and the reduction (or oxidation) is attributable to the difference between these two rates.

The exchangeable surface oxygen, n_s, of $ZnFe_2O_4$ is about five times larger than that of $ZnCr_2O_4$ and about thirty times larger than that of $ZnAl_2O_4$. This relationship is in qualitative agreement with the order of the amounts of ^{18}O transferred to carbon monoxide (Table II): $ZnFe_2O_4 > ZnCr_2O_4 > ZnAl_2O_4$. The tendency of the catalysts to be reduced or oxidized coincides with their oxidizing power; $ZnFe_2O_4$ will oxidize this gas more readily than $ZnCr_2O_4$, while $ZnAl_2O_4$ will reduce it slightly, as one might predict from its tint.

Now let us consider the nature of the surface state of these catalysts. No transfer of ^{18}O to carbon monoxide was observed even at 300° with grayish green $ZnCr_2O_4$ which had been slightly reduced with hydrogen at 100 mm. for 30 minutes at 480°. Another sample of $ZnCr_2O_4$, which had been evacuated at 10^{-3} mm. at 500° for 1 hr., also lost its catalytic activity. Neither treatment caused any change which could be observed by X-ray diffraction analysis. This suggests that the excess oxygen on the surface of $ZnCr_2O_4$, a p-type semi-conductor, is essential for its catalytic activity. Hence, for $ZnCr_2O_4$, (K)O in (2) represents the presence of excess oxygen and (K) its disappearance, which is caused by reduction by the ambient gas.

$ZnAl_2O_4$ and $ZnFe_2O_4$ are *n*-type semi-conductors; $ZnAl_2O_4$ prepared in this study was reduced somewhat from the stoichiometric composition. In $ZnFe_2O_4$, and inverse spinel, the iron ions distributed as Fe^{+++} both in the 8f and 16c positions are liable to exchange the valency as $Fe^{+++} \rightleftarrows Fe^{++}$. Accordingly, (K) and (K)O correspond in $ZnAl_2O_4$ to the defect of surface oxygen and to the state where the defect is filled with oxygen atoms; and in $ZnFe_2O_4$, to the site around a reduced iron ion, and to that around which all the iron ions are oxidized.

For the elucidation of the precise nature of (K)O and (K) and the identification of the rate-determining steps, further investigation is necessary.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, CORNELL UNIVERSITY]

The Structure of Tetragonal Boron[1]

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The fifty boron atoms of the tetragonal unit are divided among four approximately regular icosahedra centered in the positions $^1/_4\ ^1/_4\ ^1/_4$, $^3/_4\ ^3/_4\ ^1/_4$, $^3/_4\ ^1/_4\ ^3/_4$, $^1/_4\ ^3/_4\ ^3/_4$ of $P4_2/nnm$ with two individual atoms in 2b:00 $^1/_2$, $^1/_2\ ^1/_2$ 0. Each boron atom of an icosahedron forms six bonds directed toward the corners of a pentagonal pyramid, five within the same icosahedron, the sixth to an adjacent icosahedron or to an atom in 2b. The resulting framework is continuous in three dimensions. Typical intra- and intericosahedral bond distances are, respectively, 1.805 ± 0.015 and 1.68 ± 0.03 Å. Available single crystals of tetragonal boron are subject to a large and variable degree of internal disorder: the diffraction data afforded by different specimens are notably diverse as regards strength of diffuse scattering, distribution of Bragg intensities, and lattice constants. Typical values of lattice constants are $a = 8.75$, $c = 5.06$ Å.

Introduction

For many years only microcrystalline and often quite impure preparations of elemental boron were available, yielding X-ray powder diffraction patterns of notable complexity and diversity. Recent single crystal studies of three different modifications show boron exhibiting a remarkably wide range of structural complexity. The most recently discovered and structurally simplest modification[2] is *rhombohedral* with but one icosahedral B_{12} group within the unit cell. The structural arrangement[2] is intimately related to that of boron carbide,[3] $B_{12}C_3$. The most easily prepared but structurally by far the most complex modification of boron also is *rhombohedral*,[4] with 108 atoms in the unit cell. We have in progress intensive studies aimed at a determination of structure for this form. The *tetragonal*[5] modification of boron has been most studied.[6] The present paper reports the detailed structural investigation of the tetragonal single crystals (appearing in two widely dissimilar growth habits) prepared by Laubengayer, *et al.*,[6] through reduction of boron tribromide with hydrogen on a hot filament; the fundamental atomic arrangement within the fifty-atom cell of the earlier brief report[5] is confirmed.[7]

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(1) Supported by the Atomic Energy Commission under Contract No. AT(30-1)-878 and by the Research Corporation through a grant for purchase of major equipment used in this study.

(2) L. V. McCarty, J. S. Kasper, F. N. Horn, B. F. Decker and A. E. Newkirk, THIS JOURNAL, **80**, 2592 (1958).

(3) H. K. Clark and J. L. Hoard, *ibid.*, **65**, 2115 (1943); G. S. Zhdanov and N. G. Sevast'yanov, *Compt. rend. acad. sci. U.R.S.S.*, **32**, 432 (1941).

(4) D. E. Sands and J. L. Hoard, THIS JOURNAL, **79**, 5582 (1957).

(5) J. L. Hoard, S. Geller and R. E. Hughes, *ibid.*, **73**, 1892 (1951).

(6) A. W. Laubengayer, D. T. Hurd, A. E. Newkirk and J. L. Hoard, *ibid.*, **65**, 1924 (1943).

(7) Based on the free use of authoritative single crystal data, we expect to prepare (or persuade others[2] to prepare) for publication definitive tables for identifying the known modifications from X-ray powder data. We note here that the powder diffraction pattern[6] for "needle crystals" includes lines not characteristic of tetragonal boron. In taking "clusters" of needles for powdering a good deal of the microcrystalline matrix (formed at a higher temperature since it directly ensheathed the filament) must have been included. The microcrystalline sheath formed in a run with a *filament* temperature of about 1350° gave a powder pattern now identifiable[4] as that of complex

Crystallography of Tetragonal Boron.—Crystals of two distinct habits were found in the preparation[6] of tetragonal boron. Most common were needles growing out from the heated filament more or less along the thermal gradient. The larger specimens, about 0.25 mm. in diameter, gave multiple diffraction spots; less imperfect smaller specimens about 0.10 mm. thick were found to be most useful. All needles showed the full diffraction symmetry of D_{4h}-4/mmm with the unique axis parallel to the needle axis. Twinning on (130) was invariably observed, the individual members being virtually equal in volume. The particularly small rods mentioned[6] as rarely observed gave (weak) diffraction patterns which showed them to be early (but twinned) versions of the needles. Specimen needles large enough to give a useful range of diffraction intensities tended to be carrot-shaped with the blunt end away from the filament. It would appear that at the low temperature (relative to the melting point) of deposition, boron from the vapor phase was deposited on the nearest available sites with little subsequent rearrangement.

The second less commonly represented habit in the preparation[6] was that of plates less than 0.05 mm. thick, virtually regular hexagons in outline, with an effective diameter up to about 0.3 mm. The plates generally were attached to the filament along an edge with the plate face approximately parallel to the thermal gradient. Despite all appearances to the contrary, the plates were shown to have the same fundamental structure as the needles, although lacking the invariable twinning of the latter. The following considerations may account in part for the simultaneous growth of crystals having such widely different habits.

