distances in $AgNO_2$ and $AgClO_4$. 3 dioxane (see Table 7), structures in which ionic bonding must be fairly important. Although the apparent bending of the fulminate groups must be regarded as rather uncertain – the temperature factor for the O atom is much larger than for the C and N atoms – it is interesting that it appears to occur *towards* the neighbouring Ag atom at 2·45 Å distance, thus suggesting some bonding interaction between the residual negative charge on O and the residual positive charge on Ag. The next shortest $Ag \cdots O$ distances are 2·89 Å and 2·92 Å and must correspond to much weaker interactions.

Silver fulminate is held in poor regard as a detonator, as is shown by the following quotation (Rinkenbach, 1951): *Unlike mercuric fulminate, silver fulminate as ordinarily produced consists of fine amorphous aggregates instead of crystals. While normally it is slightly less sensitive to impact and more sensitive to heat than mercury fulminate, it has been found that under certain conditions of temperature some small clusters of crystals are formed that are much more sensitive than the amorphous aggregates. This explains the general conclusion that silver fulminate is dangerously sensitive.*

We did not find the amorphous form mentioned, but we did find these two polymorphs, both formed near room temperature in the same sample. They have quite different molecular volumes (see Table 1) as well as structures, and it seems likely that the difference in sensitivity depends on the presence or absence of the second form. Since these are both crystalline modifications with presumably a well-defined transition temperature, it should be possible to avoid the formation of the unstable form by careful control of the temperature in the manufacturing process.

This work was performed during the tenure of a fellowship for which D.B. would like to thank the National Science Foundation. The preliminary calculations for both structures were carried out on the IBM 1620 computer of this laboratory, using programs prepared by M. Dobler, H.C. Mez, P. Strickler, and H. P. Weber. The least-squares calculations were carried out on the CDC 1604 computer at the Numerical Analysis Center of the University of Minnesota, using programs prepared at Princeton University under the direction of Professor R. Jacobson. This part of the work was performed by Mr E. O. Schlemper, and supported by a grant from the National Science Foundation. We thank them all for their help.

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The Crystal Structure of ScB_2C_2

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A compound of synthetic composition ScB_2C_2 was prepared, and its crystal structure was established by X-ray diffraction procedures. The presence of graphite lines in powder patterns of this material as well as small variations in lattice constants from preparations on the boron-poor side of ScB_2C_2 indicates some amount of compositional variation. Crystals are orthorhombic with space group *Pbam*. Lattice constants for the particular crystal used are $a = 5·175 \pm 0·005$, $b = 10·075 \pm 0·007$, $c = 3·440 \pm 0·005$ Å. A novel feature of the structure is the incorporation of boron and carbon into nets of aromatic-like five- and seven-membered rings. The scandium atoms lie between the seven-membered rings of adjacent layers. In addition to these 14 light atoms, each Sc is surrounded by 5 other Sc atoms at distances which are nearly the same as in metallic scandium.

Introduction

In a recent investigation of the ternary compounds formed between rare earth elements (M) and boron and carbon, Smith (1964) has reported the occurrence of a stable, high-melting compound, MB_2C_2, for nearly all of the lanthanides studied. X-ray diffraction studies clearly indicated that this phase is identical with the one previously thought to be either a pure boride or a boride stabilized by carbon. A notable feature of the structure proposed by Smith (1964; see also Smith & Giles, 1965) is the incorporation of boron and carbon into nets of fused four- and eight-

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membered heterocyclic rings sandwiching the metal atoms.

The present investigation of the Sc–B–C system near this same composition also shows an air-stable, high-melting compound which, however, is not isostructural with the lanthanide borocarbides. We place the stoichiometry as ScB_2C_2, although there is evidence of some solid solution between boron and carbon. In the crystal structure, herein reported, the B,C nets are composed of fused five- and seven-membered rings. Scandium atoms are situated above and below the seven-membered rings, whereas in the rare earth series the metals are between eight-membered rings.

