

Mechanical Robustness in Fused Polyhedral Borane Crystals through Persistent Weak Intermolecular Interactions

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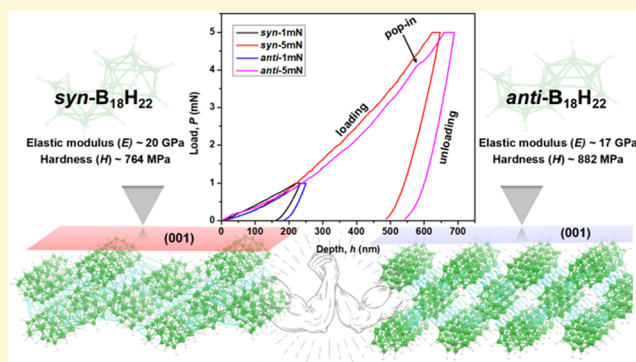


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ABSTRACT: Borane clusters represent a unique class of molecular materials featuring electron-deficient bonding and diverse polyhedral architectures. While their electronic, photophysical, and chemical properties have been extensively explored, the influence of polyhedral architecture on their mechanical behavior remains largely unknown. Here, we investigate the nanomechanical properties of two prototypical-dicosahydrooctadecaborane isomers (*syn*-B₁₈H₂₂ and *anti*-B₁₈H₂₂) through nanoindentation experiments, density functional theory (DFT) calculations, crystallographic and energy-framework analyses. The crystals exhibit exceptional mechanical robustness, displaying elastic modulus (*E*) of ~20 GPa for *syn*-B₁₈H₂₂ (*syn*-B₁₈) and ~17 GPa for *anti*-B₁₈H₂₂ (*anti*-B₁₈), despite being composed exclusively of boron and hydrogen atoms and lacking conventional strong hydrogen-bonding networks. Structural analyses reveal that both isomers adopt three-dimensional interlocked packing arrangements sustained by multiple B...μHBB, B-H...B, and B...B contacts. In contrast, the parent single-polyhedral borane crystal of B₁₀H₁₄ exhibits a substantially lower elastic modulus (~9 GPa) and has lower-dimensional interaction networks in the solid state. The structure-mechanical property correlation presented here establishes a clear relationship between polyhedral architecture, intermolecular interaction topology, and mechanical performance in borane molecular crystals. More broadly, this work identifies macropolyhedral fusion as a structural design strategy for enhancing the mechanical robustness of cluster-based molecular solids and expands the emerging materials chemistry of borane-derived crystalline materials.



INTRODUCTION

Understanding how molecular architecture and crystal packing govern mechanical behavior is a central theme in the design of functional molecular materials. Mechanical properties such as elasticity (resistance toward elastic deformation) and hardness (resistance toward plastic deformation) influence the performance, processability, and long-term stability of materials employed in electronic, optical, and energy-related applications.^{1–5} Although the mechanical behavior of metals, ceramics, and polymers has been extensively investigated, molecular crystals have only recently emerged as a distinct class of materials whose mechanical properties can be systematically tailored through crystal engineering.^{1,6–18} Recent advances in nanoindentation techniques have revealed that molecular solids exhibit a remarkably broad spectrum of mechanical responses, ranging from highly compliant crystals to mechanically robust materials.^{1–5,7,8,19–23} Previous studies have established that crystal packing, intermolecular interactions, and molecular geometry collectively determine both qualitative and quantitative mechanical performance of crystalline materials.^{7,10,18,20,22,24} In many mechanically robust molecular solids, strong hydrogen-bonding networks are

frequently invoked as key structural motifs responsible for enhanced rigidity.^{1,4,8,21} However, whether mechanically resilient molecular crystals can be achieved through alternative interaction networks (e.g., without having strong hydrogen bond-forming functional groups) and molecular architectures remains an open question. Addressing this challenge requires the exploration of molecular systems that possess fundamentally different bonding paradigms from those found in conventional organic solids.

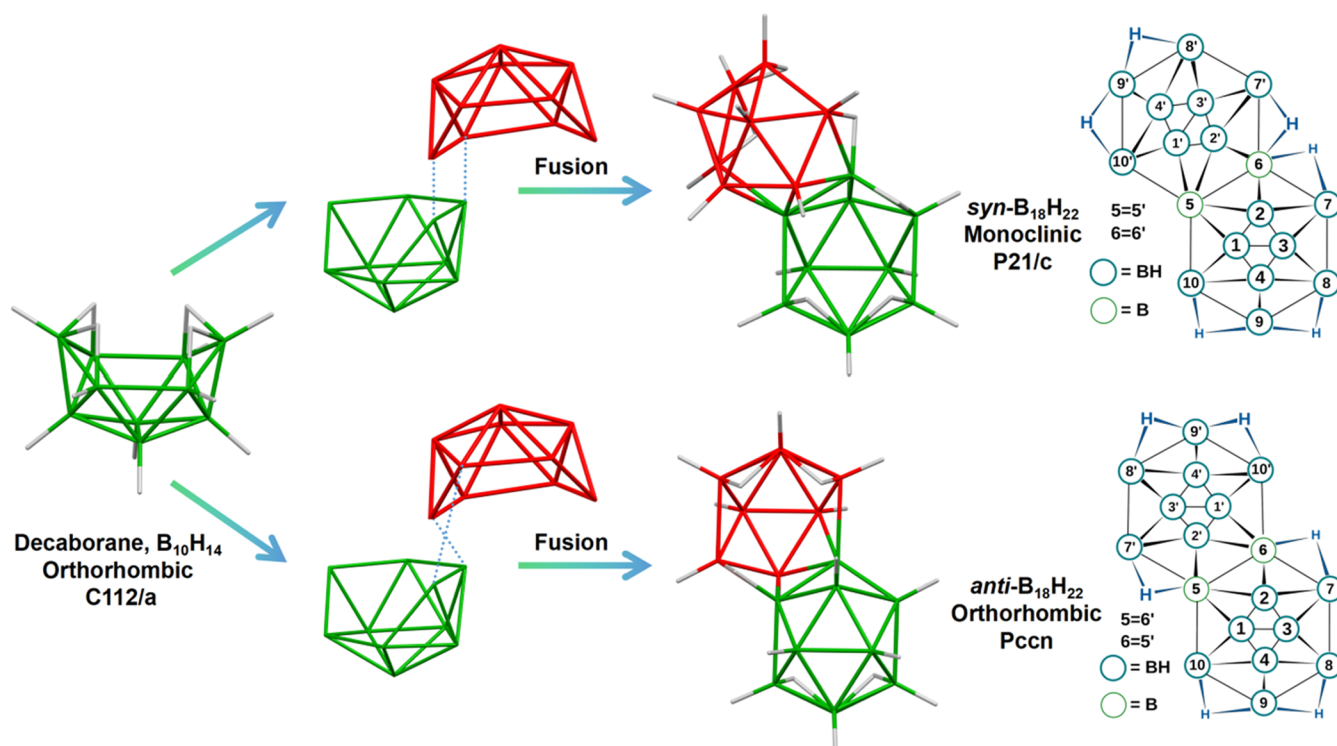
In this regard, borane clusters provide a unique platform for investigating these questions. Boranes are electron-deficient boron–hydrogen compounds characterized by multicenter bonding and polyhedral molecular architectures that have significantly expanded modern understanding of chemical bonding and molecular structure.^{25–27} Unlike hydrocarbons,

