

## A Neutron Diffraction Study of Orthoboric Acid $D_3^{11}BO_3$

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A neutron-diffraction study of orthoboric acid  $D_3^{11}BO_3$  has shown that the O-D...O hydrogen bonds joining the  $D_3BO_3$  molecules are essentially straight, confirming the result obtained by Zachariasen from an X-ray diffraction study of  $H_3BO_3$ . The coherent neutron scattering length for  $^{11}B$  has been determined ( $0.61 \pm 0.01 \text{ cm}^{-12}$ ).

### Introduction

Orthoboric acid ( $H_3BO_3$ ) was one of the first hydrogen-bonded crystal structures to be examined by X-ray diffraction methods (Zachariasen, 1934) and, ever since, it has been a textbook example of the hydrogen bonding of molecules to form extensive sheets. In a later analysis based on X-ray counter-diffractometer data, Zachariasen (1954) determined precisely the geometry of the boron and oxygen atoms and gave evidence for the hydrogen atoms being in positions such that the hydrogen bonds O-H...O were more or less collinear.

Cowley (1953) investigated the structure of orthoboric acid in projection, using electron-diffraction data from micro-crystals containing faults in the stacking of the hydrogen-bonded sheets, and the structure analysis necessarily involved deductions as to the nature of the disorder. However, Cowley's results were in agreement with those of Zachariasen, except that the hydrogen atoms were found to be systematically displaced from a collinear arrangement in each hydrogen bond.

The observed proton magnetic resonance absorption spectrum of polycrystalline  $H_3BO_3$  was reported (Kume & Kakiuchi, 1960) to agree with the electron diffraction results, but Ibers & Holm (1961) showed that when interactions between boron and hydrogen nuclei were taken into account, agreement was obtained with a model structure based on collinear hydrogen bonds.

This paper describes a neutron diffraction study of orthoboric acid undertaken in order to study the details of the hydrogen bonding.

### Experimental

To carry out the experiment, it was necessary to use boric acid enriched in the  $^{11}B$  isotope, because of the excessive neutron absorption by  $^{10}B$  (4010 barns, natural abundance 18.8%). Boric acid enriched to 99%  $^{11}B$  was obtained from 20th Century Electronics Ltd. This material was subsequently deuterated by three

recrystallizations from solution in 99%  $D_2O$  in order to take advantage of the higher coherent neutron scattering length of deuterium, and to avoid the high incoherent scattering characteristics of hydrogen. Small crystals grew readily; however, they were usually multiply twinned on the plane (001). After some effort, a single crystal was grown which measured  $1.0 \times 2.0 \times 5.0 \text{ mm}^3$ , with the long axis parallel to  $c$ .

The extent of replacement of hydrogen by deuterium was estimated by dissolving a known weight of deuterated boric acid crystals in pure  $D_2O$  and determining the intensity of the HDO infrared absorption band at  $2.95\mu$  (Gaunt, 1954). This is the standard technique for measuring the degradation of  $D_2O$  in the Australian Atomic Energy Commission's reactor, HIFAR. Replacement was found to be  $93 \pm 2\%$ .

The cell data for orthoboric acid are shown in Table 1. The reciprocal cell translations for  $D_3^{11}BO_3$  were measured by Bond's method (1960) and agree with the corresponding parameters for  $H_3BO_3$  (Zachariasen, 1954). The X-radiation used was  $CrK\alpha_1$  ( $\lambda = 2.2896 \text{ \AA}$ ). The cell angles for  $D_3^{11}BO_3$  were assumed to be the same as for  $H_3BO_3$ .

Since the crystal structure of orthoboric acid consists of hydrogen-bonded molecules in almost coplanar sheets repeating after every second sheet, the distribution of intensity data in reciprocal space is similar for the even layers of  $l$ , and likewise for the odd layers of  $l$ .

Table 1. *Crystal data for orthoboric acid*

Crystal system: Triclinic

Space group:  $P\bar{1}$  (by structure analysis)

Cell parameters:  $H_3BO_3$  (Zachariasen, 1954)

$a = 7.039 \pm 0.002 \text{ \AA}$                        $\alpha = 92.58 \pm 0.02^\circ$

$b = 7.053 \pm 0.002$                          $\beta = 101.17 \pm 0.02$

$c = 6.578 \pm 0.002$                          $\gamma = 119.83 \pm 0.02$

$Z = 4$  molecules per unit cell

Cleavage plane: (001), perfect.