Experimental

The preparations were made by arc-melting approximately 0·5 g of Sc metal filings with appropriate amounts of boron and carbon powders in a thorium-gettered argon atmosphere. These starting materials had been well mixed and pressed into a pellet under greater than 3·5 kg.mm^{-2} pressure. Each preparation was turned and remelted to homogenize the sample. A piece of the arc-melted ingot was annealed at ~2100°C by induction heating in a graphite crucible under a vacuum of 10^{-5} torr. After cooling to room temperature, well-developed, plate-like crystals having a dark metallic lustre were readily found.

The scandium metal was obtained from American Scandium Company, and spectroanalyses showed 0·043–0·43% impurities consisting mainly of Al, Ca, Pb, and Ta. Crystalline boron, reported to be 99·1% pure, was obtained from U.S. Borax Research, Anaheim, California. Spectroanalyses showed it to contain 0·24–2·4% impurities consisting mainly of Ca, Cr, Cu, Fe, Mg, Mn, Mo, Ni, and Si. Grade SP-1C graphite powder from National Carbon Company was used. Maximum spectroscopic impurities were certified to be 6 ppm by weight.

ScB_2C_2 was also found as a major phase in preparations of initial composition $ScBC_2$, ScB_2C, ScBC, and ScB_3C_3 but was not present in a preparation of initial composition Sc_2BC_2. Debye–Scherrer patterns showed that the *d* spacings in the $ScBC_2$ and ScBC batches differed slightly from a set which characterized the other preparations. In addition, the 002 line of graphite was present with weak-to-medium intensity in nearly all of the patterns. Whether this is unreacted graphite or graphite which came out of solution during cooling is not known.

When lattice constants from single-crystal work became available, only the batches at ScB_2C_2 composition were found to have powder patterns approaching that of a single phase. A chemical analysis of a preparation at this composition gave these percentages: Sc, 48·60 ± 0·08; B, 23·55 ± 0·07; C, 26·97 ± 0·43. Corresponding theoretical percentages (for ScB_2C_2) are 49·62, 23·87, and 26·51, respectively. The analysis corresponds to a Sc:B:C atomic ratio of 1·000 ± 0·002:2·015 ± 0·006: 2·08 ± 0·03. Excess carbon was detected (as graphite) in the powder pattern; this was the only impurity line observed.

Single-crystal oscillation and Weissenberg photographs showed orthorhombic symmetry. The observed systematic extinctions (0*kl* for *k* odd; *h*0*l* for *h* odd) are characteristic of the space groups *Pbam* and *Pba*2 (*International Tables for X-ray Crystallography*, 1952). Lattice constants obtained from measurements on a single-crystal orienter with Mo $K\alpha$ radiation ($\lambda = 0·7107$ Å) are: $a = 5·175 \pm 0·005$, $b = 10·075 \pm 0·007$, $c = 3·440 \pm 0·005$ Å. The crystal was from a $ScBC_2$ batch which contained a number of crystals suitable in size and quality for intensity data collection. Lattice constants of crystals from stoichiometric preparations are larger: $a = 5·23 \pm 0·01$, $b = 10·12 \pm 0·01$, $c = 3·45 \pm 0·01$ Å. Smaller values on the boron-poor side are to be expected if carbon substitutes for boron, the respective single-bond radii being 0·77 and 0·80 Å (Pauling, 1960).

Intensities were measured diffractometrically using a stationary-crystal stationary-counter technique (Furnas, 1957), zirconium-filtered Mo $K\alpha$ radiation, and pulse-height discrimination. The crystal shape approximated a parallelepiped, 0·12 × 0·16 × 0·08 mm, along *a*, *b*, and *c*, respectively. 147 independent reflections were recorded (up to $2\theta \simeq 45°$). The intensities were corrected for a small φ-dependent absorption, a 2θ-dependent absorption (assuming the crystal to be a sphere, $\mu R = 0·3$), and converted to a set of relative $|F|$'s through the application of Lorentz-polarization factors.