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Scheme 1. Schematic of $B_{10}H_{14}$ and $B_{18}H_{22}$, Illustrating the Nominal Fusion of Two $\{nido-B_{10}\}$ Sub Clusters- One Colored Red and the Other Green, with H Atoms Omitted for Clarity-to Form the Two Isomers of Octadecaborane(22): $syn-B_{18}H_{22}$ and $anti-B_{18}H_{22}$ ^a



^aIn $syn-B_{18}$, the fusion of two $\{B_{10}\}$ units occurs *via* a shared $B(5)-B(6)$ edge, resulting in a 2-fold symmetry axis along $B(5) \equiv B(5')$ and $B(6) \equiv B(6')$. In the $anti-B_{18}$ isomer, $B(5) \equiv B(6')$ and $B(6) \equiv B(5')$, producing inversion symmetry. The numbering system is shown in the net-like representations.

which predominantly form chain-like or planar molecular frameworks, boranes adopt three-dimensional cage-like geometries stabilized through delocalized bonding interactions. Depending on their size and electron count, boranes exist as *closo*, *nido*, *arachno*, and more complex macropolyhedral structures, offering a diverse structural landscape for investigating relationships between molecular architecture and materials properties.^{28,29} While their electronic structures, photophysical properties, luminescence behavior, and chemical reactivity have been studied extensively, their nanomechanical properties remain largely unexplored.^{26,30–36}

Among the various borane clusters, the macropolyhedral isomers $syn-B_{18}H_{22}$ and $anti-B_{18}H_{22}$ represent particularly attractive model systems.^{33,34,37} These clusters are formed through the fusion of two *nido*- $\{B_{10}\}$ polyhedral units, generating large cage-like architectures that retain the characteristic electron-deficient bonding of boranes while introducing increased structural complexity. Although $syn-B_{18}H_{22}$ and $anti-B_{18}H_{22}$ possess identical chemical compositions, differences in their molecular symmetry and crystal packing arrangements provide an opportunity to investigate how subtle variations in molecular architecture and intermolecular interaction topology influence mechanical response (Scheme 1). Furthermore, the availability of the parent single-polyhedral borane $B_{10}H_{14}$ and related thiolated derivatives offers a useful framework for evaluating the effects of polyhedral fusion and functional-group substitution on mechanical behavior.^{30,38–41}

Here, we investigate the nanomechanical properties of the macropolyhedral borane crystals of $syn-B_{18}H_{22}$ and $anti-B_{18}H_{22}$ isomers through nanoindentation experiments, density functional theory (DFT) calculations, crystallographic and energy-frameworks analyses. Both the crystals exhibit exceptional mechanical robustness, displaying elastic moduli of approximately 20 and 17 GPa, respectively. Comparative studies involving the parent single-polyhedral borane $B_{10}H_{14}$ and related thiolated derivatives reveal substantially lower mechanical performance, highlighting the influence of polyhedral architecture on crystal rigidity. By correlating nanomechanical behavior with crystal packing and intermolecular interaction topology, we establish a clear structure–mechanical property relationship in borane molecular crystals and identify macropolyhedral fusion as a structural feature associated with enhanced mechanical robustness in cluster-based molecular solids.^{8,10–15,42–44}

EXPERIMENTAL SECTION

Materials

$syn-B_{18}H_{22}$ and $anti-B_{18}H_{22}$ were purchased from Katchem s.r.o. (Czech Republic) and used as received. Thiolated derivatives were synthesized following reported literature procedures.³⁰ Solvent-grade dichloromethane (DCM), hexane, and diethyl ether were obtained from Rankem and Finar India. All other commercially available chemicals were used without further purification.

In the following, we present the essential details of the experimental and computational methods. Additional experimental procedures, measurement parameters, data analysis, and computational details are provided in the Supporting Information.

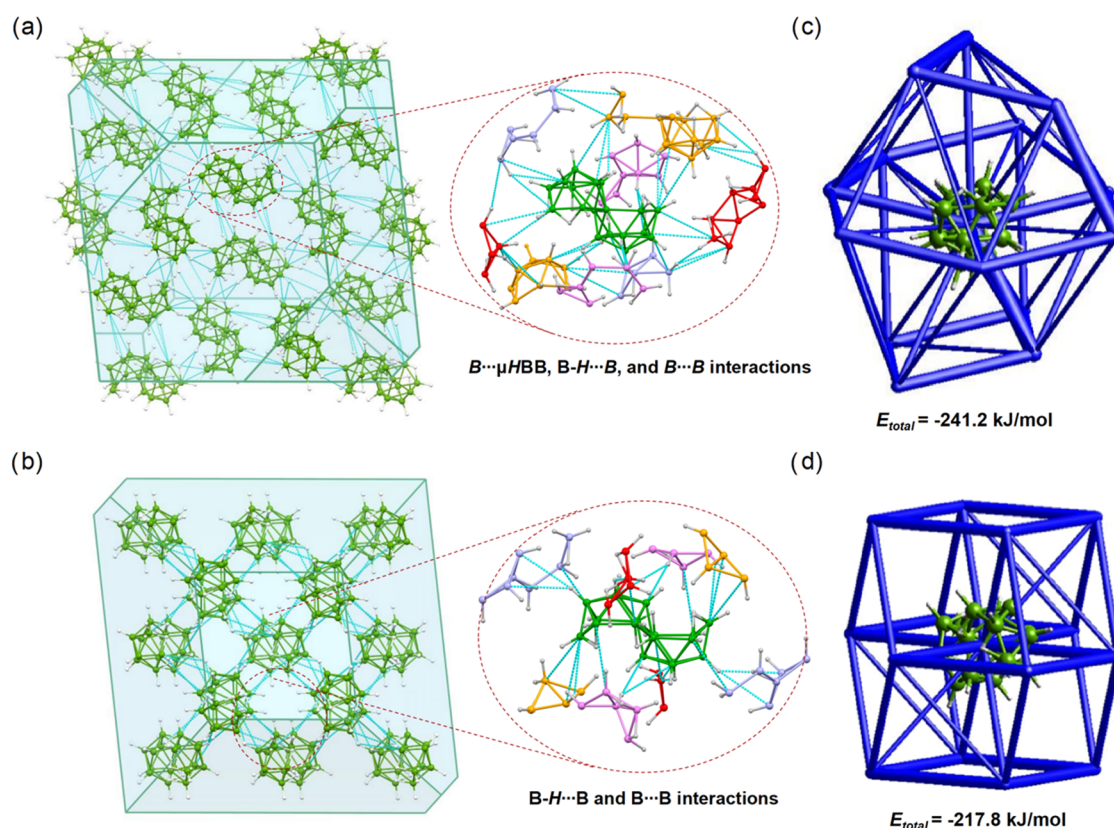


Figure 1. (a and b) Bravais-Friedel-Donnay-Harker (BFDH) morphological representation of the extended crystal packing of *syn*-B₁₈ (top) and *anti*-B₁₈ (bottom) clusters as viewed along the *a*- and *c*-axes, respectively. In the zoomed images, cyan-colored dotted lines indicate intercluster interactions involving green-colored boron atoms from distinct boron skeletons B $\cdots\mu$ HBB, B-H $\cdots$ B, and B $\cdots$ B interactions (neighboring extra skeletons are removed for clarity). (c and d) Skeleton of the total interaction energy tubes (thickness of the tube is proportional to the amount of energy) obtained from energy frameworks analysis representing pairwise interaction energies experienced by the *syn*-B₁₈ (top) and *anti*-B₁₈ (bottom) molecules present at the center of the skeleton. The tube size was kept at 100 and the interaction energy cutoff was 10 kJ/mol.