The axial ratio a/c of the tetragonal cell is almost precisely $\sqrt{3}$ with c, the shortest and structurally simplest rational translation, as the probable direction of most rapid growth in a homogeneous environment. Formation of a nucleus with c even roughly along the high thermal gradient should result in a crystal of exaggerated needle-like habit. Formation of a nucleus with c parallel to the filament surface and a secondary axis, say a_2 along the thermal gradient might encourage growth in the latter direction comparable with that along c, giving rise to a crystal plate-like on (100). If, in addition, lateral faces ±(010), ±(011), ±(01̄1) were about equally developed, the resulting crystal would appear as a hexagonal plate.

The plate crystals had this aspect, although closer scrutiny indicated that eight extremely narrow faces of the form {111} usually substituted in pairs for the four faces of {011} cited above. One of the three face diagonals of the hexagon was along c; this unique direction was indicated by (easily overlooked) fine parallel striations present in the surface. Examination of several plates showed that the ragged edge of the hexagon, presumably indicating the line of attachment to the filament, was nearly parallel to the striations, *i.e.*, to c. On several specimens three consecutive angles of the hexagon could be measured on the microscope stage, each to better than one degree. Measured angles were often found to depart from 120° by 2–4°, with the sum of three consecutive angles not equal to 360° within the errors of measurement. The ideal crystallographic angles certainly were not preserved during rapid deposition in the high thermal gradient. Anomalous optical properties[6] must surely be anticipated for very hard crystals grown in such an environment.

Experimental

The structural conclusions of this paper are based upon spectrometrically measured intensity data afforded by two specimens selected from among about twenty examined by X-ray methods. A number of complicating features arising from various unsatisfactory characteristics of the boron crystals are summarized at this point.

In addition to the invariable twinning on (130) of every needle, all specimens were split into at least two macroscopic components, albeit the departure from parallel alignment in favorable cases corresponded to less than ten minutes of angular rotation. On Weissenberg or rotation photographs, nevertheless, the doublet or multiplet character of the specimen was rather commonly obscured by heavy diffuse scattering concentrated in the immediate vicinity of the Bragg direction; by setting the crystal at the Bragg angle so as to limit the angular range for diffuse scattering (most conveniently on the spectrogoniometer with photographic recording) resolution of the macroscopic structure of the specimen and, in the appropriate $\sin \theta/\lambda$ range, of the Kα doublet of the radiation became apparent. The intensity of the diffuse scattering varied a good deal from one crystal to another, being a minimum for the needle (III) chosen for spectrometric measurements, and substantially stronger for the selected plate. Both needle and plate were macroscopic doubletons.

Accompanying the variations in diffuse scattering as between specimens were measurable differences in lattice translations and in the general distribution of Bragg intensities. Thus for Needle I (used in the original photographic work[5] and for preliminary spectrometric measurements), we obtained $a = 8.743 \pm 0.015$, $c = 5.030 \pm 0.003$ Å.; for Needle III (chosen as best for spectrometric measurements), $a = 8.740 \pm 0.015$, $c = 5.068 \pm 0.010$ Å.; for Needle IV (showing the largest value of c), $c = 5.090 \pm 0.003$ Å.; and for the specimen plate, $a = 8.771 \pm 0.013$, $c = 5.088 \pm 0.015$ Å. Comparing Needles I and IV, a minimum difference in c of 1% is established. The existence of variations in a, though probable, is not certainly established.

For fifty[5] atoms within the cell the calculated density of needle III is 2.33 g./cc. and of the plate, 2.29 g./cc. The density of one of the needles as determined by flotation was reported[5] as 2.31 g./cc.

Photographic intensity data obtained by Dr. S. Geller for all reflections lying within the limiting sphere defined by the Cu Kα wave lengths were used to determine the approximate structure of tetragonal boron. It was clear that many reflections at still higher $\sin \theta/\lambda$ must have large structure factors (the intensity distribution[8,9] was somewhat hypercentric for general reflections and completely so for the *hk*0 and *hhl* data), but photographic recording with Mo Kα radiation was not practicable for the available undersized specimens. The optimum thickness of sample for boron, taken as the reciprocal of the linear absorption coefficient, is about 1.5 mm. with Cu Kα or 10 mm. with Mo Kα radiation. Our best crystal, Needle III, was 0.1 mm. thick, 0.26 mm. long; our plate was 0.3 mm. in maximum diameter, but only 0.03 mm. thick. However, we found it feasible with Mo Kα to record spectrometrically virtually all reflections within the Cu Kα sphere plus a good many at higher $\sin \theta/\lambda$; about half of the *hk*0 and *hhl* data from Needle III (Table I) were not accessible to Cu Kα radiation.

Intensity measurements were carried out on a General Electric XRD-3 Geiger Counter Spectrometer adapted for single crystal work. The counter was mounted on an arc to

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rhombohedral boron. This result and the observed[3] transformation of the simplest modification suggest that the most complex structural form is thermodynamically stable from the melting point downward to about 1200° or perhaps lower.

(8) E. R. Howells, D. C. Phillips and D. Rogers, *Acta Cryst.*, **3**, 210 (1950).

(9) H. Lipson and M. M. Wolfson, *ibid.*, **5**, 680 (1952).

swing about the specimen in a vertical plane (normal beam Weissenberg geometry). Integrated intensities were measured with a stationary crystal in a convergent beam.[10] Assuming a mosaic spread of 0.5° in the crystal and uniform production of X-rays over the focal area of the tube, the final assembly theoretically permitted satisfactory recording of equatorial reflections from a stationary crystal of 0.56 mm. maximum diameter, about twice the largest dimension of any specimen employed. Any one of several carefully calibrated filter combinations could be quickly and reproducibly located to cover the (wide open) counter window, thus permitting measurement at low counting rates. Positions of crystal and counter were adjusted independently but systematically to maximize the intensity, the scaler being used in the final stages. The background correction was taken as the averaged number of counts measured for settings of the counter about two degrees above and below the position of maximum intensity. The complete operation of measuring an intensity required about 15 minutes.