Zachariasen (1954),  $H_3BO_3$       Present results,  $D_3^{11}BO_3$

$d_{100} = 5.9135 \pm 0.002 \text{ \AA}$                $5.9126 \pm 0.0005 \text{ \AA}$

$d_{010} = 6.0335 \pm 0.002$                  $6.0319 \pm 0.0005$

$d_{001} = 6.3654 \pm 0.002$                  $6.3628 \pm 0.0005$

The X-ray analysis of Zachariassen (1954) was based on data for  $l=0, 1$ . In the present analysis, intensity data in the layers  $l=3, 5$  were also collected in order to investigate the slight atomic displacements from coplanarity in the planes  $z=\frac{1}{4}, \frac{3}{4}$ .

The neutron intensity data were measured on a single-crystal diffractometer on the reactor HIFAR. The crystal was mounted on a General Electric goniostat with  $e^*$  along the  $\Phi$  axis and the crystal angle settings were calculated from the formulae developed by Sabine (1963). So that maximum use could be made of the reactor operating cycle, goniostat angles for each reflexion were set hourly by the reactor operating staff and the diffractometer allowed to step scan in the  $\theta/2\theta$  mode through  $4^\circ$  in  $2\theta$  in  $3'$  steps. The spectrometer was monitor controlled and the flux at the specimen was approximately  $2.8 \times 10^5$  n.cm<sup>2</sup>.sec<sup>-1</sup>

at a wavelength of  $1.10 \text{ \AA}$ . The second order contamination of the monochromatic beam was  $0.25\%$ .

Because of other demands on the neutron diffractometer, the data were subdivided into five groups, each group containing data collected under the same experimental conditions. Many of the data were measured more than once to correlate the various groups. The integrated intensities were measured for 589 distinct reflexions and, of these, 154 were too low to be observed. Although the internal consistency of the results of this analysis indicates the presence of some systematic errors in the intensity data (see below), the origin of these remains unknown. In particular, there was no evidence for the presence of serious extinction effects. The measured intensities were placed on an absolute scale by comparison with the intensity of the 200 reflexion from a standard potassium bromide crystal