Determination of structure

The calculated density (3·35 g.cm^{-3}) which appeared most reasonable was for four ScB_2C_2 units per unit cell. The scandium atoms may be placed in general positions of *Pba*2 or in special fourfold positions of *Pbam*. However, because of the polar nature of *Pba*2, the *z* parameter of Sc can be fixed at zero, in which case the general positions in *Pba*2 are identical with the 4(*g*) positions in *Pbam* $[\pm(x, y, 0); \pm(\frac{1}{2}+x, \frac{1}{2}-y, 0)]$. Of the other fourfold positions in *Pbam*, the 4(*f*) and 4(*e*) sets both place Sc atoms too close to one another (at best, *c*/2 apart) and the 4(*h*) positions are equivalent to 4(*g*) but shifted by $\frac{1}{2}$ along *z*. Thus, the question of space group assignment depends here on the behavior of the light atoms.

Examination of the 2*k*0 and 4*k*0 reflections indicated the *x* parameter of Sc to be $\sim\frac{1}{8}$; acceptable distances between Sc atoms were obtained for $y \simeq \frac{1}{7}$. A three-dimensional Patterson synthesis confirmed these values, and showed other strong vector interactions at $W = \frac{1}{2}$.

A 'heavy atom' electron density synthesis exhibited light atom peaks only on the plane $Z = \frac{1}{2}$. Connexity of the layer was established as fused five- and seven-membered rings, the latter centered over Sc atoms. This structure model, based on *Pbam* with Sc in 4(*g*) and the light atoms in four sets of 4(*h*) positions, was refined by the full-matrix least-squares program of Gantzel, Sparks & Trueblood (ACA Program No. 317, unpublished). Atomic scattering factors used were those listed in *International Tables for X-ray Crystallography* (1962) for the neutral atoms. As an approximation to a weighting scheme appropriate for diffractometric data (Smith & Alexander, 1963) the following weights were used: $w=F_o^{1/4}, F_o<A$; $w=A^{5/4}F_o^{-1}, F_o>A$. When the structure factors were placed on an absolute scale, A was 27. Five cycles of least-squares refinement with anistropic temperature factors reduced the conventional R index to 2·6% (all reflections). Changes in the parameters at this point were about 0·1–0·01 times the estimated standard deviations. Difference maps showed no tendency of the light atom to deviate from the mirror at $Z=\frac{1}{2}$. There is thus no disagreement with the more symmetric space group, *Pbam*.

Remarks on atom identification and stoichiometry

We regard the agreement for an ordered, fully stoichiometric (ScB_2C_2) compound as quite excellent, even though, as noted above, the crystal used came from a boron-poor preparation. There is little in the behavior of the temperature parameters to suggest a gross misidentification of boron and carbon. Nevertheless, we decided to check further on the correctness of the atomic designations.

The original assignment of boron and carbon as such was based on peak heights which appeared in the 'heavy-atom' synthesis. Preparation of a complete electron density function now gave the following peak heights (in e.Å^{-3}): C(1), 5·9; C(2), 5·5; B(1), 4·9; B(2), 5·5. A difference synthesis from which Sc had been subtracted gave these peak heights (again in e.Å^{-3}): C(1), 4·9; C(2), 4·3; B(1), 4·1; B(2), 3·5.

With these somewhat uneven results in mind (and ignoring for the moment our chemical analysis), we carried out least-squares refinements for the following compositions: $ScBC_3$, ScB_3C, and one for ScB_2C_2 in which the form factors of B(2) and C(2) were interchanged. In all three cases, the R value was higher, if only nominally so (R=3·1–3·6%). More importantly, the thermal parameters refined to less plausible values.

Refinement of the data above $\sin\theta/\lambda=0{\cdot}30$ for our original model and preparation of a difference Fourier synthesis on the remaining data did not prove especially helpful. The value of R for this refinement was 1·9%. However, the biggest effect in the difference map was not at the boron and carbon positions, but rather, there was a hole ($-0{\cdot}2$ e.Å^{-3}) at the Sc positions.