SC-XRD and Face Indexing

SC-XRD data for *syn*-B₁₈H₂₂ and *anti*-B₁₈H₂₂ were collected at 298 K using a Bruker D8 VENTURE FIXED CHI diffractometer equipped with a PHOTON III CPAD detector and graphite-monochromated Mo K α radiation ($\lambda = 0.71073$ Å). Crystal face indexing was performed using APEX-6 software.

Nanoindentation Measurements

Nanomechanical measurements were performed using a Hysitron TI Premier Nanoindenter equipped with a Berkovich diamond indenter. Single crystals of *syn*-B₁₈H₂₂ and *anti*-B₁₈H₂₂ were affixed to glass slides and subjected to load- and displacement-controlled nanoindentation measurements. Load-displacement curves were used to determine the mechanical properties. Creep and stress-relaxation measurements were also performed.

Nano Dynamic Mechanical Analysis Measurements

Nano-DMA measurements were performed using load-controlled frequency-sweep and CMX loading modes. The storage modulus, loss modulus, and damping factor were determined from the dynamic load and displacement response.

Energy Frameworks Calculations

Intermolecular interaction energies and energy frameworks were calculated using CrystalExplorer^{19,45} based on Gaussian B3LYP/6-31G(d,p) wave functions and the experimental crystal structures. The total interaction energy was evaluated from its electrostatic, polarization, dispersion, and exchange-repulsion components. The X-H bond lengths are normalized by Crystal Explorer to be the same as those obtained from neutron diffraction experiments.⁴⁶

Computational Details

The elastic properties of borane clusters (B₁₈H₂₂) were investigated using plane-wave density functional theory (DFT) as implemented in the Vienna Ab initio Simulation Package (VASP).^{47–49} Projector-augmented wave (PAW) pseudopotentials and the Perdew–Burke–Ernzerhof (PBE) exchange-correlation functional^{50,51} within the generalized gradient approximation (GGA)⁵² were employed, with Tkatchenko–Scheffler dispersion corrections.⁵³ A plane-wave cutoff of 500 eV and a k-point mesh width of 0.33 Å^{−1} were used. The elastic constants were obtained from energy-strain relationships by applying controlled strains within the elastic regime and fitting the resulting energies to a quadratic function. The crystal symmetries of *syn*-B₁₈H₂₂ (monoclinic) and *anti*-B₁₈H₂₂ (orthorhombic) were considered in determining the independent elastic constants. The details of computational information have been documented in github (GitHub - prnrvs/elastic_vasp)⁵⁴ and relevant analyses are provided in the Supporting Information.

RESULTS AND DISCUSSION

Crystal Structure Analysis and Supramolecular Packing of *syn*-B₁₈ and *anti*-B₁₈ Crystals

Due to their identical chemical composition, isomers serve as ideal models for investigating how both the molecular structure as well as their 3D arrangements influences various physical properties of the crystals. We examined the crystal structures of the B₁₈H₂₂ isomers, *syn*-B₁₈ and *anti*-B₁₈. Crystallization from diethyl ether yielded well-developed single-crystals suitable for X-ray diffraction and nanomechanical studies (Figures S1 and