TABLE I

AMPLITUDE DATA FOR *hk*0 REFLECTIONS

Needle			Plate		Needle			Plate	
F	*Fc*[a]	*hk*	*F*	*Fc*[a]	*F*	*Fc*[a]	*hk*	*F*	*Fc*[a]
4.0	10.1	11	2.0	6.8	6.2	6.3	10·4	..	4.8
31.0	35.7	20	36.0	38.4	16.2	16.0	11·1	9.2	13.5
..	4.8	22	1.0	2.7	17.2	16.6	88	17.2	17.1
6.0	7.9	31	3.0	5.5	8.2	10.4	11·3	9.2	9.3
..	3.4	40	3.0	3.7	5.2	6.5	97	5.2	4.7
9.0	8.5	33	6.0	8.8	12.2	13.8	10·6	12.2	14.5
8.0	6.2	42	10.0	6.5	22.2	21.6	12·0	19.2	19.6
..	1.0	51	1.0	1.0	14.2	14.6	11·5	13.2	12.0
30.0	26.6	44	30.0	26.4	12.2	13.0	12·2	11.2	11.1
4.0	3.9	53	3.0	2.8	15.3	15.1	12·4	15.3	14.1
31.1	32.8	60	27.1	28.4	10.3	10.0	99		
36.1	36.7	62	35.1	36.1	3.3	3.4	13·1		
17.1	14.5	55	9.1	9.6	5.3	3.7	10·8		
..	1.0	71	3.1	1.0	6.3	6.6	13·3		
15.1	14.1	64	16.1	15.8	4.3	4.4	12·6		
4.1	3.8	73	7.1	5.7	7.3	6.8	10·10		
10.1	10.4	80	10.1	12.3	6.3	7.5	11·9		
..	1.0	82	2.1	2.8	10.4	11.7	13·7		
7.1	7.7	66	7.1	7.7	5.4	6.8	14·6		
7.1	5.8	75	4.1	5.3	13.4	11.6	11·11	8.4	7.2
..	2.1	84	..	2.0	11.5	11.8	12·12		
22.1	23.8	91	16.1	18.1	8.5	9.3	16·8		
..	1.0	93	..	1.0	9.5	10.6	18·2		
24.2	22.7	77	17.2	18.3	4.5	4.5	17·7		
3.2	2.2	86	4.2	2.3	10.6	11.0	13·13		
8.2	6.4	10·0	3.2	2.2	5.6	6.5	18·4		
4.2	3.9	10·2	3.2	5.6	4.6	4.6	14·14		
18.2	19.4	95	14.2	14.9	3.7	5.2	20·4		

[a] Calculated *F*'s differ for needle and plate because atomic coördinates and distributions of occasional atoms in holes are somewhat different. See text.

For any one crystal the reproducibility of intensity measurement was excellent; the agreement between structurally equivalent reflections corresponding to very different orientations of the specimen in the beam (excepting a few reflections only fractionally above background) was within 4%. (The absolute absorption of Mo $K\alpha$ radiation by the specimens was essentially negligible.) In a careful check of the tetragonal symmetry of the plate, discrepancies in intensity among equivalent reflections of a form were reduced below 2%.

Intensities were measured for two zones, *hk*0 and *hhl*, of Needle III, and for all *hkl* from the plate. In the latter case, the spectrometric analog of the normal beam Weissenberg method was used for zero, first and second layer reflections with each of three rotation axes. The few reflections not thus included were obtained from higher layers with the plate normal as rotation axis. As compared with a needle, the plate offered both easy orientability along any rational axis and freedom from twinning.

The *hk*0 Bragg amplitudes of Needle III and the plate are compared in Table I. (The data from Needle I more closely resembled those from the plate.) Most striking is the greater range of the needle data, with nineteen reflections recorded in the high range of $\sin \theta/\lambda$ where but one appears for the plate. This observation correlates qualitatively with very different values (Table II) for the two specimens of the effective "thermal" parameter *B* (to be called the Debye parameter since it is largely non-thermal in this case). The phenomenon of rather sharp cut-off in the plate data probably is understandable in terms of inadequate correction of the Bragg intensity for diffuse background, which later was experimentally a maximum just at the Bragg angle. It would appear that so long as the relatively sharp Bragg reflection was detectable, its intensity was overestimated monotonically with the diffuse intensity. This implies that the *B*-values of Table II are in fact too small, a conclusion easy to accept in view of the obvious strength of the diffuse scattering.

TABLE II

PARAMETER DATA FOR TETRAGONAL BORON

Needle					Plate			
x	*y*	*z*	*B*, Å.^{2}	Atom	*x*	*y*	*z*	*B*, Å.^{2}
0.3253	0.0883	0.3985	0.76	B_1	0.3255	0.0875	0.4005	1.29
.2272	.0805	.0865	.73	B_2	.2265	.0825	.0895	1.56
.1195	.1195	.3780	.79	B_3	.1245	.1245	.3870	1.62
.2425	.2425	.5815	.67	B_4	.2490	.2490	.5865	0.66
0	0	$^1/_2$	.52	B_5	0	0	$^1/_2$	.68

Determination of Space Group.—The structure to be described is based upon the space group $P4_2/nnm$, consistent with the X-ray symmetry and requiring the extinction[11] of all reflections *hk*0, $h + k$ odd and 0*kl*, $k + l$ odd. Selection of this space group was attended by certain complications. The original photographic data[5] included some three or four weakly observable reflections *hk*0, $h + k$ odd forbidden by $P4_2/nnm$, and we supposed that the structure as reported[5] would need to be modified in accordance with the lesser symmetry[11] of either $P4nm$ or $P\bar{4}n2$. Spectrometric measurements turned up some additional, barely detectable reflections of this type (with a notable lack of correspondence between specimens) and also three of the type 0*kl*, $k + l$ odd. Of the five space groups consistent with 4/mmm while requiring no special vanishings,[11] only $P\bar{4}2m$ would allow nearly or exactly the ideal structure based on $P4_2/nnm$. $P\bar{4}2m$ offered the not entirely implausible possibility for initiating distortion in the structure through a selective partial filling of natural holes (*vide infra*) in the framework. Extensive study of such possibilities as they affected the Fourier syntheses and calculated reflection amplitudes of the centrosymmetric zones gave negative results: not even qualitative agreement could be achieved for the weak reflections forbidden by $P4_2/nnm$, and no reversal of phase for a permitted reflection occurred.[12] In fact, we became convinced that any structural modification introduced through changing the space group would be trivial as compared with the real differences in structure between our two selected specimens.

On the other hand, we were able to find convincing evidence[12] for interpreting the weak reflections forbidden by $P4_2/nnm$ as resulting from double reflection.[13] The prevalence of large unitary structure factors in the amplitude data combined with some relaxation of the geometrical requirements

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(10) W. Cochran, *Acta Cryst.*, **3**, 268 (1950).

(11) "International Tables for X-Ray Crystallography," Vol. I, The Kynoch Press, Birmingham, England, 1952.

(12) For the detailed analysis see Donald E. Sands, "The Crystal Structure of Boron," Cornell University Thesis, Cornell University Library, 1955.

(13) M. Z. Renninger, *Z. Krist.*, **97**, 95 (1937); *Z. Physik*, **106**, 141 (1937).

through slight misalignment of the macroscopic components of the split crystals were favorable to double reflection. A much more substantial easing of the geometric restrictions arose in the spectrometric measurements through use of the convergent beam with maximization technique.