Evidently the diffraction data are relatively insensitive to the form factors of the light atoms.* However, among the various models tested, our original model gave the best agreement and the most satisfactory set of thermal parameters. This model, moreover, is in agreement with chemical analyses and in part is directly supported by the bond data (see below). Because of small variations in the lattice constants, our results admit, at the same time, of some compositional variation. It seems most likely that substitutional effects occur in the light atom positions, accompanied possibly by changes in the Sc content; there is no indication of interstitial atoms in any of our difference maps.

Table 1. *Final parameters*

E.s.d.'s in parentheses. $\beta_{13}=\beta_{23}=0$ for all atoms.
Temperature factor expressed as: $\exp[-(h^2\beta_{11}+k^2\beta_{22}+l^2\beta_{33}+hk\beta_{12})]$

Atom	$10^4 x$	$10^4 y$	z	$10^4\beta_{11}$	$10^4\beta_{22}$	$10^4\beta_{33}$	$10^4\beta_{12}$
Sc	1375(2)	1488(1)	0	29(5)	2(1)	79(12)	−1(5)
C(1)	3904(12)	446(7)	$\frac{1}{2}$	67(22)	16(6)	101(52)	9(22)
C(2)	2948(12)	3122(6)	$\frac{1}{2}$	94(27)	15(7)	183(57)	1(20)
B(1)	3608(14)	4667(6)	$\frac{1}{2}$	48(24)	1(6)	55(55)	−3(26)
B(2)	4836(14)	1900(7)	$\frac{1}{2}$	50(24)	8(8)	121(64)	21(23)

Table 2. *Observed and calculated structure factors* (×10)