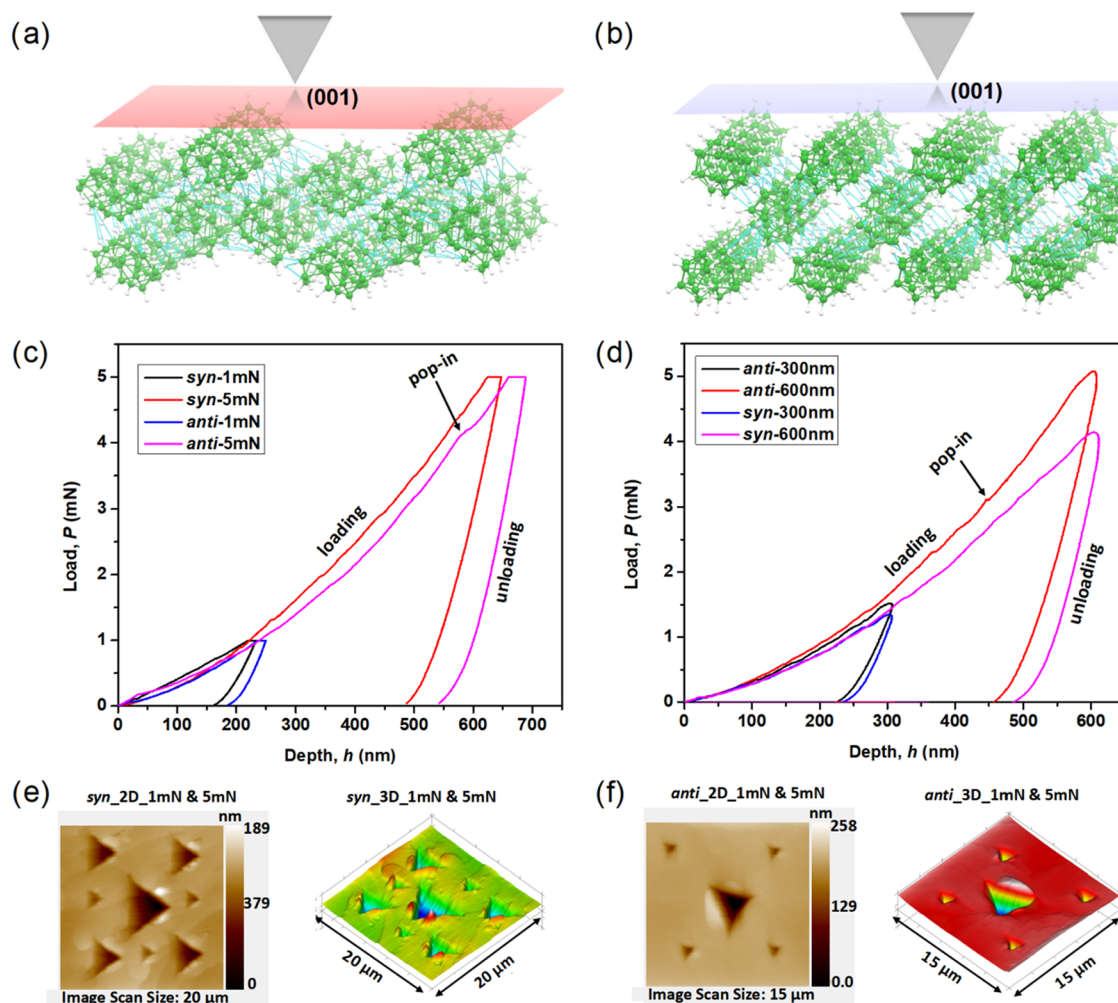


Figure 2. Nanoindentation of *syn-B*₁₈ and *anti-B*₁₈. The upper panel represents the schematic of the crystal packing along with a (001) plane (major faces for both the crystals) perpendicular to which nanoindentation experiments were performed for *syn-B*₁₈ and *anti-B*₁₈, from left (a) to right (b). (c) Load controlled load–displacement curves of both crystals under a fixed load of 1 mN and 5 mN using a load function of 5–2–5 s. (d) Depth controlled load–displacement curves with a fixed displacement of 300 and 600 nm for both the crystals, together using a load function of 5–2–5 s. Arrows indicate pop-in events occurring during nanoindentation experiments. The lower panel (e and f) represents the 2D and 3D indent impression images at different peak loads (1 mN and 5 mN) together for both the crystals (corresponding height profiles are presented in the Supporting Information).

S2). Their comparative analysis reveals how differences in the molecular structure and supramolecular interactions can profoundly influence the physical properties of borane clusters. While being compositionally identical, they exhibit distinct crystal structures arising from differences in their molecular geometry and packing. The *anti-B*₁₈ forms a centrosymmetric orthorhombic lattice with space group *Pccn*,³³ while *syn-B*₁₈ adopts a monoclinic structure with space group *P2*₁/*c* and C2 symmetry.³⁰ The unit cell in each of the two distinct structures contains four molecules. The difference in crystal symmetry between the two isomers is significant: *syn-B*₁₈'s monoclinic structure exhibits lower molecular and crystal symmetry with higher density (1.036 g/cm³) and higher packing coefficient (0.789), whereas *anti-B*₁₈'s orthorhombic lattice is more symmetric having lower density (1.026 g/cm³) and lower packing coefficient (0.786) than *syn-B*₁₈. A key factor differentiating the supramolecular packing of *syn*- and *anti-B*₁₈ is the role of bridging hydrogen atoms (Figures 1 and S3,S4). In *syn-B*₁₈, boron atoms interact strongly with the acidic μ HBB bridging hydrogens. Both isomers have intense IR

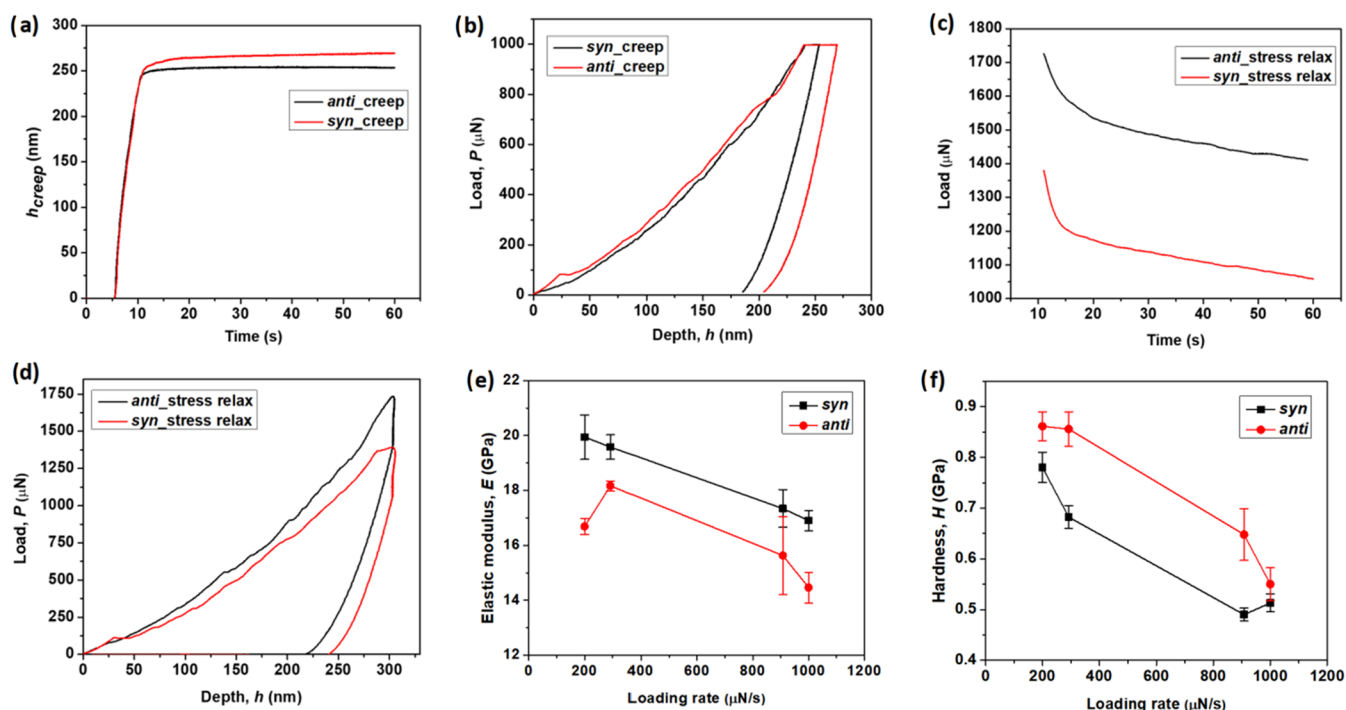
absorption bands near 1490 cm^{−1} (B–H stretching) and 1950 cm^{−1} (μ HBB bridge) (Figures S5 and S6). In *syn-B*₁₈ each molecule forms direct connections to eight neighboring clusters through B–H...B, B–H... μ HBB and B...B short contacts, resulting in an interlocked, complex, and entangled 3D networks (Figures 1a and S4a). In contrast, *anti-B*₁₈ lacks the same degree of interlocked interactions because of high symmetry of the molecule. Its supramolecular packing is also dominated by B–H...B and B...B short-contacts with H...H distances ranging from 2.55 to 2.83 Å, typical for van der Waals interactions for both the isomers (Figures 1b and S4b). Each *anti-B*₁₈ molecule also connects through short contacts to eight neighboring molecules, but these contacts are more directional and more evenly distributed, resulting in a close-packed, isotropic lattice (Figure 1).