Determination of Parameters.—The approximate structure of tetragonal boron, derived[5] with the aid of numerous two-dimensional, and sections of three-dimensional Patterson syntheses, was then found[5] to account with remarkable fidelity for all Patterson syntheses. It is convenient at this point to consider the general character[5] of the structure. The fifty-atom unit (Fig. 1) consists of four approximately regular icosahedra (of minimum symmetry 2/m) centered in the positions[11] 4e: $^1/_4\ ^1/_4\ ^1/_4\ ^1/_4$; $^3/_4\ ^3/_4\ ^1/_4$; $^3/_4\ ^1/_4\ ^3/_4$; $^1/_4\ ^3/_4\ ^3/_4$ of $P4_2/nnm$, and two additional atoms in 2b: 0 0 $^1/_2$; $^1/_2\ ^1/_2$ 0. Each boron atom of an icosahedron forms six bonds directed toward the corners of a pentagonal pyramid, five bonds to atoms within the same icosahedron and the sixth to an atom of an adjacent icosahedron or to an atom in 2b. An atom in 2b forms but four bonds directed toward the corners of a flattened bisphenoid ($\bar{4}2m$) but is needed to perpetuate the characteristic three-dimensional bonding pattern of icosahedral atoms. There remain natural holes in the framework at 2a: 0 0 0; $^1/_2\ ^1/_2\ ^1/_2$; 4c: 0 $^1/_2$ 0, $^1/_2$ 0 0, 0 $^1/_2\ ^1/_2$, $^1/_2$ 0 $^1/_2$; 4d: 0 $^1/_2\ ^1/_4$, $^1/_2$ 0 $^1/_4$, 0 $^1/_2\ ^3/_4$, $^1/_2$ 0 $^3/_4$; and (the icosahedron centers) 4e. Evidence will be presented to show that there is partial filling of such holes with extra boron atoms but in variable concentrations as between specimens. The holes 2a are so large as to suggest the alternative use of positions 4g: 0 0 z: 0 0 $\bar{z}$; $^1/_2$, $^1/_2$, $^1/_2 + z$; $^1/_2$, $^1/_2$, $^1/_2 - z$, with $z \leqslant 0.183$. 4d appears to offer a structurally less satisfactory, unused alternative to 4c. Occupation of icosahedral centers seems possible only if there are neighboring framework vacancies.

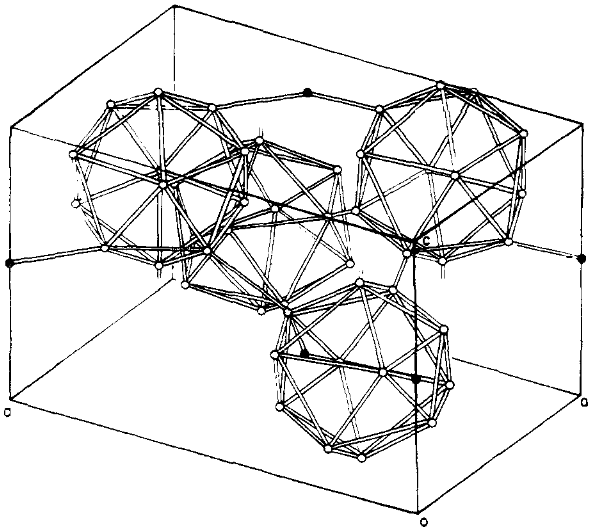

Fig. 1.—Diagram of the structure of tetragonal boron.

A Fourier synthesis, $\rho(x,y)$ of $hk0$ amplitudes (Fig. 2) shows remarkably good resolution with no overlapping between icosahedra. A quasi-fivefold axis of an icosahedron is virtually parallel to the projection axis c: consequently ten of the twelve atoms appear as individual peaks almost equally spaced along an approximate circle surrounding the central doubled peak of two equivalent (B_4) atoms. A representative icosahedron, *e.g.*, that centered at $^1/_4\ ^1/_4\ ^1/_4$, has four atoms in the mirror plane $y = x$ and eight in positions of no required symmetry. Analytical description of the complete framework requires the eightfold positions[11] 8m: xxz; etc., used twice, the general positions 16n: xyz; etc., also used twice, together with the special positions 2b. There are ten variable parameters to be determined, and the excellent resolution of $\rho(x,y)$ enables us to derive at once good if not entirely final values for the x and y coördinates of all atoms. The $\rho(x,y)$ projection for the needle specimen (Fig. 2) is superior to that for the plate (not reproduced, but see Fig. 3 for $\rho(x,x,z)$) in providing smoother contours, more nearly uniform peak densities for individual atoms and less apparently false detail. Real differences of the order of 0.005 in the parameters of certain atoms as between needle and plate are indicated and are confirmed by the subsequent analysis. Minor but substantial peaks at $^1/_2$,0 and 0,$^1/_2$ on both projections are interpretable as partial filling by boron atoms of natural holes corresponding to 4c or 4d. Similarly, excess electron density associated with the peaks 2b indicates partial occupancy of 2a or 4g.

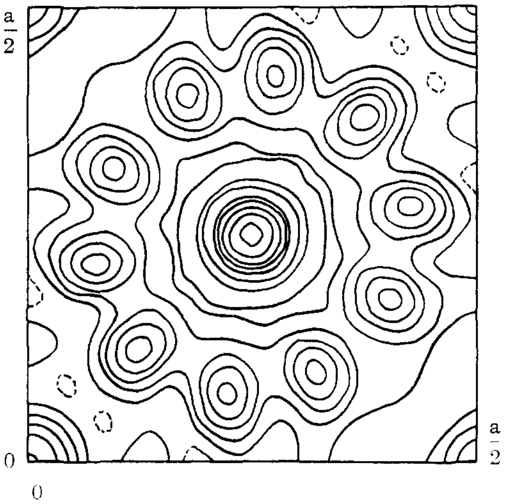

Fig. 2.—Projected electron density, $\rho(x,y)$, for the needle specimen.

The following additional Fourier syntheses of amplitude data for the plate were used in the evaluation of atomic parameters: $\rho(y,z)$, showing excellent resolution of B_2 and B_5; $\rho(x,x,z)$, reproduced in Fig. 3, showing complete resolution of B_3, B_4, B_5; the projected section $\rho(y,z)$ for $x = 0 \rightarrow {}^1/_4$, giving data on every variable parameter save one; line syntheses of hkl data through B_1 and B_2 parallel to c to give z-coördinates of these atoms. Despite the erratic background (*cf.* Fig. 3), the agreement in parameter values among the several syntheses was rather good. The coördinates adopted as best representing the Fourier data for the plate were, for each structural class of atom, essentially those given by syntheses showing complete resolution for atoms of the class. The maximum deviation for any synthesis of any x or y parameter from the weighted mean value was 0.0013; the mean deviation (all syntheses and all structural classes) from the weighted means of x and y coördinates was 0.0005, corresponding to about 0.0045 Å. The mean deviation (all syntheses and all classes) from the weighted mean values of z-coördinates was 0.0014, corresponding to about 0.007 Å., a lower degree of consistency than that obtained for x and y parameters.

The positions thus obtained (to be called the *Fourier* values) for the basic framework in the plate are subject to further refinement provided we can calculate amplitudes from a satisfactorily realistic model; there is some doubt on this point, at least for the plate. (The determination of z-coördinates in the needle, for which only zonal *hhl* data are available, is described later.) Using the Fourier values of the atomic coördinates and an isotropic effective Debye parameter of 1.05 Å.^{2}, the value of $R = \Sigma||F_0| - |F_0||/\Sigma|F_0|$, is 0.16 for *hkl* plate data.

Difference synthesis,[14] $\rho_0 - \rho_c$, corresponding to the more pertinent Fourier projections and sections mentioned earlier, but with only the basic frameworks contributing to calculated amplitudes,[15] confirm the existence of probably significant differences between needle and plate, both as regards atomic positions in the basic structure and the degree of filling of natural holes. We estimate this latter roughly as follows: needle: $^1/_4$ in 2a or $^1/_8$ in 4g, $^1/_{16}$ in 4c; plate: $^1/_{16}$ in 4g, $^1/_8$ in 4c.

