in the DOS. For each
crystal, there are two very broad peaks below the HOMO
levels, suggesting band formation because of the intermolecu-
lar hybridization of the Zn–C bonding orbitals (around
−3 eV) and a hybridization between Me and Et groups of
adjacent molecules (around −5 eV and lower). For α-Me₂Zn,
the HOMO-1 has only two nodal planes along the molecular axis
such that the broadening in the DOS arises from the
overlap of the terminal lobe in one molecule with the central
lobe of its neighbor. Finally, the relative orientation of
the methyl groups is governed by the degenerate HOMO-2 and
HOMO-3 levels, which allow for greater intermolecular
overlap for the staggered conformation. Similar arguments
explain the DOS for Et₂Zn. Overall, our analysis shows that
overlap for the staggered conformation. Similar arguments
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Keywords: density functional calculations · organometallic compounds · solid-state structures · X-ray diffraction · zinc

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ment in space group Pn̅2₁/n as a pseudo-merohedral twin: a = 6.856(5), b = 6.842(5), c = 4.182(3) Å, β = 89.970(11)°, V =
196.2(2) Å³, Z = 2, ρ = 1.616 g cm⁻³, Rᵣ = 0.0197. Alternative
refinement in Pn̅m̅m̅n̅n with a split C-position: a = 6.849(4), c =
4.183(2) Å, V = 196.2(2) Å³, Z = 2, ρ = 1.616 g cm⁻³, Rᵣ = 0.0149.
Theory: a = 6.798(8), c = 4.04(9), Eₘₙ = 0.61(4) eV per molecule.
β-Me₂Zn: CH₂Zn, Mᵣ = 95.44, T = 150 K, Pn̅2₁/n, a = 7.475(13),
b = 7.497(14), c = 7.484(13) Å, β = 114.12(3)°, V = 381.91(12) Å³,
Z = 4, ρ = 1.660 g cm⁻³, Rᵣ = 0.0566. Et₂Zn: CH₃Zn, Mᵣ =
123.49, T = 100 K, Pbn̅2₁, a = 9.893(7), b = 5.300(4) Å, V =
518.8(6) Å³, Z = 4, ρ = 1.581 g cm⁻³, Rᵣ = 0.0286. Theory: a =
10.07(6), b = 5.21(6), Eₘₙ = 0.88(6) eV per molecule.
CCDC 835339, 835340, 835341, 835342 contain the supplemen-
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