Nanomechanical Investigation of Isomorphous *syn-B*₁₈ and *anti-B*₁₈ Crystals

We investigated the mechanical properties of B₁₈H₂₂ crystals using a Hysitron TI PremierNanoindenter with a 150 nm Berkovich tip. For both the cluster *syn-B*₁₈ and *anti-B*₁₈,

Table 1. Mechanical Properties of *syn*-B₁₈ and *anti*-B₁₈ Obtained by Different Nanoindentation Measurements (σ Represents Standard Deviation)

Crystal systems		<i>syn</i> -B ₁₈ H ₂₂		<i>anti</i> -B ₁₈ H ₂₂	
Different measurements		<i>E</i> (GPa)	<i>H</i> (MPa)	<i>E</i> (GPa)	<i>H</i> (MPa)
Load controlled	1 mN	19.94 ($\sigma = 0.8$)	780 ($\sigma = 29$)	16.68 ($\sigma = 0.29$)	861 ($\sigma = 28$)
	5 mN	16.9 ($\sigma = 0.36$)	513 ($\sigma = 17$)	14.46 ($\sigma = 0.56$)	550 ($\sigma = 32$)
Displacement controlled	300 nm	19.58 ($\sigma = 0.45$)	682 ($\sigma = 22$)	18.16 ($\sigma = 0.18$)	856 ($\sigma = 34$)
	600 nm	17.34 ($\sigma = 0.69$)	490 ($\sigma = 12$)	15.63 ($\sigma = 1.42$)	648 ($\sigma = 51$)

**Figure 3.** Nanoindentation of *syn*-B₁₈ and *anti*-B₁₈. (a) Creep test (under load-controlled mode) showing the indenter displacement during the hold time for both the crystals and the corresponding *P*-*h* curves (b). (c) Stress-relaxation experiment under depth-controlled mode showing the indenter displacement during the hold time of 50 s and the corresponding *P*-*h* curves for both the crystals together (d). (e) and (f) represent the loading rate dependency of elastic modulus and hardness for both the crystals, respectively.

indentations were performed on the (001) planes, which represent the major faces of crystals (Figures S1 and S2). To ensure consistent load–displacement responses, at least five indentations were made on five crystals each for both samples at different regions of the crystal surface (Figures S7–S23).

Initial experiments involved quasi-static measurements, where the load was applied to the crystals without frequency, followed by dynamic measurements with frequencies from 20 to 200 Hz. To evaluate material resilience under stress, load-controlled nanoindentation tests were conducted using 1 mN and 5 mN peak loads. This selection aimed to examine elastic properties as a function of applied force. All measurements used a trapezoidal load function with different loading rates, achieved by adjusting loading–holding–unloading times (seconds) to 5–2–5, 1–30–1, and 5–50–5, respectively. Displacement-controlled experiments were also carried out at two different depths of 300 and 600 nm, respectively employing displacement functions of 5–2–5 s. To understand time-dependent mechanical behavior, we investigated stress relaxation, creep behavior, and dynamic mechanical analysis, elaborated in the subsequent sections.

First, load-controlled nanoindentation studies were performed on both crystals at a fixed load of 5000 μ N using a trapezoidal load function of 5–2–5 s. The load–displacement

curves (Figure 2a) revealed displacements of approximately 678 nm for *syn*-B₁₈ and 710 nm for *anti*-B₁₈, indicating that *anti*-B₁₈ is less stiff than *syn*-B₁₈. Residual displacements of 149 nm for *syn*-B₁₈ and 161 nm for *anti*-B₁₈ further supported this observation. Additional load-controlled indentations at varying load functions with different loading rates, holding time, etc. (1–30–1 and 5–50–5 s) and different loads (1000 μ N) consistently showed that *anti*-B₁₈ undergoes larger displacements than *syn*-B₁₈ for the same maximum load (Figures S7–S16). Displacement-controlled nanoindentation studies at fixed depths of 300 and 600 nm (Figures S17–S23) also demonstrated similar mechanical properties between *syn*-B₁₈ and *anti*-B₁₈. Multiple indentation tests provided reproducible load–displacement curves, enabling the determination of elastic modulus (*E*, resistance to elastic deformation) and hardness (*H*, resistance toward plastic deformation) through Oliver and Pharr method.⁵⁵ Statistical analysis yielded mean *E* values of 19.94 ($\sigma \approx 0.80$) GPa for *syn*-B₁₈ and 16.68 ($\sigma \approx 0.29$) GPa for *anti*-B₁₈, with corresponding hardness values of 780 ($\sigma \approx 29$) MPa and 861 ($\sigma \approx 28$) MPa, respectively (Table 1). Multiple *P*-*h* curves at different loads and different displacements, and the Gaussian distribution of these values validated the consistency and reliability of the measurements (Figures S8–23).

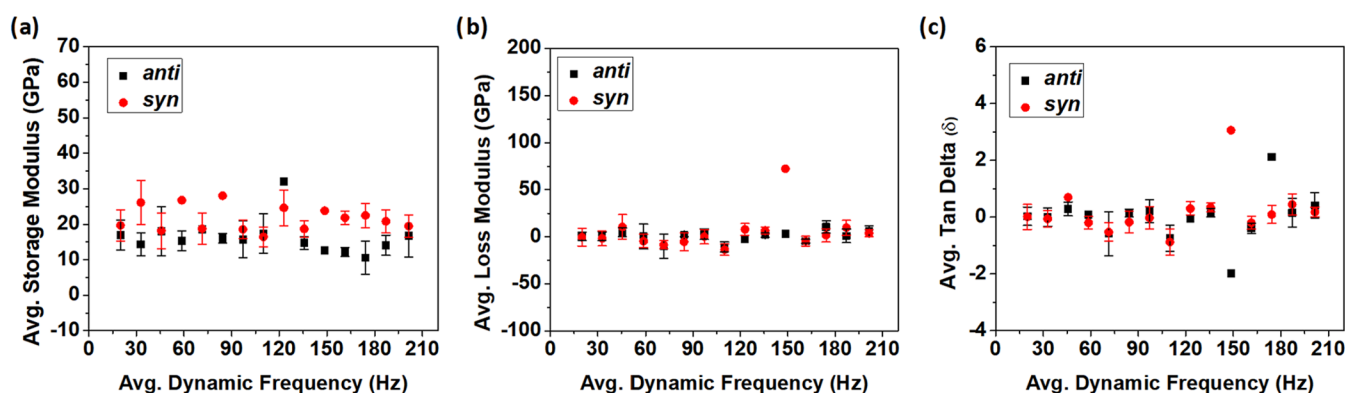


Figure 4. Nano-DMA analysis of *syn*-B₁₈ and *anti*-B₁₈. (a–c) Frequency dependent variation of average storage modulus, loss modulus, and tan-δ, respectively (error bars are omitted for outliers' data points).

During indentation studies, significant “pop-in (displacement-bursts)” events were observed in the load–displacement curves of both crystals, suggesting dislocation of molecular layers within the crystal lattice (Figure 2a,b). These events result from the slipping or breaking of crystal planes. This anisotropic behavior is consistent with direction-dependent mechanical responses observed in other molecular crystals.⁸ However, our study was limited to specific crystal planes (major faces) due to the challenges related to mechanical manipulation with tiny crystals and accessing minor faces.