The attempted further refinement of x and y-coördinates applied the least squares technique to the *hk*0 data, programmed to allow redetermination during each computational cycle of the scale factor for experimental amplitudes and the effective Debye parameter for each structural class of atom and to take account of the special symmetry of B_3 and B_4 atoms. At most five iterations were needed to attain convergence of the computational cycle. The refinement was carried out (I) with only framework atoms used to calculate amplitudes, (II) with inclusion of contributions from extra atoms as specified in the preceding paragraph and (III), for the needle only, with just the extra contribution from 4g (or 2a). The positions obtained for framework atoms in each specimen were found to be virtually independent of the choice of model and in no case more than 0.025 Å. from the Fourier positions. However, the quality of the agreement between calculated and observed reflection amplitudes was obviously better for the extra atom models. The amplitude data of Table I and the effective Debye parameters of Table II are those resulting from the least squares treatment based upon the models (II).

The value of R for the needle data of Table I, every listed reflection being included, is 0.114; it is 0.135 for the plate data, unobserved reflections being omitted. Both values are 0.02–0.03 less than the best figures attainable with any simple framework model. Substantial discrepancies between calculated and observed amplitudes are virtually limited (Table I) to a few weak or unobserved reflections of very simple indices, *i.e.*, reflections of especially small unitary structure factor: *cf.*, 110, 220, 400 of the needle data. In most cases the introduction of extra atoms has materially lessened the range of disagreement. The remaining discrepancies must arise from some other form of short-range disorder, as is strongly implied by the strange variability (Table II) observed in the effective Debye parameters.

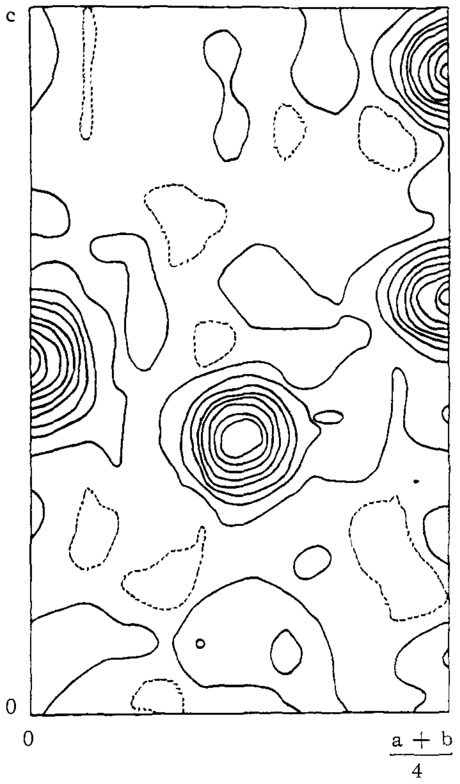

Fig. 3.—Fourier section, $\rho(xxz)$, for the plate specimen.

Rating just below diamond in hardness,[6] boron at room temperature would be expected to have a true thermal parameter not much larger than that of diamond,[16] for which $B = 0.147$Å.^{2} (mostly from zero-point vibrations). It appears certain that even for the needle the larger part of the effective B-values must arise from disorder[17] other than thermal motion. All evidence[6] speaks against appreciable contamination of our crystals. The dominant type of disorder probably consists of vacancies in the fundamental framework, existing in much larger concentration in the plate specimen.

If vacancies (or other substitutional defects) were distributed uniformly throughout the framework, the least squares method as set up for the ideal framework would choose a compensatingly large scale factor for experimental amplitudes, and we would expect to find rather uniform B-values

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(14) *Cf.* H. Lipson and W. Cochran, "The Determination of Crystal Structures. The Crystalline State," Vol. III, G. Bell and Sons Ltd., London, 1953.

(15) Using the atomic form factors of R. McWeeny, *Acta Cryst.*, **4**, 513 (1951).

(16) R. W. James, "The Optical Properties of the Diffraction of X-Rays. The Crystalline State," Vol. II, G. Bell and Sons Ltd., London, 1954, p. 225.

(17) *Cf.* W. H. Zachariasen, "Theory of X-Ray Diffraction in Crystals," John Wiley and Sons, Inc., New York, N. Y., 1945.

for the several structural classes of boron atoms. Perhaps this case is not too badly approximated by the needle data (Table II); hence we accept the least squares results as the final values for x and y parameters in this specimen. If, on the other hand, the concentration of vacancies in any structurally equivalent set were especially large, we must expect to obtain an artificially large B for it, since the least squares method will surely underestimate the scattering power of this set at large angles in the attempt to compensate on the average for the inevitable overestimation (despite some accompanying adjustment of the over-all scale factor) at small angles. We do not suppose that the unduly large values of the effective Debye parameter for B_1, B_2 and B_3 of the plate (Table II) are attributable solely to correspondingly large concentrations of vacancies in these positions; we do conclude that the ideal framework, even as modified by the addition of extra atoms in natural holes according to the earlier discussion, cannot provide an altogether realistic model for refinement of parameters. The final x and y coördinates in the plate (Table II) are averages, rounded off to the nearest 0.0005, of the values given by the direct Fourier and least squares methods. In but one case is a final projected position farther than 0.01 Å. from the least squares result, namely, 0.013 Å. for B_1. The mean deviation for all projected positions is 0.006 Å.

The corrections to z-coördinates in the plate given by difference syntheses of *hkl* data along lines parallel to c through atomic centers were, rather unexpectedly, too small to occasion worry about the unrealistic character of the model. The largest shift indicated for any z-coördinate was 0.008 Å., the mean shift but 0.004 Å.

Spectrometrically measured amplitudes for 70 *hhl* forms were available for determination of z-coördinates in the needle. Computation and interpretation of the Fourier syntheses were simplified by the transformations

$$\vec{A}_1 = \vec{a}_1 + \vec{a}_2; \qquad H = h + k; \qquad u = (x + y)/2$$

$$\vec{A}_2 = \vec{a}_2 - \vec{a}_1; \qquad K = k - h; \qquad v = (y - x)/2$$

$$\vec{C} = \vec{c}; \qquad L = l; \qquad Z = z - {}^1/_4$$

Thus *hhl* becomes *H0L* and $\rho(u, Z)$ corresponds to projection along A_2 onto the new (010). In Fig. 4, $\rho(u, Z)$ is unchanged by reflection across the boundary lines $Z = 0$ or ${}^1/_2$, $u = {}^1/_4$ or 0 (although only $u = 0$ is a true mirror plane of the structure), or by inversion through 00, ${}^1/_4\,{}^1/_2$, $0\,{}^1/_2$, ${}^1/_4\,0$.

A pair of icosahedra centered at 0, $\pm{}^1/_4$, ${}^1/_2$ are exactly superposed in projection to give doubled peaks for every structural type of atom. However, the excellent resolution (Fig. 4) of B_3 and B_4 along 0, Z was achieved only by removing the peak at $0\,{}^1/_4$ for the 2b atom, B_5. The B_1 and B_2 peaks for this pair of icosahedra occur at approximately the same Z (*ca.* 0.34), are about 0.60 Å. apart along A_1 and are consequently not completely resolved. A second pair of icosahedra centered at ${}^1/_4\,00$, ${}^1/_4\,{}^1/_2\,0$ and related by the twofold axis along ${}^1/_4\,{}^1/_4\,Z$ are partially resolved from one another in projection, although two B_4 atoms of identical Z and nearly identical u (0.2425, 0.2575) are superposed. The single B_3 and the exactly doubled B_1 peaks belong to the icosahedron centered at ${}^1/_4\,0\,0$, the exactly doubled B_2 peak to the other. The B_1 and B_2 peaks, again at approximately the same Z (*ca.* 0.16), are about 0.70 Å. apart along A_1. $\rho(u,Z)$ is thus seen to furnish mutually perpendicular views of the asymmetric unit.

