

(8) Amorphous powder; IR 3300, 1780 cm^{-1} ; NMR (CDCl_3) δ 1.49 (9 H, s), 2.12 (3 H, s), 3.20 and 3.40 (2 H, AB q, $J = 18$ Hz), 3.58 (3 H, s), 4.58 (1 H, s), 4.93 (1 H, s), 8.35–9.08 (3 H, m).

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Icosahedral Boron Frameworks. The Structure of $\gamma\text{-AlB}_{12}$

Sir:

We have determined the structure of $\gamma\text{-AlB}_{12}$. The solution to this long-standing problem has contributed significantly to our understanding of the structural chemistry of elementary boron and icosahedral borides. The structure is based upon a framework of boron icosahedra that is intimately related to the frameworks in $\alpha\text{-AlB}_{12}$ ¹ and BeB_6 .² Moreover, we have determined that all of these structures are derivative from a parent framework, that of β -rhombohedral boron,³ the thermodynamically stable form of the element.⁴ We also suggest that such derivative frameworks will be appropriate for the description of another preparation of boron⁵ and for a variety of nonstoichiometric borides.⁶

A single crystal of $\gamma\text{-AlB}_{12}$ was kindly provided by Dr. J. A. Kohn.⁷ Diffraction symmetry and extinctions corresponded to $P2_12_12_1$ with $a = 16.623 \pm 0.005$, $b = 17.540 \pm 0.005$, and $c = 10.180 \pm 0.005$ Å. The densities $D_m = 2.56$ and $D_x = 2.55$ g cm^{-3} correspond to a unit cell content of $\text{B}_{352}\text{Al}_{27.9}$. Intensities were measured in a θ - 2θ scan mode with Mo $K\alpha$ radiation on a Picker card controlled diffractometer; of 5539 non-absent independent reflections investigated ($\sin \theta/\lambda \leq 0.7456$), a total of 5439 were statistically observable. With 427 independent parameters in the refinement, this provided a data-parameter ratio of 12.7. No corrections were made for extinction or absorption.

The structure was solved by iterative Fourier methods using initial models derived from stereochemical principles for icosahedral boron framework structures that were developed in this laboratory.⁸ Final block diagonal least-squares refinement of the structure yielded a standard residual $R = 0.059$ for the observed data; a weighted residual $R_2 = [\sum w(|F_o| - |F_c|)^2 / \sum w |F_o|^2]^{1/2} = 0.078$ was obtained with unit weights. Isotropic thermal parameters were used for all boron atoms but six fully occupied and two partially occupied aluminum sites were refined anisotropically. Final difference Fourier syntheses were featureless with background noise at a level of $\sim 0.5 \text{ e } \text{Å}^{-3}$.

Icosahedral structures can be described in remarkably diverse but nevertheless complementary ways depending upon the basic unit of structure that is selected for emphasis.⁴ Because of this diversity we now introduce a nomenclature that characterizes the symmetry of selected boron subunits with standard Schoenflies notation. Thus, the now conventional representation⁹ of the β -rhombohedral boron structure, $\beta\text{-B}_{105}\text{-(R}\bar{3}m)$, would be described as a rhombohedral (quasi-cubic) framework of $\text{B}_{84}\text{-(I}_h)$ units interbonded through rhombohedrally directed pentagonal faces with holes in the framework filled by $\text{B}_{10}\text{-(C}_{3v})$ units that fully interlink the equatorial pentagonal faces. This succinct statement provides a graphic description of a complex structure that requires only a moderate familiarity with the $\text{B}_{84}\text{-(I}_h)$ unit. An alternative description is required, however, to reveal the hitherto unnoted relationships to the framework structures of $\alpha\text{-AlB}_{12}$ and $\gamma\text{-AlB}_{12}$.

Boron icosahedra can be centered at all of the vertices of a regular 3636 kagomé plane net¹⁰ with twofold axes perpendicular to the net and then oriented so as to fully satisfy the