For better understanding and comparison of their mechanical responses, and to probe their time-dependent behavior, if any, creep and stress relaxation tests were conducted for *syn*-B₁₈ and *anti*-B₁₈ crystals. Creep tests (Figures 3a and S26–28) revealed primary creep in both crystals, with *anti*-B₁₈ exhibiting an initial displacement of 250 nm compared to the *syn*-B₁₈ (270 nm) under a 1000 μN load. However, neither crystal showed secondary or tertiary creep, indicating stability under stress. Stress relaxation behavior was observed in both the crystals (Figure 3c), though it was less pronounced in the creep tests (Figure 3a). Stress relaxation tests demonstrated a gradual decrease in load over time, indicating a gradual release of internal stress. This behavior is akin to that of elastomers and thermosetting polymers, which exhibit stress relaxation without substantial creep due to their ability to adapt to deformed states or resist flow under sustained loads.⁵⁶ Stress reduction in molecular crystals may occur through mechanisms such as molecular rotations or vibrations, and lattice rearrangements. Indentation tests at varying loading rates (Figures S7–S18) revealed that *E* and *H* values decreased with increasing loading rates from 200 to 1000 μN/s (Figure 3e). Higher *E_r* at lower loading rates is likely due to atypical or unique molecular reorganization under slower deformation.

Dynamic Mechanical Analysis (DMA) of *syn*-B₁₈ and *anti*-B₁₈ Crystals

The time-dependent properties observed in the quasi-static nanoindentation experiments, such as creep and stress relaxation behaviors, prompted us to investigate the dynamic mechanical response of the crystals at the nanometer length scale. A viscoelastic material is expected to exhibit both viscous (capability of dissipating energy) as well as elastic (ability to deform reversibly) behaviors simultaneously. We determined the time dependent response or the viscoelastic behavior of both the *syn*-B₁₈ and *anti*-B₁₈ crystals using a typical frequency sweep nano-DMA test.^{42,50} The viscoelastic properties, such as

storage modulus (*G'*), loss modulus (*G''*), and tan-δ, are plotted as a function of frequency, as shown in Figure 4a–c. Generally, viscoelastic materials show frequency dependency of the storage and loss modulus and thus exhibit damping behaviors. We found that, both the storage modulus which represents the energy stored within the system, and the loss modulus which characterizes energy dissipation or the viscous part of the sample, remained nearly constant across all measured frequencies. Both the crystals exhibited similar sensitivity to frequency changes (Figure 4a,b). The complex modulus shows higher mean values which are consistent with the values obtained from the quasi-static indentation method. The low or nearly negligible values of tan δ (Figure 4c) further confirmed that both crystals exhibit minimal energy dissipation and a negligible phase lag between applied stress and resulting strain, indicating more of elastic behavior than the viscous nature.

Structure–Property Correlation in Borane Clusters

The mechanical response of *syn*-B₁₈ and *anti*-B₁₈ is intimately linked to their distinct structural characteristics, particularly the arrangement of their macropolyhedral frameworks and the network of B–H···μHBB, B–H···B, and B···B interactions/short contacts within the crystal lattice (Figure 1a and 1b). The *syn*-B₁₈ demonstrates a higher elastic modulus of approximately 20 GPa and a hardness of around 764 MPa, attributable to its more compact and highly interconnected crystal packing. The dense, mechanically interlocked networks of B–H···μHBB, B–H···B, and B···B interactions in the *syn*- isomer serves as an effective reinforcing scaffold, distributing mechanical stress and enhancing the overall rigidity of the lattice. In contrast, *anti*-B₁₈ exhibits a slightly lower elastic modulus of around 17 GPa but a higher hardness value of approximately 882 MPa. This distinction stems from its alternative packing motif with more isotropic arrangements of boron cages and B–H···B, and B···B short contacts than in the *syn*- isomer. While this leads to a marginally more flexible lattice, it also results in localized strengthening, enhancing resistance to plastic deformation and increasing hardness.

The mechanical behavior of both *syn*- and *anti*-B₁₈ crystals correlates directly with the presence and cumulative energy of B···μHBB, B–H···B, and B···B interactions/short-contacts embedded in their frameworks. Although these noncovalent short contacts are individually weak (estimated at ~2–4 kJ/mol per interaction),^{30,41,58} they form a dense network that reinforces the crystal structure. The elastic modulus is particularly sensitive to the number and geometric arrangement of these

Table 2. Comparison of Mechanical Properties of *syn*-B₁₈ and *anti*-B₁₈ with Various Other Types of Materials Obtained by Different Nanoindentation Measurements

Different systems		Crystal classes	Elastic modulus, E (GPa)	Hardness, H (MPa)	refs
Metal clusters	$[\text{Ag}_{29}(\text{1,3-BDT})_{12}(\text{PPh}_3)_4]^{3-}$	Cubic	5.66 ± 0.44	282 ± 53	43
	$\text{Cu}_4(\text{oCBT})_4$ (001)	Trigonal ($P3_121$)	9.79 ± 0.98	534 ± 82	42
Active pharmaceutical ingredients	Isoniazid (010)	Orthorhombic ($P2_12_12_1$)	18.82 ± 1.25	610 ± 13	21
	Saccharin (100)	Monoclinic ($P2_1/c$)	13.36 ± 0.05	610 ± 10	12
MOF (001)		Monoclinic ($P2_1/c$)	≈ 6.79	≈ 790	44
COF (thin film)		—	≈ 1.46	≈ 23	57
Mechanically responsive organic crystals	BH_3NMe_3 (010) (3D plastic crystal)	Trigonal ($R3m$)	0.21 ± 0.04	9.9 ± 2.6	13
	α -Glycine (001) [amino acid (brittle)]	Monoclinic ($P2_1/n$)	44 ± 1	—	8
	SB1 (100) [Plastically bendable]	Monoclinic ($P2_1/c$)	8.4 ± 1	317 ± 33	14
	BPNA (100) [Elastically flexible]	Hexagonal ($P6$)	7.7 ± 0.8	200 ± 10	15
Boranes	<i>syn</i> - $\text{B}_{18}\text{H}_{22}$	Monoclinic ($P2_1/c$)	19.94 ± 0.8	780 ± 29	This work
	<i>anti</i> - $\text{B}_{18}\text{H}_{22}$	Orthorhombic ($Pccn$)	16.68 ± 0.29	861 ± 28	This work

weak interactions. The higher the density and connectivity of these interactions, the higher is the elastic modulus observed in these systems. This highlights the crucial role of weak, directional interactions in dictating the bulk mechanical properties of boron cluster crystals and provides a molecular-level explanation for their observed nanomechanical behavior. In contrast, several reported organic crystals that exhibit higher hardness and elastic modulus values have been predominantly attributed to strong intermolecular interactions, particularly hydrogen-bonding networks (Table 2). A diverse range of materials including MOFs, COFs, metal-nanoclusters, organic crystals with different mechanical responses were chosen for comparison because of their well-studied quantification of mechanical properties and provide relevant benchmarks for assessing the mechanical robustness of the present borane crystals. The comparison therefore highlights the role of intermolecular interactions in determining the mechanical response of molecular solids.