h k ℓ	$\lvert F_o\rvert$	F_c	h k ℓ	$\lvert F_o\rvert$	F_c	h k ℓ	$\lvert F_o\rvert$	F_c	h k ℓ	$\lvert F_o\rvert$	F_c	h k ℓ	$\lvert F_o\rvert$	F_c	h k ℓ	$\lvert F_o\rvert$	F_c	h k ℓ	$\lvert F_o\rvert$	F_c
0 2 0	156	-162	2 6 0	62	- 63	4 7 0	0	0	1 9 1	153	-153	4 1 1	120	121	1 6 2	225	220	4 2 2	56	- 57
0 4 0	346	-366	2 7 0	74	75	5 1 0	32	-36	1 10 1	0	- 13	4 2 1	261	267	1 7 2	262	263	4 3 2	42	48
0 6 0	514	517	2 8 0	35	- 34	5 2 0	263	260	2 0 1	92	- 83	4 3 1	21	18	1 8 2	218	-216	4 4 2	184	190
0 8 0	30	- 40	2 9 0	228	-234	5 3 0	128	130	2 1 1	541	-556	4 4 1	331	331	2 0 2	63	- 63	0 0 3	105	104
0 10 0	326	-334	2 10 0	52	54	5 4 0	166	-166	2 2 1	25	17	4 5 1	118	-118	2 1 2	252	-251	0 2 3	128	-129
1 1 0	208	199	3 1 0	333	-323	5 5 0	0	6	2 3 1	269	-258	4 6 1	279	-273	2 2 2	19	18	0 4 3	348	-343
1 2 0	406	-411	3 2 0	327	-324	6 0 0	171	169	2 4 1	63	59	4 7 1	46	47	2 3 2	58	- 58	0 6 3	156	158
1 3 0	326	-344	3 3 0	464	463	0 0 1	33	65	2 5 1	314	315	5 1 1	112	-108	2 4 2	54	51	1 1 3	164	159
1 4 0	122	121	3 4 0	163	163	0 2 1	253	-234	2 6 1	37	- 41	5 2 1	303	300	2 5 2	459	464	1 2 3	284	-281
1 5 0	52	- 52	3 5 0	116	-118	0 4 1	576	-574	2 7 1	263	-265	5 3 1	101	96	2 6 2	48	- 48	1 3 3	240	-239
1 6 0	288	282	3 6 0	52	50	0 6 1	241	237	2 8 1	0	- 8	5 4 1	153	-151	2 7 2	63	66	1 4 3	192	188
1 7 0	331	323	3 7 0	265	-265	0 8 1	316	317	2 9 1	323	-324	0 0 2	803	843	2 8 2	24	- 31	1 5 3	13	18
1 8 0	268	-262	3 8 0	175	-174	0 10 1	326	-328	3 1 1	155	-158	0 2 2	109	-108	3 1 2	251	-250	1 6 3	106	106
1 9 0	94	- 89	3 9 0	162	164	1 1 1	304	309	3 2 1	145	-143	0 4 2	282	-267	3 2 2	244	-246	2 0 3	57	- 59
1 10 0	33	- 26	4 0 0	427	-416	1 2 1	499	-513	3 3 1	255	254	0 6 2	406	395	3 3 2	355	360	2 1 3	321	-327
2 0 0	99	-101	4 1 0	73	67	1 3 1	407	-390	3 4 1	90	86	0 8 2	35	- 34	3 4 2	130	132	2 2 3	18	20
2 1 0	316	-336	4 2 0	59	- 63	1 4 1	338	333	3 5 1	136	137	1 1 2	146	142	3 5 2	98	-100	2 3 3	160	-164
2 2 0	30	37	4 3 0	55	59	1 5 1	28	24	3 6 1	189	188	1 2 2	292	-286	3 6 2	33	44	2 4 3	36	39
2 3 0	57	73	4 4 0	234	226	1 6 1	163	158	3 7 1	308	-310	1 3 2	236	-233	3 7 2	217	-227	2 5 3	207	211
2 4 0	69	69	4 5 0	88	- 91	1 7 1	212	204	3 8 1	149	-147	1 4 2	111	107	4 0 2	338	-345	3 1 3	96	-100
2 5 0	594	593	4 6 0	203	-210	1 8 1	280	-279	4 0 1	317	-320	1 5 2	44	- 40	4 1 2	52	57	3 2 3	97	-100

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* This is not to say that the data are insensitive to the presence of boron and carbon. The R value for Sc alone is 30%.

The parameters from our original refinement were accepted as final. These are given in Table 1. In Table 2 are listed the observed and calculated structure factors.

Discussion of structure

Fig. 1 illustrates the two types of planar layers which alternate along the *c*-axis direction. Within the boron–carbon layer, each atom is bonded to three other atoms so as to form a network of fused, aromatic-like five- and seven-membered rings. Each seven-membered ring contains 3C and 4B; each five-membered ring contains 3C and 2B. Since these are odd membered rings, at least one *homopolar* bond in each is unavoidable. Otherwise, boron and carbon alternate to produce a maximum number of *heteropolar* bonds.† Continuous layers of fused five- and seven-membered rings constitute a novel structural feature. While there are apparently no other known examples, this arrangement, interestingly enough, was anticipated by Wells (1954) as one of the denumerable ways of dividing a plane into polygons such that each point is connected to three others.

The scandium layer, separated by $c/2$ from the light atoms, is not close-packed; rather, each Sc is situated in the interstices of the heptagonal prisms. Nonetheless, Sc–Sc distances of 3·295 ± 0·003 and 3·319 ± 0·003