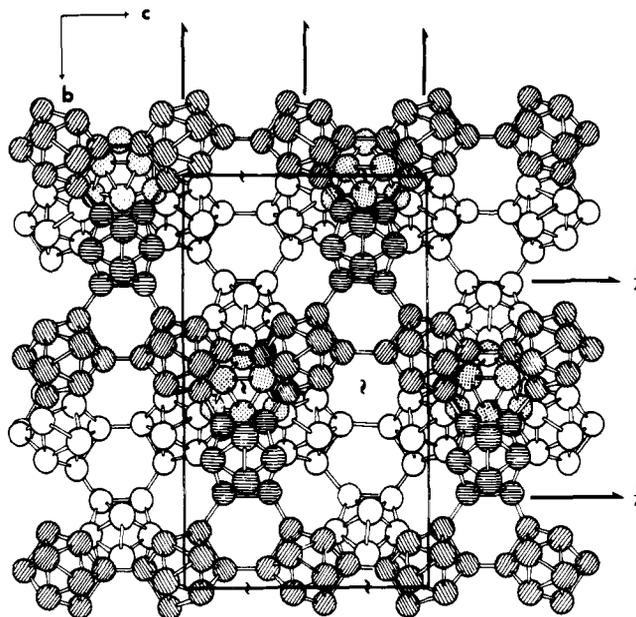


Figure 1. A projection along the a axis of the framework of boron icosahedra in $\gamma\text{-AlB}_{12}$. Two kagomé nets and the interleaving triangular net frame the truncated tetrahedral holes.

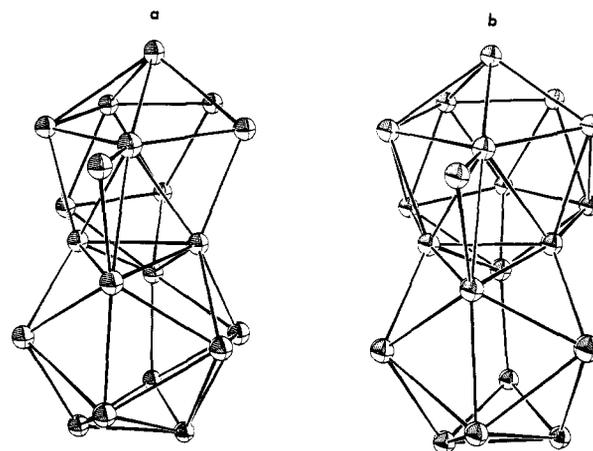


Figure 2. Condensed units of boron icosahedra and icosahedral fragments: a, $\text{B}_{20}\text{-(C}_2)$ unit, found in $\alpha\text{-AlB}_{12}$ and $\gamma\text{-AlB}_{12}$; b, $\text{B}_{20}\text{-(C}_2)$ unit, found in $\gamma\text{-AlB}_{12}$.

symmetry of the plane group $p6m$; indeed, the resulting sheet of icosahedra also possesses mirror symmetry in the net plane. If additional boron icosahedra (with threefold axes perpendicular to the plane net) are suitably centered at the tetrahedral apices above one of the two subsets of triangular sites in the kagomé net, the effective plane group symmetry of the array becomes $p3m1$. A tetrahedron of four boron icosahedra possesses the full symmetry of the tetrahedral group and is designated as the $\text{B}_{48}\text{-(T}_d)$ unit. The bi-layered sheet of icosahedra comprised of a kagomé layer of interconnected $\text{B}_{48}\text{-(T}_d)$ units is the basic layer of structure in the frameworks of $\gamma\text{-AlB}_{12}$, $\alpha\text{-AlB}_{12}$, and β -rhombohedral boron. The frameworks are simply generated by appropriately stacking these layers and it is important to emphasize that in every case all intericosahedral bonds in the frameworks closely satisfy the preferred pentagonal pyramidal bonding for elementary boron.⁴

There are two distinct stacking operators that relate successive $\text{B}_{48}\text{-(T}_d)$ kagomé layers so as to preserve the directed geometry of icosahedral bonding. The first, a 2_1 operator normal to the layer and colinear with the "local" threefold axes of the $\text{B}_{48}\text{-(T}_d)$ units, generates the framework of $\gamma\text{-AlB}_{12}$ as depicted in Figure 1. The appropriate metrics of the orthorhombic cell are preserved in a framework of symmetry

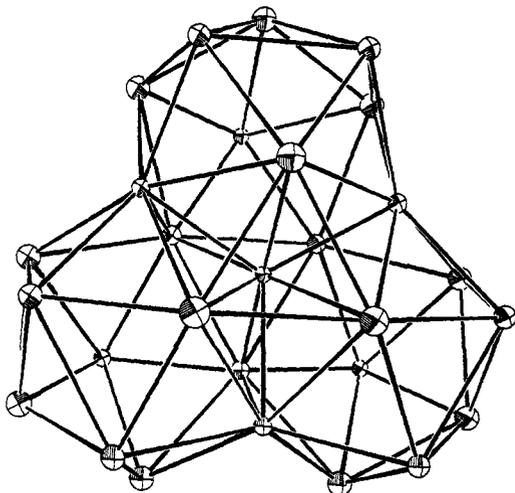


Figure 3. Condensed unit of three boron icosahedra, $B_{28}(C_{3v})$, found in β -rhombohedral boron.