Taking the u and v coördinates as known from the earlier analysis, two *quasi*-independent values of Z for each structural class were read from $\rho(u,Z)$. Difference syntheses, using a common Debye parameter for all atoms, were carried through three cycles of refinement with the following results: Indicated corrections along A_1 were small, and none were introduced into the computation cycle. Convergence to a common value of the two determinations of Z was satisfactory for B_4. The unresolved single peak was assigned minor weight in the refinement of Z_3, which oscillated about but returned to within 0.0005 of the Fourier value. From the outset the *quasi*-independent corrections to the Z-coördinate of B_2 were in opposite directions; even though the mean coördinate oscillated within a restricted range (<0.01 Å.), we were left with equal and opposite indicated corrections of about 0.015 Å. A similar result, but with apparent corrections less than half as large, was obtained for B_1. A further reduction of the residual gradients at atomic positions through introduction of individual Debye parameters (with modification of the scale factor) was not attempted, since our experience with difference syntheses of the probably somewhat higher quality *hk*0 needle data had not been very encouraging. In this latter case we were happy to use the automatic least squares procedure and to find that it gave corrections to atomic coördinates in fair agreement with those indicated by one cycle of difference synthesis. The presence of so many high frequency Fourier coefficients of substantial magnitude (*cf.* Table I), and the use of a model based upon a completely ordered structure were not conducive to the construction of a completely satisfactory difference synthesis.

Striking discrepancies between calculated and observed *H0L* amplitudes were limited, as for the *hk*0 data, to a few weak or missing reflections of simple indices (and even L), again reflections of very small unitary structure factor. Occasional atoms in 2a or 4g, which contribute only to reflections with L even, were ignored in computing amplitudes. Values of R for various classes of reflections are: 0.15 for L even, 0.12 for L odd, 0.14 for all *H0L* and 0.15 for all *H0L* (half the total) lying outside the Cu Kα limiting sphere. This last result engenders confidence in the parameter data, more particularly since the agreement is fully as good for large L as for large H.

The unit cell has two large holes at 000, ${}^1/_2$, ${}^1/_2$, ${}^1/_2$, each of which, according to $\rho_0(x,y) - \rho_c(x,y)$ and the least squares treatment, contains scattering material statistically equivalent to about ${}^1/_4$ of a boron atom. It is dimensionally feasible to use 2a, 4g with either one or two boron atoms in a given hole or any statistical combination of these three. The excess electron density along $u = 0$ of $\rho_0(u,Z)$

TABLE III

BOND LENGTHS IN TETRAGONAL BORON

Needle, Å.	Bond	Plate, Å.	Needle, Å.	Bond	Plate, Å.
		A. Within an icosahedron			
1.846[c] $\pm$ 0.025	B_1–B_1[a]	1.873[c]	1.813[c] $\pm$ 0.014	B_2–B_2[a]	1.786[c]
1.800 $\pm$ .019	B_1–B_2[b]	1.804	1.785 $\pm$ .018	B_2–B_3[b]	1.796
1.812 $\pm$ .010	B_1–B_2[b]	1.821	1.786 $\pm$ .013	B_2–B_4[b]	1.741
1.822 $\pm$ .008	B_1–B_3[b]	1.794	1.837 $\pm$ .012	B_3–B_4[a]	1.848
1.789 $\pm$ .012	B_1–B_4[b]	1.831	1.806 $\pm$ .015	Av.	1.805
		B. External bonds of an icosahedron			
1.858 $\pm$ 0.020	B_1–B_1[b]	1.837	1.709 $\pm$ 0.030	B_4–B_4[a]	1.664
1.658 $\pm$ .020	B_2–B_2[b]	1.710	1.601 $\pm$ .005	B_3–B_5[a]	1.648

[a] Two equivalent bonds of this type/icosahedron. [b] Four equivalent bonds of this type/icosahedron. [c] Rounding off to the nearest 0.005 A. (occasionally to 0.01 Å.) is indicated for most of the calculated distances.

$-\ \rho_c(u,Z)$ is best interpreted in terms of the last possibility; perhaps as much as half of the excess corresponds to $2a$ (larger impurity atoms?), the remainder to $4g$ with z roughly estimated as 0.16. This fragmentation into peaks of density rather smaller than that of a single hydrogen atom is, to say the least, uncertain. The agreement for *HOL*, *L* even, reflections is slightly improved by including contributions from 2a and 4g with any reasonable distribution of the excess scattering power between them.

Discussion of Results

Calculated bond distances, with estimated standard deviations in the case of the needle, are given for both specimens in Table III. The least squares program for determination of x and y-coördinates gave standard deviations as follows: needle: $\sigma_x \approx \sigma_y = 0.007$ Å. for both B_1 and B_2, σ_x $(\equiv \sigma_y) = 3.5 \times 10^{-4}$ Å. for B_3 and B_4; plate: $\sigma_x \approx \sigma_y = 0.0010$ Å. for B_1 and B_2, $\sigma_x = 5 \times 10^{-4}$ Å. for B_3, 0.004 for B_4. Since variations in the theoretical model of the sort described earlier produce changes in position for B_3 and B_4 of the order of 5×10^{-4} Å., we have arbitrarily used $\sigma_x = 0.003$ Å. for B_3 and B_4 of the needle, 0.004 Å. for B_3 and B_4 of the plate. Even so, the differences as between specimens in the projected positions (along $y = x$) of B_4 and B_3 are significant: 0.093 ± 0.007 Å. for B_4, 0.062 ± 0.007 Å. for B_3. Values of σ_z as estimated by Cruickshank's procedure[14] for z-coördinates in both needle and plate were generally between 0.010 and 0.015 Å. The less certain estimated standard deviations in bond lengths for the plate run from 0 to 75% larger than corresponding values in the needle. Only one calculated difference in bond length as between specimens meets the conditions for objective significance[14]: for B_3–B_5 we obtain 1.601 ± 0.005 and 1.648 ± 0.006 Å.

Within an icosahedron the thirty bonds are classified into nine structurally distinct sets by the required minimum symmetry 2/m. From the needle data we obtain an averaged length with root-mean-square deviation for all thirty bonds of 1.806 ± 0.019 Å., for the nine bond types of 1.810 ± 0.021 Å.; from the plate data we get. respectively, 1.805 ± 0.033 Å. and 1.810 ± 0.036 Å. The r.m.s. deviation from the average, *ca.* 0.020 Å. for the needle data, may be compared with $\sigma = (\Sigma \sigma_i^2/n)^{1/2} = 0.015$ Å., calculated from the individual bond σ_i (with averaging either over all bonds or all bond types). We suggest 1.805 ± 0.015 Å. as the most probable value for the edge of a regular boron icosahedron on the basis (A) that the first type of averaging is appropriate to this case and (B) that strains introduced through formation of external bonds are more likely to result in a net extension rather than compaction of intraicosahedral bonds. This value is 0.04 Å. or more larger than averaged values of (highly variable) B–B distances reported[18] for fragments of icosahedra in the boron hydrides.