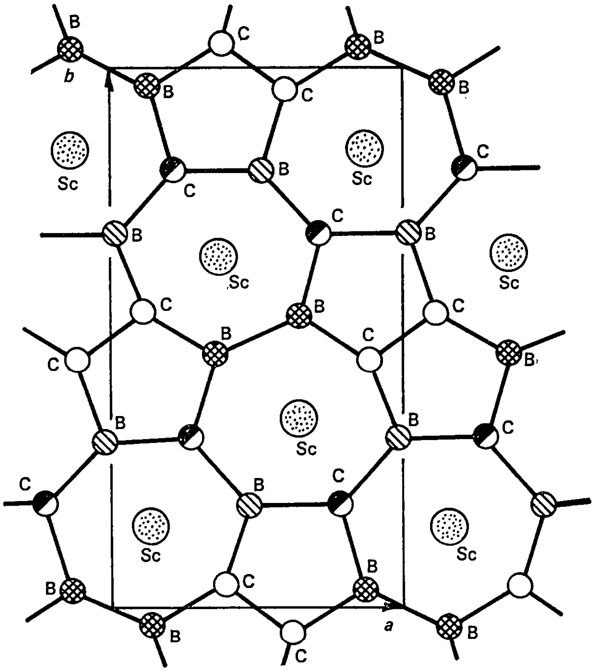

Fig. 1. Projection of ScB_2C_2 along the *c* axis. Scandium atoms are at $Z=0$; the boron-carbon net is at $Z=\frac{1}{2}$. Equivalent atoms are indicated.

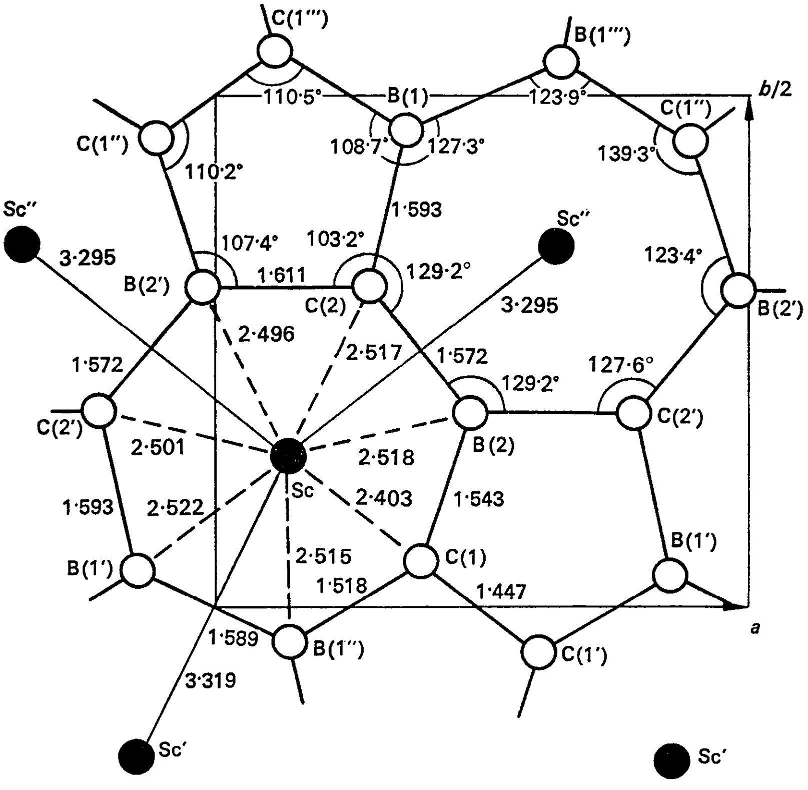

Fig. 2. Bond data for ScB_2C_2. Distances in Å. Numbering of atoms follow that of Table 3.

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† The situation is just reversed in stoichiometric boron carbide where the boron atoms are grouped together as icosahedra and the carbons as linear C_3 units (Clark & Hoard, 1943).

Å (Fig. 2 and Table 3) are very nearly the same as in h.c.p. scandium metal (Spedding, Daane & Herrmann, 1956). Two additional Sc atoms at ±c (=3·440±0·005 Å) complete a 19-fold ligancy about each Sc. With this arrangement, the calculated bulk density is actually higher than in metallic scandium, 3·35 *vs.* 2·985 g.cm^{-3}, respectively.