Table 2. Observed and calculated structure amplitudes and standard deviations

H	K	L	O	H	K	L	O	H	K	L	O	H	K	L	O	H	K	L	O	H	K	L	O												
1	204	-224	18	-13	106	93	10	-2	-74	L=1	23	-1	-44	23	-1	-2	20	18	5	174	-198	15	H=8	L=1	1	38	-49	8	H=-3	L=5	5	289	264	33	
2	152	-177	12	9	106	93	10	-6	142	-148	13	-6	23	-23	23	7	44	-52	11	6	23	20	23	-9	22	-7	22	2	19	-0	15	-3	19	-47	19
3	34	-23	18	-8	118	-147	10	0	194	183	12	-5	223	207	44	-9	74	L=1	11	-7	301	-300	23	H=0	L=1	1	19	-10	19	1	144	-147	10		
4	35	-21	35	7	38	30	11	1	102	-95	8	-4	186	-232	16	-8	237	239	15	-5	188	170	11	H=0	L=3	3	2	73	-75	10	2	73	-75	10	
6	116	113	18	-2	20	-36	13	2	341	-320	30	-2	82	72	9	-7	157	151	9	-4	23	-44	23	-6	20	-40	20	-6	20	-40	20	4	52	-48	11
7	140	161	19	5	38	30	11	3	118	123	8	-1	20	108	10	-5	237	239	15	-2	59	61	9	-2	59	61	9	4	52	-48	11	4	52	-48	11
8	43	-19	43	-4	143	-150	18	4	47	-53	9	-2	60	54	8	-6	363	-369	37	-3	23	-23	23	-5	19	21	19	4	52	-48	11	4	52	-48	11
H=1	L=0	0	0	-3	35	64	10	5	22	-19	22	0	120	108	10	-5	82	81	7	-3	225	219	17	0	136	-120	9	-3	189	-191	19	-3	189	-191	19
-9	42	-58	42	-2	121	151	10	6	120	116	8	2	381	-477	60	-2	99	97	5	-1	232	232	23	-1	232	232	23	-1	232	232	23	-1	232	232	23
-10	43	-17	43	-1	39	42	9	7	263	-208	25	3	404	-493	58	-1	37	36	8	-1	232	232	23	-1	232	232	23	-1	232	232	23	-1	232	232	23
-11	46	-61	7	0	17	20	17	8	47	-55	14	4	51	-59	9	-1	37	36	8	-1	232	232	23	-1	232	232	23	-1	232	232	23	-1	232	232	23
-12	202	233	10	1	237	-250	22	9	23	-33	23	4	51	-59	9	-1	37	36	8	-1	232	232	23	-1	232	232	23	-1	232	232	23	-1	232	232	23
-13	151	-157	9	2	29	-9	13	-4	139	-137	12	7	82	-5	22	2	20	170	14	1	63	63	7	-5	262	-242	25	2	262	-256	52	2	196	155	16
-14	377	451	36	3	135	-127	11	-4	139	-137	12	7	82	-5	22	2	20	170	14	1	63	63	7	-5	262	-242	25	2	196	155	16				
-15	24	-29	6	4	20	1	20	-3	46	-54	14	7	82	-5	22	2	20	170	14	1	63	63	7	-5	262	-242	25	2	196	155	16				
-16	189	-207	14	5	20	-50	20	-2	23	-4	23	8	23	-15	23	3	410	-454	55	-2	148	-157	9	-2	148	-157	9	-2	148	-157	9				
0	231	-249	10	H=6	L=0	0	0	-1	22	-27	22	9	45	-41	15	5	113	112	12	2	287	304	29	-2	2	-39	22	5	19	2	19	-2	148	-157	9
1	252	274	16	-17	144	-140	11	0	96	76	11	-8	23	-19	23	6	23	-2	23	0	1232	-1342	232	-6	92	-97	6	-6	92	-97	6				
2	316	-6	16	-7	54	59	27	1	46	-77	13	-7	23	-19	23	6	23	-2	23	0	1232	-1342	232	-6	92	-97	6	-6	92	-97	6				
4	104	-89	8	-6	47	69	17	3	264	-296	26	-6	22	28	22	-10	31	-26	19	-2	343	281	39	-4	256	255	22	-1	18	24	18				
5	29	-23	13	-5	138	185	33	4	21	16	21	-5	20	156	21	-9	204	-176	18	-9	204	-176	18	-3	82	-80	5	0	30	56	13				
6	91	-6	9	-4	403	-405	63	5	131	-135	12	-4	131	124	12	-8	101	-79	11	-4	53	35	11	-2	15	-0	15	1	30	-5	18				
7	83	54	20	-3	349	-427	25	6	115	-121	12	-3	52	-43	9	-7	376	359	48	0	95	-90	10	0	40	19	8	3	36	-18	13				
8	42	-10	42	-2	146	135	23	7	113	114	12	-2	348	-487	60	-2	148	-157	9	0	95	-90	10	0	40	19	8	3	36	-18	13				
H=2	L=4	0	0	0	30	-40	19	9	30	-40	19	-0	21	-13	9	-5	58	-63	10	1	37	37	12	2	213	212	16	-3	40	-44	8	-3	40	-44	8
-10	139	111	11	0	63	-77	22	H=5	L=1	1	1	1	133	136	13	-3	327	-363	34	-4	19	-13	19	2	139	-148	12	2	213	212	16	-5	19	27	19
-9	20	-42	20	1	69	75	9	-5	87	71	11	1	133	136	13	-3	327	-363	34	-4	19	-13	19	2	139	-148	12	2	213	212	16	-5	19	27	19
-8	20	-2	20	2	20	12	20	-4	388	344	69	2	20	20	20	-1	118	115	9	4	261	255	22	3	18	-29	18	-3	18	-29	18				
-7	39	36	13	3	20	-17	3	3	170	-155	15	3	120	-118	11	-1	19	-13	19	4	19	19	19	5	89	93	10	4	102	92	9	-4	102	92	9
-6	267	-25	17	4	18	-22	18	4	22	22	22	4	270	329	30	0	19	12	19	5	89	93	10	4	102	92	9	-4	102	92	9				
-5	84	66	6	H=7	L=0	0	0	-1	34	29	16	5	20	16	20	1	45	-20	12	6	99	-94	8	6	99	-94	8	6	99	-94	8				
-4	78	-84	6	-8	100	-70	14	0	20	18	20	6	99	-94	8	1	45	-20	12	6	99	-94	8	6	99	-94	8	6	99	-94	8				
-3	202	-236	22	-6	18	-12	18	2	396	461	60	6	99	-94	8	1	45	-20	12	6	99	-94	8	6	99	-94	8	6	99	-94	8				
-2	36	-36	36	-5	18	-27	18	3	118	79	11	6	99	-94	8	1	45	-20	12	6	99	-94	8	6	99	-94	8	6	99	-94	8				
-1	24	-39	6	-5	18	-27	18	3	118	79	11	6	99	-94	8	1	45	-20	12	6	99	-94	8	6	99	-94	8	6	99	-94	8				
0	40	-394	41	-2	209	167	27	4	20	-20	20	6	99	-94	8	1	45	-20	12	6	99	-94	8	6	99	-94	8	6	99	-94	8				
1	131	127	7	3	238	240	38	5	29	-36	10	-8	122	129	11	-10	35	28	17	4	8	52	10	4	8	52	10	4	8	52	10				
2	81	-2	81	-2	273	-233	48	6	43	56	9	-8	122	129	11	-10	35	28	17	4	8	52	10	4	8	52	10	4	8	52	10				
3	49	-72	21	-1	18	36	18	7	425	412	106	-5	20	-7	20	-8	203	193	15	5	2	375	-361	52	5	2	375	-361	52						
4	69	61	9	0	107	-89	19	8	178	-165	16	-4	36	95	12	-6	40	-51	11	-3	177	163	12	-6	302	270	27	-6	302	270	27				
5	322	-325	20	1	256	273	42	9	47	65	14	-2	341	-376	57	-5	21	26	21	-2	136	141	12	-2	278	-278	19	-2	278	-278	19				
6	64	-86	23	2	19	-51	19	H=4	L=1	1	-2	341	-376	57	-5	21	26	21	-2	136	141	12	-2	278	-278	19	-2	278	-278	19					
7	62	70	10	3	36	-30	11	-6	45	-37	10	-2	341	-376	57	-5	21	26	21	-2	136	141	12	-2	278	-278	19	-2	278	-278	19				
8	29	-40	13	H=12	L=0	26	4	-5	23	66	23	-2	341	-376	57	-5	21	26	21	-2	136	141	12	-2	278	-278	19	-2	278	-278	19				
H=3	L=3	L=3	L=3	-8	121	-95	26	-3	157	-163	9	2	371	379	52	-2	371	379	52	-2	371	379	52	-2	371	379	52	-2	371	379	52				
-9	76	-59	21	-7	200	184	35	-2	151	179	13	3	243	-234	26	1	22	12	5	-2	371	379	52	-2	371	379	52	-2	371	379	52				
-8	67	-58	9	-6	19	-24	19	-1	20	29	20	4	27	-35</																					