To investigate the role of functional group substitution and polyhedral architectures, if any, we studied the mechanical properties of SH-*syn*-B₁₈H₂₁ (which is a derivative of *syn*-B₁₈H₂₂), B₁₀H₁₄ (with only single polyhedral) and its thiolated analogue, SH-B₁₀H₁₃ (Figures S24–27). We found that the macropolyhedral SH-*syn*-B₁₈H₂₁ has almost similar higher values of *E* (~15 GPa) and *H* (~540 MPa) as that of *syn*- or *anti*-B₁₈H₂₂, however, the *E* and *H* values decrease significantly in case of single polyhedral systems. The *E* and *H* values were ~9 GPa and ~142 MPa for B₁₀H₁₄, and ~11 GPa and ~590 MPa for SH-B₁₀H₁₃, respectively. To rationalize the differences in mechanical properties, we have performed energy frameworks analysis of *syn*-, *anti*-B₁₈H₂₂ and B₁₀H₁₄ (please see SI for details of calculations, Figures S28–30).^{19,45} We found that the aggregate total pairwise interaction energies (*E*_{total}) shared by each molecule of *syn*-B₁₈H₂₂ is highest among all other systems which corresponds well with its highest *E* value compared to other systems. The *E*_{total} values of these systems are as follows: *syn*-B₁₈H₂₂ (−241.2 kJ/mol) > *anti*-B₁₈H₂₂ (−217.8 kJ/mol) > B₁₀H₁₄ (−154.2 kJ/mol), which correlates well with their mechanical properties as follows: *syn*-B₁₈H₂₂ (*E* ~ 19 GPa) > *anti*-B₁₈H₂₂ (*E* ~ 17 GPa) > B₁₀H₁₄ (*E* ~ 8 GPa).

Computational Insights

To support and interpret the experimental observations, we performed first-principles calculations of the elastic properties of *syn*- and *anti*-B₁₈ isomorphs using plane-wave density functional theory (DFT),^{46,47} as implemented in the Vienna *ab initio* Simulation Package (VASP).⁴⁸ The core–valence electron interactions were described using projector augmented-wave (PAW) pseudopotentials, and the exchange–correlation energy was treated within the generalized gradient approximation (GGA) using the Perdew–Burke–Ernzerhof (PBE) functional.^{49,51,52} To accurately account for long-range van der Waals (vdW) interactions, which are particularly important in molecular crystals where weak intermolecular forces influence structural and mechanical behavior, we incorporated the Tkatchenko–Scheffler (TS) dispersion correction scheme.⁵³ The TS approach provides an efficient and physically grounded correction by deriving environment-dependent dispersion coefficients from the electron density, thereby improving the reliability of DFT predictions for noncovalently bonded systems. This combined methodology enabled us to achieve a more realistic description of the elastic response of B₁₈H₂₂ isomorphs and to better understand the influence of weak intermolecular interactions on their mechanical properties. Each of the unit cells has been distorted with small amount of shear strains as mentioned in the Experimental Section (average errors in lattice parameters below 0.7%).

The distinct elastic behaviors of *syn*-B₁₈ (monoclinic) and *anti*-B₁₈ (orthorhombic) originate from their crystallographic symmetries, which govern both experimental measurements and computational modeling approaches. As shown in Table S1 monoclinic systems, with a single plane of symmetry, require 13 independent elastic constants to describe directional stiffness variations caused by coupled shear–normal deformations (e.g., *C*₁₆, *C*₂₆). In contrast, orthorhombic structure possesses three mutually perpendicular symmetry planes, resulting in higher crystallographic symmetry. Consequently, it is characterized by only 9 independent elastic constants, with all shear–normal coupling terms eliminated. This structural dichotomy is captured computationally by symmetry-specific strain configurations in the Python code (GitHub code provided in SI) and elsewhere,⁵⁴ which automates VASP^{48,49} input file generation for DFT calculations. For example,