Of the 14 atoms in the heptagonal prisms, 12 are nearly equidistant from a given Sc. Thus, B(1), B(2), B(1′) and B(2′) as well as C(2) and C(2′) all have bond distances to Sc within a range 2·496–2·522 Å (σ's= 0·005–0·006 Å). These scandium–boron distances compare favorably with the Sc–B distance of 2·528 Å in the parameterless ScB$_2$ structure (Donnay, 1963). The exceptional atom is C(1) which is only 2·403±0·005 Å distant from Sc. In addition, the angle at C(1) is significantly larger (139·3°) than the other heptagonal angles, and C(1) forms shorter bonds within the light-atom network than does the other carbon atom, C(2). As seen in Fig. 2, the neighbors of C(1) are two boron atoms at 1·518 and 1·543 Å and a carbon at 1·447 Å. Those of C(2) are three boron atoms at 1·572, 1·593 and 1·611 Å.

We note, however, the special role of C(1) in the network. C(1) is bonded to only two scandium atoms, whereas B(1), B(2) and C(2) are bonded to four scandium atoms. Stated somewhat differently, C(1) is at a junction of two pentagons and one heptagon; the other light atoms are at junctions of one pentagon and two heptagons. Simple geometric considerations show that these polygons cannot be regular in this arrangement; were they regular, the sum of angles around a junction of the type at C(1) would be 344·6° (=2×108·0+128·6) and at the other type the sum (2×128·6+108·0) would in fact exceed 360°. It is thus clear that readjustments of bond angles within the light-atom layer must be made to preserve a planar network. Of the two types of junction, the one at C(1), however, requires the greater departures from regular angles.

On the basis of a lower coordination number (C.N.) for C(1) a smaller Sc–C(1) distance is not surprising. Moreover, the observed shortening is accompanied by changes in angles which serve to relieve most of the exigencies of network formation with planar pentagons and heptagons. As indicated in Fig. 2, the angle B(2)–C(1)–B(1″) is opened up by about 10·6°, and in consequence the immediately adjacent angles at B(2) and B(1″) are closed by about half this amount. It remains only for the B(1)–C(2)–B(2′) angle to be closed by about 5°. None of the remaining angles deviate by more than 2·5° from the angles required for regular polygons of this kind.

It is to be noted that the carbon atoms are bonded to only three other atoms in the network so that an additional electron from each might be presumed available for double-bond formation. A number of valence structures involving double bonds can be written, which, with the donation of two electrons from each electropositive metal atom, result in an octet of electrons for each light atom. However, the B–C distance in trimethylboron is 1·56±0·02 Å (Pauling, 1960). Using this as a single-bond norm for tricovalent boron, we see that the B–C distances involving C(2) (1·57, 1·59, 1·61 Å) are all somewhat longer. There is thus little evidence for double-bond character in the bonding about C(2). Subtracting the single-bond radius of carbon from 1·56 Å leads to a B–B single-bond distance of 1·58±0·02 Å. The B(1)–B(1‴) distance of 1·589±0·014 Å compares excellently with this value, and again gives no indication of partial double-bond character. Against this behavior, the B–C distances involving C(1) (1·52 and 1·54) do suggest double-bond formation whereby C(1) achieves an octet of electrons. We would envisage a resonance of the double bond among three intralayer bonds formed by C(1). In this connection we observe that the value of C(1)–C(1′) is close to the bond distance of 1·42 Å (Pauling, 1960) in graphite where the bond order should be (practically) identical.