which had been shown to be free from extinction effects (volume  $2.87 \text{ mm}^3$ ), assuming the thermal parameters determined by Pryor (1965).

### The analysis of the data

An estimated standard deviation (e.s.d.) was assigned to every observed integrated intensity  $P$ , according to the expressions

$$\begin{aligned}\sigma^2(P) &= \sigma_1^2(P) + \sigma_2^2(P) \\ \sigma_1(P) &= (P + 2B)^{\frac{1}{2}} \\ \sigma_2(P) &= \alpha + \beta P + \gamma P^2\end{aligned}$$

where  $B$  was the total background intensity associated with the integrated intensity  $P$ , and  $\alpha$ ,  $\beta$ ,  $\gamma$  were constants whose values were somewhat arbitrarily defined for each of the five subgroups of the data. Thus, the variance in  $P$  was taken as the sum of the variance due to the counting statistics  $\sigma_1^2(P)$  and a factor  $\sigma_2^2(P)$  designed to account for possible systematic errors in the data, such as the error in assessing the true background  $B$ . The five groups of data were reduced to the same scale by comparison of the intensities of those reflexions common to more than one group. Standard deviations in these internal scaling factors were estimated and taken into account. The unobserved reflexions were assigned an intensity corresponding to half the minimum observable intensity under the particular experimental conditions. The data were then reduced to neutron structure amplitudes with their e.s.d.'s on the experimentally determined absolute scale (Table 2).

An important parameter to be determined in this analysis was the coherent neutron scattering length for the isotope  $^{11}B$ , hitherto unknown. The total bound atom scattering cross section of  $^{11}B$  has been reported as  $4.4 \pm 0.3$  barns (Hughes & Harvey, 1955), but this should have some contribution from both coherent and incoherent scattering since the nuclear spin of  $^{11}B$  is  $\frac{3}{2}$ . The coherent scattering length for  $^{11}B$  was assumed initially to have the value  $+0.30 \times 10^{-12}$  cm.

Structure factors were calculated with atomic parameters taken from Zachariasen's (1954) X-ray analysis. A Fourier synthesis of neutron scattering density using the calculated phase angles showed the deuterium atom peaks to be in positions corresponding to collinear hydrogen bonds  $O-D \cdots O$  rather than in the positions suggested by Cowley (1953). Also, the boron atom peaks were about the same height as the oxygen atom peaks, suggesting that the coherent scattering length for  $^{11}B$  was about  $0.55 \times 10^{-12}$  cm.

In a full-matrix least-squares refinement, there would be considerable parameter correlation among the various neutron scattering lengths and the overall scale factor for the observed data. For this reason, the deuterium/hydrogen replacement factor (*i.e.* the D/H scattering length) and the data scaling factor were assumed to have their experimentally determined values (see above).

The refinement process converged after five cycles of full-matrix least squares, using the ORFLS and

ORFFE programs of Busing, Martin & Levy (1962*a*, *b*), in which the variable parameters were the positional and anisotropic thermal parameters for each atom and the scattering length for each of the two crystallographically distinct boron atoms. The final  $R$  value was 0.130 for all reflexions (0.105 for observable reflexions only), and the weighted  $R$  for all data was 0.130.