$P6_3/mmc$. The alternative operator, a 3_1 normal to the layer, produces a three-layer framework structure with the full cubic symmetry of the group $Fd\bar{3}m$. This is the framework both of α - AlB_{12} and of β - $B_{105}(R\bar{3}m)$. It should be mentioned that these frameworks can be derived equally well through formal layer twin operators.⁸

Further insight into the relationships among the structures can be achieved by focusing upon still another structural unit in which 12 interbonded icosahedra define the vertices of a regular truncated tetrahedron. Both frameworks can be generated in detail by appropriately sharing hexagonal faces of this elegant $B_{144}(T_d)$ unit. Each of the large holes thus defined has 12 internally directed, unsatisfied bonds that sharply delimit the size, the geometry, and the symmetry of the structural units contained therein. In λ - AlB_{12} , the holes are alternately occupied by one of two novel structural units condensed from boron icosahedra (Figure 2). They fully satisfy the internal bonding and interlink in a subsidiary framework through the open hexagonal faces. Along with some attendant deviations from ideality, this reduces the overall symmetry of the structure to $P2_12_12_1$. Similarly, in α - AlB_{12} , the $B_{20}(C_2)$ unit lies on the twofold axis of the hole in the $Fd\bar{3}m$ framework and the symmetry of the structure is reduced to $P4_32_12$. Finally and dramatically, the $B_{28}(C_{3v})$ unit⁴ (Figure 3) occupies the same tetrahedral hole in the β - $B_{105}(R\bar{3}m)$ structure, preserves one of the threefold axes of $Fd\bar{3}m$, and produces the observed rhombohedral symmetry.

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Supplementary Material Available. Tables of atomic positional parameters and temperature factors and of observed and calculated structure factors (32 pages). Ordering information is given on any current masthead page.

References and Notes

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Three-Carbon Annulation. Formation of Five-Membered Rings from Olefins via Diels-Alder Reactions

Sir:

Owing to the increasing appearance of cyclopentane rings in large numbers of natural products, especially those of biological importance, great effort has recently been expended to develop new synthetic methods for the construction of five-membered-ring systems.¹⁻⁸ Although many of these newly developed methods very successfully prepare five-membered rings, they are often not applicable to the closely related problem of three-carbon annulation, i.e., the attachment of a three-carbon unit to two adjacent carbons of a cyclic or acyclic precursor to form a cyclopentane ring, i.e., $[3 + 2 \rightarrow 5]$. No good general method exists for this transformation, although the two corresponding ones, $[2 + 2 \rightarrow 4]$ (photochemical cyclization of two olefins) and $[2 + 4 \rightarrow 6]$ (Diels-Alder reaction), are quite well known and are of great synthetic utility. We wish now to report the successful accomplishment of this goal of three-carbon annulation, namely, a highly versatile process for the formation of cyclopentanones from olefins in good overall yields via a Diels-Alder reaction as the key step.

The direct attachment of a three-carbon unit to an olefin by some cycloaddition process has been reported previously in the literature.¹⁻⁸ However, in nearly all cases, the double bond was activated by electron-donating substituents (usually ketone derivatives such as enol acetate,² enamine,³ trimethylsilyl enol ether,⁴ or enolate of β -keto ester⁵ or via ketones themselves^{1,6}) or electron-withdrawing substituents (normally α,β -unsaturated esters⁷ or sulfoxides⁸). To impart the greatest generality to the method, we desired to place as few restrictions as possible on the nature of the olefinic substrate so that not only electron-rich and electron-poor olefins but even simple unsubstituted olefins would afford good yields of the final cyclopentanone products. For this reason we have developed a method using the very highly reactive compound, dimethoxytetrachlorocyclopentadiene (**1**) as the diene component in a Diels-Alder reaction. The remarkable reactivity of this molecule in cycloaddition reactions was first recognized by McBee,⁹ who observed that even simple olefins such as allyl alcohol, allyl bromide, and indene gave good yields of cycloadducts. Much subsequent effort has extended the scope of this facile cycloaddition reaction to include a large variety of olefins and alkynes.¹⁰⁻¹²

The general method is outlined in Scheme I; the yields obtained in its application to a variety of olefins are listed in Table I. When the diene **1** is heated in the presence of the olefins **2a-f**, high yields of the Diels-Alder adducts **3a-f** are formed.¹³ Replacement of all the chlorine atoms in compounds **3a-f** by