

strong blue-black coloration with ferric chloride. Recrystallization from water yielded 2.35 g. of essentially the same m. p. Schmitt and Hähle³ reported m. p. 204°.

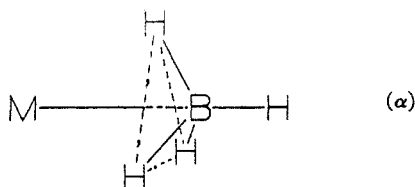
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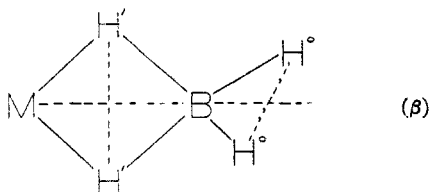
Reanalysis of the Electron Diffraction Data on $\text{Be}(\text{BH}_4)_2$ and $\text{Al}(\text{BH}_4)_3$

By S. H. BAUER*

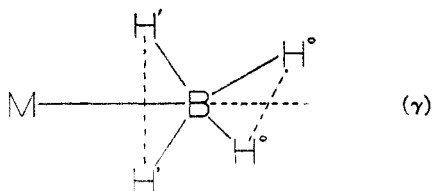
Some time ago electron diffraction data were presented in THIS JOURNAL for the borohydrides of aluminum¹ and beryllium.² These were interpreted as favoring structures of the type



The symmetrical hydrogen bridge structures



were definitely eliminated. However, highly unsymmetrical bridges



wherein the H' atoms are considerably closer to the boron than to the M atom, had not been considered. Since X-ray diffraction data indicate the presence of essentially tetrahedral BH_4^- ions in LiBH_4 ,³ NaBH_4 ,⁴ and $\text{U}(\text{BH}_4)_4$,⁵ we have reanalyzed the published electron diffraction results to check whether type γ structures are admissible. We found that when the $\angle \text{MBH}' > 50^\circ$, and the MH' distances get to be about 0.3 Å. greater than the BH' distances, the computed patterns can no longer be distinguished from those of type α , within our rather large experimental error. The same conclusion, that is, that the bridge struc-

tures must be considerably unsymmetric in order to be compatible with the infrared data, has been reached by Dr. W. C. Price.⁶

Beryllium Borohydride.—Intensity curves were computed for the following sequence of type γ models. The interatomic distances common to all are:

Be-B	1.66 Å.	$\angle \text{BBeB}$	180°	$\angle \text{H}^\circ \text{BH}^\circ$	110°		
I (α)	$\angle \text{BeBH}'$ [85°]	B-H'	1.19 Å.	Be-H'	1.87 Å.	B-H°	1.15 Å.
II	80	1.19		1.96		1.15	
III	65	1.22		1.59		1.17	
IV	50	1.26		1.29		1.20	
V	47.5	1.28		1.23		1.22	
VI	53	1.30		1.42		1.19	

The last model (VI) is the one suggested by Dr. Price, with Be-B 1.73 Å. and $\angle \text{H}^\circ \text{BH}^\circ$ 120°. Examination of the intensity curves clearly shows that the qualitative agreement between the computed and observed intensities is best for III; IV and V are definitely eliminated while I, II and VI are admissible. The quantitative agreement is best for model I (α), and gets poorer as the molecule is deformed to II, to III and to VI. It is possible that the quantitative agreement for III might have been better were the BeB/BeH' ratio made closer to 0.9, leaving the other distances as given above. Since the distant H-H terms contribute negligibly to the pattern, due to their relatively large temperature factors, one cannot tell from these diffraction data whether the bonds around the beryllium are quasi-square or quasi-tetrahedral; presumably, they are the latter.

We may now conclude that the available electron diffraction data are compatible with unsymmetric bridge models for $\text{Be}(\text{BH}_4)_2$ wherein: Be-B, 1.74 Å.; Be-H', 1.63; B-H', 1.28 Å.; B-H°, 1.22; $\angle \text{BeBH}'$, 65°.

Aluminum Borohydride.—There are two types of unsymmetric bridge models possible for $\text{Al}(\text{BH}_4)_3$. The first group, designated by γ_\perp , are those in which the three planes including $\text{AlH}'\text{H}'\text{B}_i$ ($i = 1, 2, 3$) are perpendicular to the plane of $\text{AlB}_1\text{B}_2\text{B}_3$; the second, designated by $\gamma\angle$, are those wherein these planes are inclined at 45° with respect to each other. In the former case, the H' atoms appear at the corners of a trigonal prism around the Al atom, while in the latter they form an octahedron. In both groups, the planes of $\text{H}^\circ \text{B}_i \text{H}^\circ$ are perpendicular to those of $\text{B}_i \text{H}' \text{H}' \text{Al}$.

Models A . . . E are of the γ_\perp type; the common distances are:

Al-B	2.14 Å.	B-H'	1.28 Å.	Al-H°	2.98 Å.
B-B	3.71	H°-H°	1.97	B-H°	1.20
A	$\angle \text{AlBH}' = 80^\circ$	Al-H' = 2.30 Å.		H'-H' = 2.52 Å.	
B	65	1.98		2.32	
C	50	1.64		1.96	
D	45	1.42		1.65	
E	53	1.74		2.06	

(6) W. C. Price, private communication, and W. C. Price, H. C. Longuet-Higgins, B. Rice and T. F. Young, *J. Chem. Phys.*, **17**, 217 (1949).