The final calculated structure factors together with the observed structure amplitudes and their e.s.d.'s are listed in Table 2.

The final values of the atomic parameters with their e.s.d.'s are given in Table 3. The section of the Fourier synthesis of neutron scattering density at  $z = \frac{1}{4}$  is shown in Fig. 1. The labelling of the atoms conforms with that of the X-ray analysis (Zachariasen, 1954).

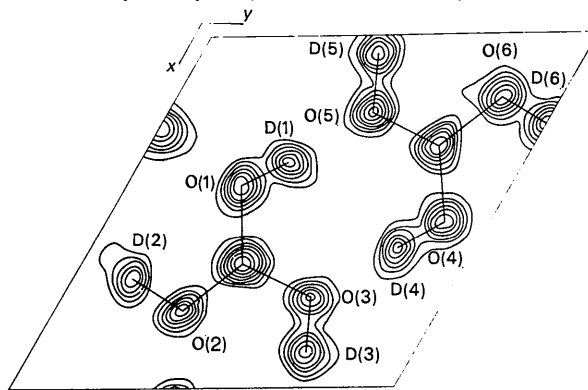


Fig. 1. Section of neutron scattering density at  $z = \frac{1}{4}$ .

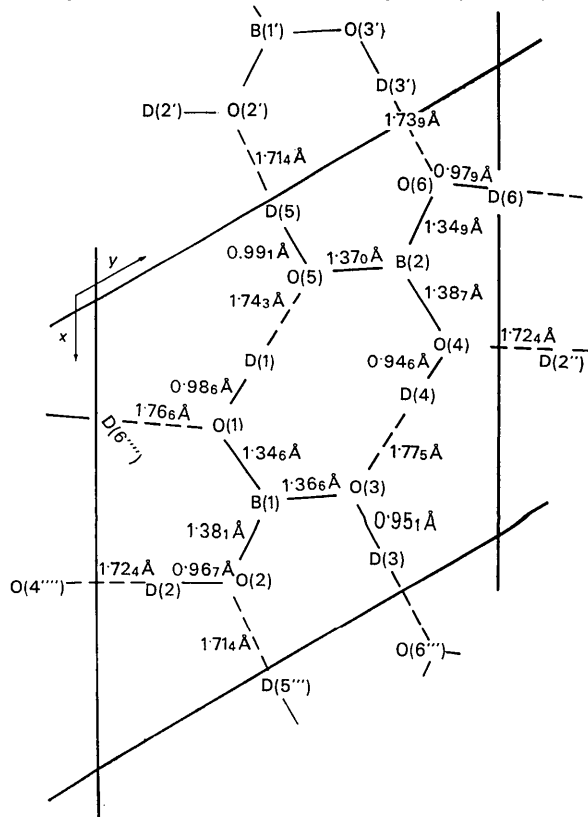


Fig. 2. Bond lengths in  $D_3^{11}BO_3$ .

### The accuracy of the structure parameters

The observed molecular parameters are shown in Figs. 2 and 3. The average values for chemically equivalent bond lengths and angles, with their e.s.d.'s, are given in Table 4. These parameters have not been corrected for the effects of thermal motion. The best least-squares plane through each of the two  $D_3BO_3$  molecules is given in Table 5. Both molecules are coplanar within experimental error.

The e.s.d.'s in the present results should lie between the limiting values shown in Table 4; e.g. for the bond

lengths B–O, the e.s.d. should be between 0.007 Å and 0.015 Å. The lower e.s.d. in each case is derived from the least-squares procedure and the higher e.s.d. from the observed distribution of those parameters which are assumed to be chemically equivalent. The least-squares e.s.d.'s are underestimates to the extent that they do not take into account possible systematic errors in the data. The e.s.d.'s from the distributions of equivalent parameters may be overestimated, since there could be small but real differences in the parameters which have been averaged. This is probably the reason for the large discrepancy between the two

Table 3. Atomic parameters and their e.s.d.'s

Positional parameters are expressed as fractions of the lattice parameters.  
Thermal parameters are in the form  $\exp[-\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{13}hl + \beta_{23}kl]$ .  
All parameters are given  $\times 10^4$ .