We observe also that the bond lengths of these homopolar bonds support the atom assignments deduced earlier from the structure analysis. That is, the B(1)–B(1‴) distance, were this actually a carbon–carbon bond, would be longer than the C–C single-bond

Table 3. *Bond distances and bond angles*

E.s.d.'s also include uncertainties in lattice constants

Sc–2C(1)	2·403±0·005 Å	C(1)–B(1″)	1·518±0·009 Å
Sc–2B(2′)	2·496±0·005	C(1)–B(2)	1·543±0·009
Sc–2C(2′)	2·501±0·005	C(2)–B(2)	1·572±0·009
Sc–2B(1″)	2·515±0·005	C(2)–B(1)	1·593±0·009
Sc–2C(2)	2·517±0·005	C(2)–B(2′)	1·611±0·009
Sc–2B(2)	2·518±0·006		
Sc–2B(1′)	2·522±0·005	C(1)–C(1′)	1·447±0·012
Sc–2Sc″	3·295±0·003		
Sc–Sc′	3·319±0·003	B(1′)–B(1″)	1·589±0·014
Sc–2Sc	3·440±0·005		
B(1)–C(2)–B(2′)	103·2±0·5°	C(1)–B(1″)–B(1′)	123·9±0·7°
C(1)–B(2)–C(2′)	107·4±0·5	C(2)–B(1)–B(1‴)	127·3±0·7
C(2)–B(1)–C(1‴)	108·7±0·5	B(2)–C(2)–B(2′)	127·6±0·5
B(2)–C(1)–C(1′)	110·2±0·7	B(1)–C(2)–B(2)	129·2±0·5
C(1)–C(1′)–B(1′)	110·5±0·7	C(2)–B(2)–C(2′)	129·2±0·5
C(1)–B(2)–C(2)	123·4±0·6	B(2)–C(1)–B(1″)	139·3±0·6

value of 1·54 Å. By the same token, the C(1)–C(1′) distance would represent an exceptionally short distance were this a boron–boron bond. As noted above, the observed length is satisfactorily close to a known carbon–carbon bond type. The bond data do not give any definitive information about the designations of B(2) and C(2). Indeed, the stereochemical behavior of these two is so similar that a substitution of C for B and B for C at these sites could well take place, the end members of such substitutions being $ScBC_3$ and ScB_3C. We stress, however, that we have no data to support as wide a solid-solution range as this. (Electronic effects must also be considered since carbon has one more electron than does boron.) Another potential source of compositional variation involves interstitial sites along the *quasi* fivefold axes of the pentagons. For example, placement of additional atoms at $z \simeq \pm 0{\cdot}23$ would 'cap' the pentagons at distances of ~1·61 Å and would provide Sc–C(or B) distances of ~2·74 Å. Difference maps, however, gave no indication of any buildup at these positions.

In considering what other metals might form a borocarbide of the present type, it is easy to foresee an upper limit to the size of the metal atom which could be accommodated within the heptagonal prisms. The distance between metal atom sites within its layer is determined by the form of the B,C network. But, because of the covalent-like character of the net, no major extension in the network and so in the metal–metal distances is to be expected. Recent work (Nordine, Smith & Johnson, 1964) has shown that the smallest rare earth element, lutetium [radius = 1·73 Å (Teatum, Gschneidner & Waber, 1959)] forms the tetragonal MB_2C_2 compound observed (Smith, 1964) for the other lanthanides, and this in spite of the more favorable bond angles afforded fused five- and seven-membered rings over fused four- and eight-membered rings. While metal atoms smaller than scandium could conceivably 'rattle around' in the sites provided, there is reason to believe the metal–metal bonding is equally important. Investigations (Glaser, 1952; Nowotny, Ruby & Benesovsky, 1961) of the borocarbides of Hf (radius = 1·58 Å) and Zr (radius = 1·60 Å) have not disclosed any MB_2C_2 compounds. It would appear that the size effects are optimal for Sc.

Finally, it is of interest to speculate on the products of an acid hydrolysis of ScB_2C_2. [The reader may recall that the boron hydrides were originally prepared by the action of acid on magnesium boride (Stock, 1933)]. In the event of bond cleavage within the light-atom network, accompanied perhaps by the evolution of diborane or methane or a C_2 species, a number of novel boron-carbon organic compounds, not otherwise obtainable, are possible. On the other hand, the B,C network might possibly be stripped off essentially intact to yield giant two-dimensional polymers.

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