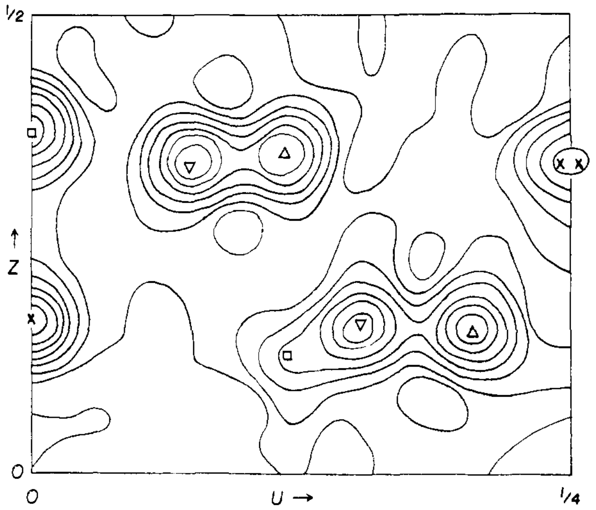

Fig. 4.—Projected electron density, $\rho(u,Z)$, for the needle specimen: △, B_1; ▽, B_2; □, B_3; ×, B_4.

Of the twelve external bonds formed by an icosahedron two (B_3–B_5) are to atoms in 2b. The bond length certainly is significantly shorter than the icosahedral average; looking especially at the needle data it appears probable that B_3–B_5 is the shortest bond in the ordered structure. The ten intericosahedral bonds are formed between structurally equivalent pairs of atoms so that the bond σ-values must be relatively high. In terms of these formally objective criteria the greater length of the B_1–B_1 bond relative to the average for other external bonds is only probably significant. Study of the structure, including the construction of a model from substantially regular icosahedra, shows that

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[18] W. N. Lipscomb, *J. Chem. Phys.*, **22**, 985 (1954); F. L. Hirshfeld, K. Eriks, R. E. Dickerson, E. L. Lippert, Jr., and W. N. Lipscomb, *ibid.*, **28**, 56 (1958).

the geometry is difficult only when forming the B_1–B_1 connections. The bond between two adjacent B_1 atoms of the same icosahedron and the external bonds formed by each (to B_1 atoms of two other icosahedra) are nearly coplanar: the two external bonds are so spread apart as to exhibit a combined angular strain of fully 40° from the ideal orientations (with the accompanying suggestion of some extension of the intraicosahedral B_1–B_1 bond). The further gross distortions of the icosahedra required to make the calculated intericosahedral B_1–B_1 bond length significantly less than the intraicosahedral average (1.805 Å.) seem to us altogether improbable.

The basic framework of one unit cell contains 148 bonds: 120 intraicosahedral, 28 external to icosahedra; these latter are distributed among four bond classes as follows: I: B_1–B_1, 8; II: B_2–B_2, 8; III: B_2–B_5, 8; IV: B_4–B_4, 4. With weighting according to these figures we calculate from the needle data various averaged values for the length of an external bond; all classes, 1.706 Å.; I omitted, 1.645 Å.; III omitted, 1.748 Å.; I and III, omitted, 1.675 ± 0.024 Å. This last value is derived from strictly intericosahedral bonds (II and IV) showing no evidence of undue strain. Giving one-third weight to the plate data, we suggest 1.68 ± 0.03 Å. as the most probable length for a typical intericosahedral bond. For all (148) framework bonds of a cell the averaged lengths are 1.786 and 1.789 Å. for needle and plate, respectively. Fourier integral analysis[19] of powder data from boron now identified[4] as the complex rhombohedral modification indicates ". . . . six nearest neighbors at an average distance of 1.89 Å. in crystalline boron."

An occasional boron atom in 4c is equidistant from four B_1 atoms of four different icosahedra at the calculated distance 1.787 ± 0.008 Å. for the needle, 1.785 ± 0.010 Å. for the plate. These results shed no light on the greater degree of filling of 4c in the plate, $\gtrsim {}^1/_8$, as compared with the needle, $\lesssim {}^1/_{16}$. (The bounds are set by the behavior of the individual Debye parameters in the least squares refinement of *hk*0 data.) The difference is perhaps a consequence of a greater probability of vacancy occurrence in the framework of the plate.

The positions 2a, 2.15 Å. from the nearest framework atoms, appear most suitable for whatever larger atom impurities might be present. Taken, for example, as representing tantalum from the filament, the maximum degree of filling of 2a permitted by $\rho_0(u,Z) - \rho_c(u,Z)$ would correspond to an atomic ratio of about ${}^1/_{1400}$ of tantalum to boron in the crystal. (The reported[6] evidence for any impurities was wholly negative.) Use of 4g with $z \lesssim 0.183$ is dimensionally more probable for occasional boron atoms. The maximum of 0.183 would put a boron atom 1.60 Å. from a B_5 atom and 1.785 Å. from each of four B_3 atoms. Simultaneous occupancy of 00*z*, 00$\bar{z}$ of the same cell with a separation of 1.60 Å. corresponds to $z = 0.157$. Limited filling of 4g neither demands a unique choice of *z* nor precludes use of 2a since there are many more available holes than occasional atoms to occupy the holes.

The shortness of the bisphenoidal B_3–B_5 bonds, 1.60 Å. in the needle, directs attention to possible replacement of B_5 atoms in 2b by carbon, nitrogen or even oxygen impurities. The absence of carbon and oxygen from the preparation was convincingly demonstrated.[6] No direct analysis for nitrogen, an unlikely impurity, was performed. Numerous total analyses for boron, perhaps likely to run low because of the fusion technique employed, ranged[6] between 99.0 and 100.2% B. It follows that no more than one-fourth, more probably, no significant fraction of the 2b atoms could have been other than boron. Furthermore, any significant degree of replacement by foreign atoms of appreciably different size is inconsistent with the small standard deviation in the B_3–B_5 bond length, less than half that of any other bond.

Intermediate between the short (1.60 Å.) bisphenoidal and the long (1.805 Å.) intraicosahedral bond lengths of tetragonal boron is the accurately determined[20] (1.716 Å.) value for the three-dimensional boron network in CaB_6. In this structure, every boron atom is bonded to five others at the corners of a square pyramid. The not very accurately determined B–B bond lengths, 1.74–1.80 Å., in boron carbide[3] are in general agreement with the results for tetragonal boron.

A most interesting theoretical treatment[21] of the electronic structure of a regular icosahedron of boron atoms leads rather naturally, as also does an earlier discussion[22] of the problem, to the conclusion that discrete molecules such as $B_{12}H_{12}$ probably are fundamentally unstable. Longuet-Higgins and Roberts[21] then discuss the structures of tetragonal boron[5] and boron carbide[3] in terms of such B_{12} icosahedra and either tetrahedral (*i.e.*, 2b) boron atoms or C_3 chains, these units to be connected by standard single bonds; they ignore the possibility of general conjugation of the three-dimensional network and any effect of the lowered symmetry of the icosahedra. When applied to the " . . . tentative structure for crystalline boron . . ." of our Communication,[5] they obtain an electron count in disagreement with the requirements of their model, and they " . . . suggest that this theoretical argument tells against the complete correctness of the proposed structure, which the authors themselves state to be only provisional." Our report[5] was highly tentative on matters dealing with the precise significance of a few weak reflections and the accurate specification of parameter values; but the fundamental structural pattern—all, we think, that was pertinent to the theory—was (and is) supported by a formidable array of data.