*Harvard University Postdoctoral Fellow 1949.

(1) J. Y. Beach and S. H. Bauer, *THIS JOURNAL*, **63**, 3440 (1940).

(2) G. Silbiger and S. H. Bauer, *ibid.*, **68**, 312 (1946).

(3) P. M. Harris and E. P. Meibohm, *ibid.*, **69**, 1231 (1947).

(4) A. M. Soldate, *ibid.*, **69**, 987 (1947).

(5) W. H. Zachariasen, private communication.

The last of these is the model proposed by Dr. Price, with

Al-B	2.19 Å.	B-H'	1.29 Å.
B-H°	1.20	B-B	3.79

The qualitative appearance of the computed intensity curves of these does not agree as well with the visual pattern as does the original model proposed by Beach and Bauer (type α); however, A and B are nevertheless admissible; C, D and E are definitely eliminated.

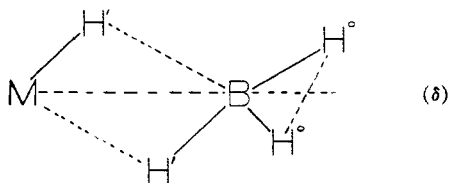
Models F ··· J are of the γ type; the common distances are

Al-B	2.14 Å.	B-H	1.18 Å.	Al-H°	2.98 Å.
F	$\angle AIBH' = 69.5^\circ$	Al-H'	= 2.20 Å.	B-H'	= 1.66 Å.
G	55.8	1.80		1.54	
H	36	1.30		1.53	
J	45	1.51		1.51	

In this group, the qualitative appearance of F and G are compatible with the experimental data.

We may therefore conclude that the available electron diffraction data are compatible with γ type models for $Al(BH_4)_3$, wherein: Al-B, 2.15 Å.; B-H' 1.28; Al-H', 2.1 Å.; B-H°, 1.21; $\angle AIBH'$, 60° . The γ_\perp are preferable to the γ_Δ configurations.

We thus find that the original conclusion that symmetrical bridge structures are inadmissible has been confirmed; however, the BH_4 tetrahedra may be oriented with a twofold axis (γ) rather than a threefold axis (α) along the M-B bond. Were larger amounts of material available so that sector photographs, and diffraction patterns covering a large angular range, could be prepared, an unambiguous decision between these two might be made. Indeed, then it would be worthwhile to test configurations of the type



However, one conclusion is pertinent—on the basis of either the α or γ model, the boron atom is surrounded by four hydrogens situated approximately at the corners of a tetrahedron, as in $LiBH_4$, etc. According to Harris and Meibohm,³ in lithium borohydride the Li^+ ions are actually surrounded by rough tetrahedra of H atoms, but each hydrogen comes from a different BH_4^- group.

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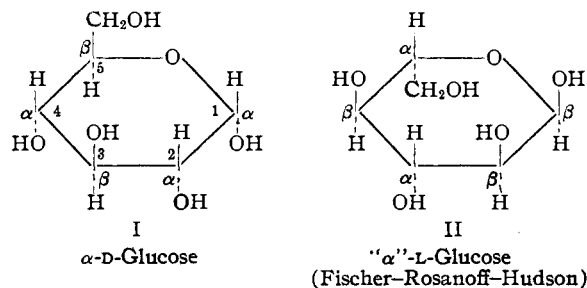
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Nomenclature of the Sugars

By LOUIS F. FIESER*

In 1909 Hudson¹ pointed out certain numerical relations in the optical rotations of glycosidic epimers of the ring forms of sugars and their glycosides, deduced a set of empirical rules, and applied these rules to definition of his familiar rules of nomenclature. After many years of search for evidence on the question of whether or not the α - and β -allocations deduced from rotatory relations are really correct, an unequivocal experimental method of determining the configurations was found in application of the elegant method of periodate oxidation of methyl glycosides,² and the results confirmed in all respects the allocations previously deduced through rotatory relations.³ Thus in the D-series, the originally trivial prefix " α " now stands for a rigorously established configuration of the glycosidic carbon atom and has the same significance in defining an orientation relative to the rest of the molecule as the prefix α does in the sterol series.⁴ When the Haworth perspective formula⁵ for α -D-glucose is oriented with the oxidic oxygen at the top or rear and C_1 to the right, the C_1 -hydrogen projects up or to the front (full line) and the C_1 -hydroxyl projects down or to the rear (dotted line). If C_1 in this



formula is defined as having the α -configuration, or if the 1-hydroxyl group is defined as α -oriented, then by logical extension the same scheme can be applied to the other four asymmetric centers: if a hydroxyl, alkyl or other substituent besides hydrogen projects down or to the rear, the carbon

* Harvard University Ph.D. 1924; Faculty 1930-.

(1) C. S. Hudson, *THIS JOURNAL*, **31**, 66 (1909).

(2) E. L. Jackson and C. S. Hudson, *ibid.*, **58**, 378 (1936); **59**, 994 (1937).

(3) Claude S. Hudson, "Collected Papers," II, Academic Press, New York, N. Y., 1948, pp. 1125-1182.

(4) L. F. Fieser and M. Fieser, "Natural Products Related to Phenanthrene," 3rd ed., Reinhold Publishing Corp., New York, N. Y., 1949.

(5) W. N. Haworth, "The Constitution of the Sugars," Edward Arnold and Co., London, 1929.