Atom	$x, \sigma(x)$	$y, \sigma(y)$	$z, \sigma(z)$	$\beta_{11},$ $\sigma(\beta_{11})$	$\beta_{22},$ $\sigma(\beta_{22})$	$\beta_{33},$ $\sigma(\beta_{33})$	$\beta_{12},$ $\sigma(\beta_{12})$	$\beta_{13},$ $\sigma(\beta_{13})$	$\beta_{23},$ $\sigma(\beta_{23})$
B(1)	6464 (7)	4263 (7)	2556 (12)	147 (12)	135 (10)	387 (27)	73 (8)	74 (16)	58 (15)
B(2)	3052 (9)	7575 (8)	2382 (24)	198 (13)	158 (11)	270 (28)	95 (9)	76 (25)	75 (33)
O(1)	4268 (8)	3020 (8)	2561 (18)	156 (11)	149 (10)	440 (30)	75 (9)	132 (19)	89 (25)
O(2)	7713 (8)	3255 (8)	2510 (22)	164 (11)	150 (11)	518 (41)	66 (9)	11 (27)	-44 (27)
O(3)	7448 (10)	6487 (9)	2599 (26)	226 (14)	188 (11)	510 (36)	132 (11)	104 (36)	69 (24)
O(4)	5334 (8)	8850 (8)	2443 (14)	196 (11)	171 (11)	507 (31)	100 (9)	121 (20)	76 (19)
O(5)	2132 (8)	5362 (7)	2479 (13)	189 (13)	154 (10)	453 (30)	102 (10)	72 (21)	76 (19)
O(6)	1777 (8)	8507 (7)	2352 (12)	174 (11)	163 (11)	429 (26)	92 (9)	112 (18)	38 (17)
D(1)	3476 (9)	3849 (8)	2505 (26)	196 (13)	208 (13)	526 (37)	127 (11)	109 (34)	101 (25)
D(2)	6863 (11)	1671 (10)	2478 (35)	272 (16)	247 (15)	485 (40)	181 (14)	136 (25)	72 (38)
D(3)	8983 (8)	7213 (8)	2523 (16)	198 (13)	191 (12)	613 (33)	119 (10)	177 (21)	136 (20)
D(4)	6047 (9)	8008 (9)	2562 (21)	209 (14)	219 (13)	567 (36)	123 (12)	94 (23)	45 (33)
D(5)	496 (9)	4775 (9)	2432 (15)	197 (14)	207 (12)	518 (33)	117 (11)	27 (21)	0 (20)
D(6)	2654 (9)	10120 (8)	2439 (15)	200 (12)	187 (12)	513 (29)	112 (11)	116 (19)	86 (20)

R.m.s. parameter changes in last cycle of least-squares refinement									
B	4	3	5	11	1	11	2	10	12
O	4	2	7	7	2	18	5	8	3
D	5	5	8	7	7	13	7	11	11

The neutron scattering lengths ( $\times 10^{-12}$  cm) were as follows:

B(1)	0.60 $\pm$ 0.01	} Structure parameters
B(2)	0.61 $\pm$ 0.01	
O	0.58	
D <sub>eff</sub>	0.58	

Assuming a D/H substitution of 93 %, and

$$b_D = 0.65$$

$$b_H = -0.38 \times 10^{-12} \text{ cm}$$

Table 4. Average interatomic distances and angles with their e.s.d.'s

Interatomic distances Atoms	$d(\text{Å})$	$\sigma(d)(\text{Å})$	
		(from distribution)	(from least squares)
B–O	1.367	0.015	0.007
O–D	0.970	0.017	0.008
O...O (intramolecular)	2.367	0.013	0.007
O...O (hydrogen bond)	2.713	0.019	0.007
D...O (hydrogen bond)	1.744	0.022	0.008
Bond angles Atoms	$\theta(^{\circ})$	$\sigma(\theta)(^{\circ})$	
		(from distribution)	(from least squares)
O–B–O	(120)	0.7	0.6
B–O–D	113.3	0.8	0.6
D...O–B (hydrogen bond)	126.9	1.1	0.6
O...D–O (hydrogen bond)	177.9	1.4	1.3

Table 5. *The best least-squares planes through the two molecules  $D_3BO_3$*

(in the crystal axes coordinate system)

Molecule 1

$$0.00622x - 0.01311y + 0.96740z = 1.60104$$

Molecule 2

$$-0.02679x + 0.01719y + 0.97229z = 1.59525$$

*x, y, z in Å*

Distances from planes for atoms forming the plane

Plane 1		Plane 2	
Atom	<i>d</i> (Å)	Atom	<i>d</i> (Å)
B(1)	0.014	B(2)	-0.038
O(1)	0.020	O(4)	-0.026
O(2)	0.000	O(5)	0.015
O(3)	0.025	O(6)	-0.021
D(1)	-0.027	D(4)	0.026
D(2)	-0.010	D(5)	0.006
D(3)	-0.023	D(6)	0.037

Distances from planes for atoms\* not forming the plane

Plane 1		Plane 2	
Atom	<i>d</i> (Å)	Atom	<i>d</i> (Å)
O(5)	-0.064	D(2'')	0.002
D(6''')	-0.038	O(3)	0.005
O(4''')	-0.012	D(1)	-0.012
D(5''')	-0.050	O(2)	0.093
O(6''')	-0.131	D(3')	0.125
D(4)	-0.018	O(1'')	0.119