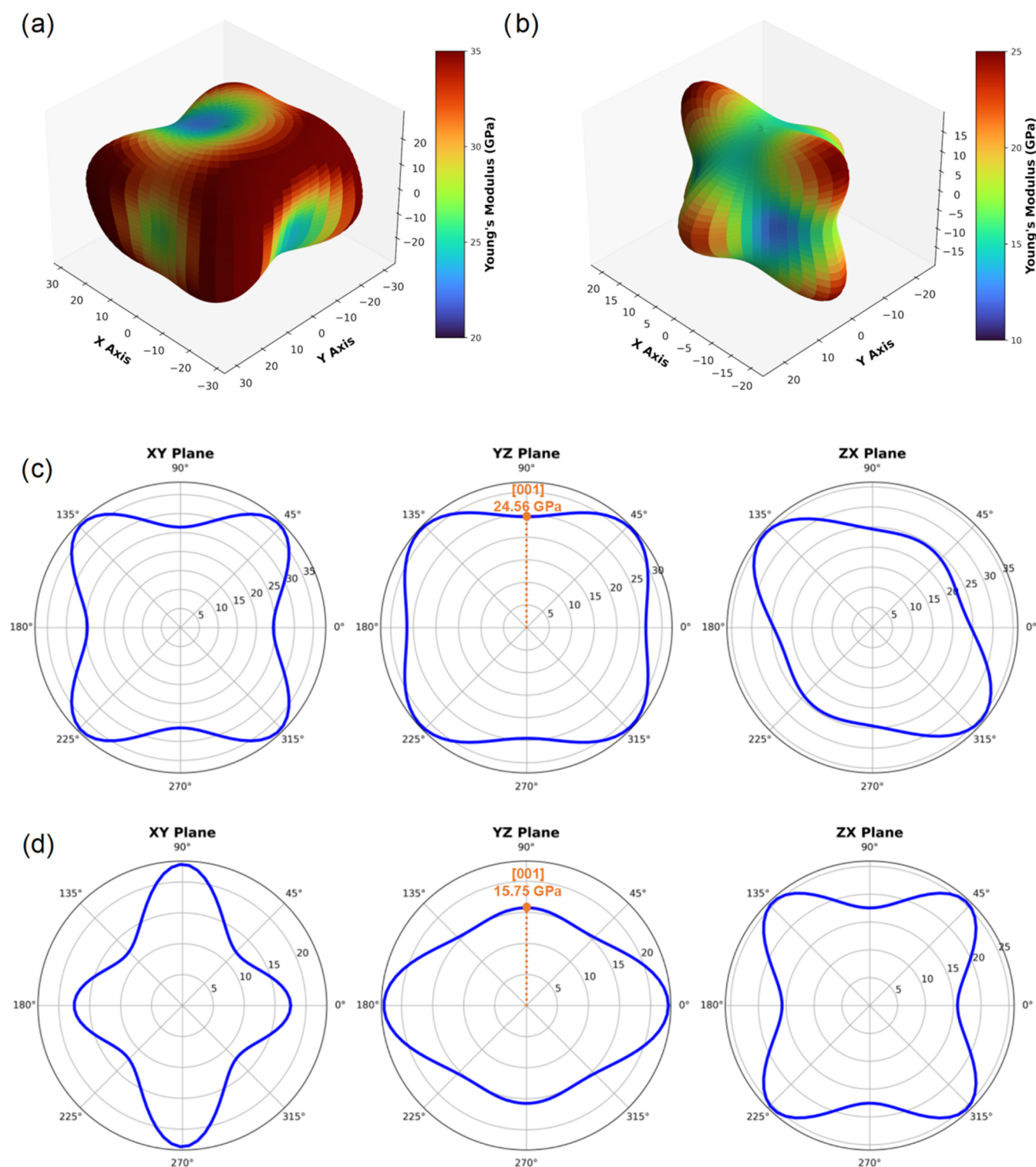


Figure 5. Computed three-dimensional representations of the directional Young's modulus for (a) *syn-B*₁₈ and (b) *anti-B*₁₈. (c, d) for each plot, *syn-B*₁₈ in (c) and *anti-B*₁₈ in (d), the distance from the origin to the surface at any point corresponds to the Young's modulus value in that specific spatial direction. Axes are labeled in GPa, with negative values indicating orientation rather than magnitude.

monoclinic simulations apply 13 unique strain patterns, while orthorhombic setups use only 9 strain deformation.

The directional elastic anisotropy visualizations for *syn-B*₁₈ (monoclinic) and *anti-B*₁₈ (orthorhombic) structures reveal profound differences in mechanical behavior that directly correlate with their crystallographic symmetries and elastic constant matrices (Figure 5, Table S2). The *anti-B*₁₈

orthorhombic structure exhibits a distinctive four-lobed diamond pattern in the XY plane (Figure 5b), indicating strong directional stiffness variations with maximum values occurring at 45° intervals, which aligns with the orthorhombic symmetry constraints that eliminate certain cross-coupling terms while preserving others. The YZ plane for this structure displays a more rounded, less anisotropic profile, suggesting

relatively uniform elastic response perpendicular to the principal crystallographic axis, while the ZX plane shows irregular triangular-like patterns with pronounced directional variations. These observations are consistent with the calculated elastic constants showing $C_{22} = 23.12$ GPa versus $C_{16} = 20.49$ GPa, creating the directional stiffness hierarchy that manifests as the observed polar plot asymmetries (Figure 5d).

In stark contrast, the *syn*- B_{18} (monoclinic) structure demonstrates significantly more complex anisotropic behavior across all three crystallographic planes, with the XY plane exhibiting a smoother, more rounded contour compared to the sharp diamond pattern of the orthorhombic phase in *anti*- B_{18} (Figure 5a and 5c). The YZ and ZX planes for the monoclinic structure show moderate to significant directional dependencies with irregular contours that reflect the presence of shear-normal coupling terms like $C_{15} = -0.69$ GPa and $C_{25} = 3.96$ GPa in the elastic constant matrix (negative values indicating orientation rather than magnitude). This coupling creates the complex mechanical response patterns visible in the polar plots, where stress applied in one direction induces strain components in multiple other directions, fundamentally altering the directional stiffness landscape compared to higher-symmetry systems (Figure 5a). The calculated elastic constants for the *syn*- B_{18} ($C_{22} = 34.71$ GPa and $C_{11} = 29.76$ GPa) are higher than the *anti*- B_{18} isomer, which correlated well with their experimentally obtained E and H values.

The three-dimensional elastic surfaces provide the most compelling evidence for the dramatic differences between these crystal structures, with the *syn*- B_{18} surface exhibiting a highly irregular, complex topology characterized by multiple lobes, indentations, and steep gradients (Figure 5a).

The red regions indicating high stiffness are concentrated in specific crystallographic orientations, creating a heterogeneous mechanical landscape that reflects the 13 independent elastic constants required to describe monoclinic behavior. Conversely, the *anti*- B_{18} surface shows a more symmetric but still significantly anisotropic topology with smoother transitions between stiff and compliant directions, demonstrating how the nine independent elastic constants of orthorhombic systems create more predictable directional behavior while still maintaining substantial anisotropy (Figure 5b). In each plot, the distance from the origin to the surface corresponds to the Young's modulus value in that spatial direction.

These computational results not only corroborate the experimental findings but also offer atomic-scale insights into the mechanisms driving the differing mechanical behaviors of the *syn*- and *anti*-isomers. The combined strength of experimental and theoretical approaches highlights the pivotal influence of crystallographic architecture and intercluster interactions in shaping the nanomechanical properties of borane clusters.

CONCLUSIONS

In conclusion, we have investigated the nanomechanical properties of the macropolyhedral borane crystals of *syn*- $B_{18}H_{22}$ and *anti*- $B_{18}H_{22}$ isomers through a combination of nanoindentation experiments, density functional theory calculations, crystallographic and energy-frameworks analyses. Both crystals exhibit exceptional mechanical robustness, displaying elastic moduli of ~ 20 and ~ 17 GPa and hardness values of ~ 764 and ~ 882 MPa for *syn*- $B_{18}H_{22}$ and *anti*- $B_{18}H_{22}$, respectively, despite being composed exclusively of

boron and hydrogen atoms. Comparative studies involving the parent single-polyhedral borane $B_{10}H_{14}$ and related borane derivatives reveal substantially lower mechanical performance, highlighting the influence of polyhedral architecture on crystal rigidity. Structural analyses indicate that the macropolyhedral $B_{18}H_{22}$ isomers form three-dimensional interlocked packing arrangements sustained by multiple $B\cdots\mu-BHB$, $B-H\cdots B$, and $B\cdots B$ contacts, whereas the reference single-polyhedral systems exhibit lower-dimensional interaction networks. Consistent with these observations, energy-framework calculations reveal a positive correlation between aggregate intermolecular interaction energies and elastic response across the borane series. The distinct mechanical behavior observed for the *syn*- and *anti*-isomers further demonstrates the sensitivity of mechanical properties to crystal packing and the intermolecular interaction topology.

Together, these findings establish a clear structure–mechanical property relationship in borane molecular crystals and identify macropolyhedral fusion as a structural feature associated with enhanced mechanical robustness in cluster-based molecular solids. In a broader perspective, this work expands the materials chemistry of borane clusters and provides insight into how molecular architecture and crystal packing can be leveraged to tailor the mechanical properties of light-element molecular materials.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.chemmater.6c01961>.

Additional experimental details; supramolecular packing and macropolyhedral cluster interactions; optical images and crystal face indexing; computational calculations of modulus values; ATR-IR spectra; energy framework calculations; load–displacement plots; statistical analysis; and scanning probe microscopy (SPM) images (PDF)

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Author Contributions

#A.M. and D.K.P. contributed equally to this work. D.K.P. and J.M. executed the experimental synthesis, characterization, and data analysis. A.M. performed the nanomechanical investigation and data analysis. P.K. and I.A. carried out the theoretical calculations. D.K.P. prepared the first draft of the manuscript and all authors contributed to the preparation of the manuscript T.P., P.G., S.G., and T.B. supervised the project.

Notes

The authors declare no competing financial interest.

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