We fear, moreover, that the apparent success[21] of the theory with boron carbide is illusory. Longuet-Higgins and Roberts[21] find a satisfactory electron count for the stoichiometric composition, $B_{12}C_3$, but the phase exists[23] over a composition range of 4-28 atomic % of carbon. There is direct evidence,[24] *e.g.*, from nuclear magnetic measurements, for substantial replacement of carbon by

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(19) T. N. Godfrey and B. E. Warren, *J. Chem. Phys.*, **18**, 1121 (1950).

(20) L. Pauling and S. Weinbaum, *Z. Krist.*, **87**, 181 (1934).

(21) H. C. Longuet-Higgins and M. de V. Roberts, *Proc. Roy. Soc.* (*London*), **230A**, 110 (1955).

(22) W. H. Eberhardt, B. Crawford and W. N. Lipscomb, *J. Chem. Phys.*, **22**, 989 (1954).

boron in the chains. Characterization[23] of the phase as a solid solution of carbon in boron is consistent with the experimental absence[24] of extrema in physical properties at any stoichiometric composition throughout the entire range. (Although it is not a system in which one imagines that complete thermodynamic equilibrium, involving the reconstitution and sorting of chains, will be readily attained.)

Acknowledgments.—We wish to thank Dr. H. A. Weakliem, Jr., for expert aid in carrying out some of the computations and the Cornell Computing Center for allowing us the necessary time on IBM equipment.

ITHACA, NEW YORK

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(23) F. W. Glaser, D. Moskowitz and B. Post, *J. App. Phys.*, **24**, 731 (1953).

(24) *Cf.*, P. J. Bray, Atomic Energy Commission Report NYO-7624.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF FLORIDA]

The Chemistry of Borazene. I. The Reaction of B-Trichloro-N-trimethylborazene with Grignard Reagents[1]

BY G. E. RYSCHKEWITSCH, J. J. HARRIS AND HARRY H. SISLER

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B-Trichloro-N-trimethylborazene reacts smoothly with Grignard reagents to give B-alkyl derivatives. B-Triethyl-N-trimethyl-, B-triallyl-N-trimethyl- and B-tri-(*n*-butyl)-N-trimethylborazene were prepared. B-Di-(*n*-butyl)-B-chloro- and B-*n*-butyl-B-dichloro-N-trimethylborazene were prepared using a deficiency of Grignard reagents.

Introduction

General methods for the preparation of B-alkyl substituted borazenes previously published involve vacuum techniques[2-4] or the use of relatively inaccessible intermediates.[5]

None of these methods is especially attractive for the synthesis of borazene derivatives containing different substituents on boron atoms in the same molecule. Redistribution reactions between substituted boranes and a borazene seem to be unsatisfactory in general, since unsymmetrical borazenes prepared from substituents that are readily redistributed in boranes may be expected to be susceptible to redistribution here, too. Another conceivable method for the preparation of unsymmetrically B-substituted borazenes could start with the desired boron substitution before the ring is formed. If, *e.g.*, a B-alkyl-B-chloroborazene is desired, this would necessitate treating a mixture of $RBCl_2$ and BCl_3 with an amine and pyrolyzing the resulting mixture of addition compounds. Since several reaction steps are involved before the borazene ring is formed in which the difference in boron substitution may exert a strong electronic or steric influence, it is highly questionable whether or not reasonable yields of the desired product can be obtained by this method.

The work reported here gives a simple synthetic method for the synthesis of B-trialkyl, B-dialkyl-B-monochloro and B-alkyl-B-dichloroborazenes from readily available starting materials through the reaction of B-trichloro-N-trimethylborazene with Grignard reagents.[6] The reaction should prove to be of general applicability in view of the similar reactivity of the boron–halogen bond in different N-substituted borazenes and the reactivity of boron halides toward a variety of Grignard reagents.

Experimental

B-Trichloro-N-trimethylborazene, $B_3Cl_3N_3(CH_3)_3$.—B-Trichloro-N-trimethylborazene was prepared from boron trichloride and methylamine hydrochloride in refluxing chlorobenzene by a slight modification of the method of Brown and Laubengayer.[7] Using a few per cent. excess boron trichloride and extending the reaction time till no more HCl was produced gave practically quantitative yields of pure product.

B-Triethyl-N-trimethylborazene, $B_3(C_2H_5)_3N_3(CH_3)_3$.—Into a 250-ml. two-neck round-bottom flask were placed 75 ml. of anhydrous ethyl ether, 9.0 g. (0.37 mole) of magnesium turnings and 25 g. (0.11 mole) of B-trichloro-N-trimethylborazene. The flask was fitted on one neck with a reflux condenser and Dry Ice cold-finger condenser in series and a dropping funnel in the other neck. The whole system was vented to the atmosphere through a Drierite tube. Forty grams (0.36 mole) of ethyl bromide slowly was added (1 to 2 hr.) through the dropping funnel to the magnetically stirred reaction mixture after adding a crystal of iodine to start the Grignard reaction. An exothermic reaction with precipitation of magnesium halide resulted. After all the alkyl bromide had been added, the reaction mixture was refluxed for another 3 to 4 hr.

The solid precipitate and any unreacted magnesium was removed by filtration through a fritted glass filter in the drybox and washed several times with dry ethyl ether. Filtrate and washings were combined and distilled, first at atmospheric pressure and then under vacuum to remove all traces of solvent. There remained a light yellow liquid. On fractionation of the crude product under reduced pressure, there was obtained 15 g. of a colorless liquid with the following physical constants: b.p. 82° (0.65 mm.), 98° (1.8 mm.), $n^{22.5}D$ 1.4791, f.p. 1–2°. The yield was 66% of theoretical. *Anal.* Calcd. for $B_3(C_2H_5)_3N_3(CH_3)_3$: B, 15.70; N, 20.33; Cl, 0.00. Found: B, 15.86; N, 19.45; Cl, 0.6.

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[1] Presented at the 132nd Meeting of the American Chemical Society, New York, N. Y., September 9, 1957. The names borazole and borazine have been used also for the compound $B_3N_3H_6$.

(2) H. I. Schlesinger, L. Horvitz and A. B. Burg, THIS JOURNAL, **58**, 409 (1936).

(3) H. I. Schlesinger, D. M. Ritter and A. B. Burg, *ibid.*, **60**, 1296 (1938).

(4) E. Wiberg, K. Hertwig and A. Bolz, *Z. anorg. Chem.*, **256**, 177 (1948).

(5) W. L. Ruigh and F. C. Gunderly, *Chem. Eng. News*, 1994 (April 23, 1956). Abstracts of papers, 129th meeting, American Chemical Society, Dallas, Texas, April 1956, 40-N.

(6) S. J. Groszos and S. F. Stafiej, Abstracts of Papers, 131st Meeting, American Chemical Society, Miami, Florida, April 1957, 53-O, report the preparation of B-trialkyl derivatives of N-triphenyl borazene through the use of Grignard reagents.

(7) C. H. Brown and A. W. Laubengayer, THIS JOURNAL, **77**, 3699 (1955).