\* These atoms may be identified from Figs. 2 and 3.

e.s.d.'s for the  $D \cdots O$  hydrogen bond distances (0.008 Å and 0.022 Å). The apparent distortions from intramolecular symmetry  $C_{3h}$  (Figs. 2 and 3) are greater than would be expected from the weak van der Waals interactions in the asymmetrical crystal environment, although there is evidence, from the assignment of a weak infrared absorption as a B-O stretching mode (Bethel & Sheppard, 1955), that there are small perturbations of the molecules in this crystal structure. However, the larger e.s.d.'s given in Table 4 are probably more realistic than the least-squares e.s.d.'s.

The e.s.d.'s derived from the distribution of equivalent bond distances and angles are considerably larger than the corresponding values in the X-ray analysis (Zachariasen, 1954)

e.g.  $O \cdots O$  (intramolecular)  $2.356 \pm 0.009$  Å and  $O \cdots O$  (hydrogen bonded)  $2.720 \pm 0.009$  Å.

### The $^{11}B$ scattering length

The values of the scattering lengths for the two crystallographically distinct boron atoms are  $0.60 \pm 0.01$  and  $0.61 \pm 0.01 \times 10^{-12}$  cm. The scattering cross section derived from these values ( $4.60 \pm 0.01$  barns) taken with the reported total scattering cross section ( $4.4 \pm 0.3$  barns), indicates that there can be very little, if any, incoherent neutron scattering from  $^{11}B$ . It was considered possible that the coherent scattering length might be an overestimate as a result of overestimating the absolute scale of the observed structure amplitudes. However, after two cycles of least-squares refinement in which the scattering length for  $^{11}B$  and the overall scale factor for the data were included as variable parameters, the scattering length for  $^{11}B$  increased to

$0.64 \times 10^{-12}$  cm and the scale factor (as applied to  $F_{obs}$ ) increased by 5%.

It is concluded that, while the reported least-squares e.s.d. may be underestimated, the large coherent scattering length for  $^{11}B$  is real.

### Description of the structure

The average B-O bond length (1.367 Å) agrees with the value ( $1.361 \pm 0.002$  Å) determined by Zachariasen, 1954, and is similar to the values for single bonds B-O in other borate crystal structures containing flat triangular  $BO_3$  groups (Zachariasen, 1963).

The average O-D bond length (0.97 Å) is normal for a long hydrogen bond (2.71 Å); cf. 1.01 Å in solid  $D_2O$  (Peterson & Levy, 1957); 0.96 Å in perdeuterated violic acid monohydrate (Craven & Takei, 1964). None of the angles at the boron atom is significantly different from  $120^\circ$ . The angles at the oxygen atoms are B-O-D,  $113.3^\circ$ ; B-O $\cdots$ D (hydrogen bond),  $126.9^\circ$ . These angles suggest that at each oxygen atom the two lone pairs and the two bonding pairs of electrons are in tetrahedrally oriented orbitals since, if the arrangement were regular, the B-O-D angle would be  $109^\circ$  and the most favourable angle for the hydrogen bond in the molecular plane would be  $125.3^\circ$ . These are the idealized angles between single-single and single-double bonds for quadricovalent atoms proposed by Pauling (1960). The observed opening of the angle B-O-D from the tetrahedral angle may be attributed to intramolecular repulsions  $D \cdots O$ .

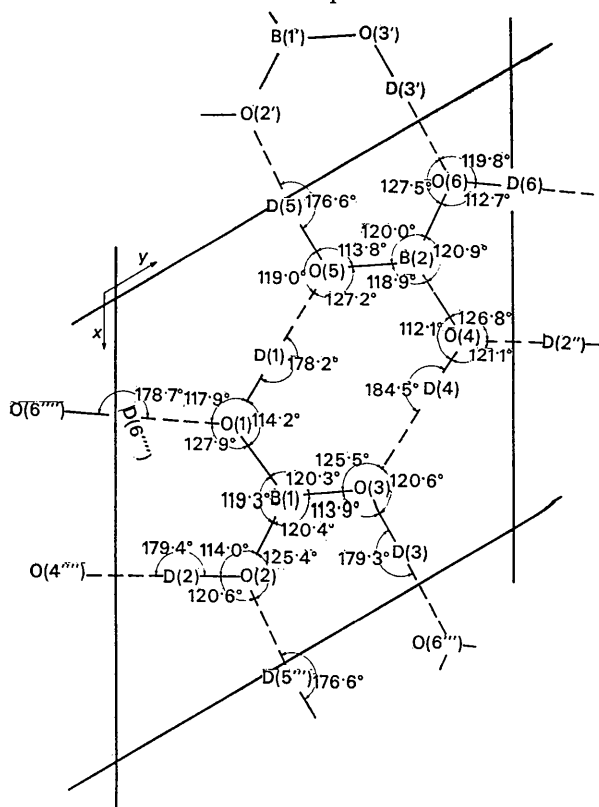


Fig. 3. Bond angles in  $D_3^{11}BO_3$ .

Zachariasen (1954) proposed that the small tilts from the plane (001) which are observed between individually coplanar molecules are predominantly the result of weak interactions between adjacent hydrogen-bonded sheets which for idealized coplanar sheets would be 3.18 Å apart in this structure.

In the neutron structure analysis the angle between the best least-squares planes through crystallographically independent molecules is found to be 9°.

While these weak interactions are undoubtedly present, it is probable that a major factor inducing the molecules to tilt is the possibility of forming stronger hydrogen bonds within the sheets since, if the structure consisted of sheets of coplanar molecules with trigonal symmetry, each molecule having the same geometry as observed in the crystal structure,\* and the hydrogen bonds were equivalent with O...O distances of 2.71 Å, the hydrogen atoms would be displaced by 0.11 Å from the line of centres O...O in each bond while the angle O-D...O would be 169.6° and the acceptor angle D...O-B would be 116.3°.

This configuration is presumably unfavourable compared with the observed one in which the molecular tilts results in a straightening of the angles O-D...O to 177.9°, and the hydrogen atoms are turned towards the lone pairs of electrons on the acceptor oxygen atoms.

Since the bending of the hydrogen bonds reported by Cowley (O-H...O, 167°) is similar to that in the hypothetical structure with strictly coplanar molecules it may be possible that in very thin disordered crystals the sheets are coplanar; however, it is difficult to see why this should be so.

The r.m.s. amplitudes of the atomic vibrations with their e.s.d.'s are given in Table 6. These have been calculated from the thermal parameter (Table 3) for the directions along the principal axes of the vibrational ellipsoids. The overall thermal vibrations are readily understood in terms of the hydrogen bonding of orthoboric acid molecules into compact sheets parallel to (001), with much weaker interactions between neighbouring sheets. For all atoms, the direction of maximum thermal vibration is the normal to the plane (001) (i.e. along  $c^*$ ), within the e.s.d.'s derived from the least-squares refinement. Thus the other principal axes of the ellipsoids ( $u_1$  and  $u_2$ ) lie in the plane (001). Within the plane (001) the thermal vibrations are essentially isotropic. The average r.m.s. amplitude of vibration in the plane (001) is 0.17 Å, agreeing with the value (0.17 Å) derived from the X-ray data for H<sub>3</sub>BO<sub>3</sub> (Zachariasen, 1954).

*Note added in proof.* - Since this paper was submitted for publication a report of measurements of the coherent scattering length of <sup>11</sup>B by mirror reflexion (Donaldson, Passell, Bartolini & Groves, 1964) has

\* Chidambaram (1962) has shown that hydrogen bonds are more easily deformable than covalent bonds, so the hypothetical coplanar sheets are expected to have an intramolecular geometry very similar to that observed.

Table 6. *The atomic thermal vibrations*

The r.m.s. amplitudes  $u_1$ ,  $u_2$ ,  $u_3$  correspond to directions parallel to the principal axes of the thermal displacement ellipsoids. The angles between the directions of maximum displacement and the reciprocal lattice vector  $c^*$  are also given. The corresponding e.s.d.'s are in brackets.

Atom	$u_1$	$u_2$ (Å × 10 <sup>2</sup> )	$u_3$	Angle $u_3c^*$ (°)
B(1)	15(1)	16(1)	28(1)	4(3)
B(2)	16(1)	19(1)	24(1)	14(10)
O(1)	15(1)	17(1)	30(1)	6(3)
O(2)	16(1)	18(1)	34(2)	7(3)
O(3)	16(1)	20(1)	32(1)	2(6)
O(4)	17(1)	18(1)	32(1)	1(3)
O(5)	16(1)	18(1)	31(1)	8(4)
O(6)	16(1)	17(1)	30(1)	7(3)
D(1)	17(1)	19(1)	33(1)	6(3)
D(2)	17(1)	22(1)	31(1)	4(4)
D(3)	16(1)	17(1)	36(1)	7(2)
D(4)	18(1)	20(1)	34(1)	6(4)
D(5)	18(1)	20(1)	34(1)	5(3)
D(6)	17(1)	18(1)	32(1)	3(3)

become available to us. They obtained  $0.66 \pm 0.3 \times 10^{-12}$  cm, which is in good agreement with the present value.

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