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Further Refinements of Some Rigid Boron Compounds

BY G. S. PAWLEY*

Department of Chemistry, Harvard University, Cambridge, Massachusetts 02138, *U.S.A.*

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A number of suitable rigid-molecule structures of boron compounds have been refined primarily to test a method of constraining the anisotropic temperature factors to agree with rigid motion. The structures reported have a wide range of success and should serve as a basis for comparing later work. In addition to giving greater accuracy in estimating the rigid molecular motion, the method yields more reliable bond lengths for the same initial data and a considerable economic advantage. All significant improvements are listed and also the new corrected bond lengths, which should be of interest in theoretical boron chemistry.

1. Introduction

Boron framework structures provide ideal examples of crystals composed of rigid molecules. Pawley (1964) has described a method of structure refinement in which the anisotropic temperature factors of the atoms in a molecule are constrained to agree with rigid-body translational and rotational movement of that molecule. Previously the atomic anisotropic temperature factors were refined individually and were analysed in terms of the molecular mean square translational and rotational tensors, **T** and **ω**, only at the conclusion of refinement (Cruickshank, 1956*a*). The new refinement method includes a variation of the origin of **ω**, shown to be necessary by Pawley (1963). However, no attempt has been made to include the screw-rotation coefficients that the full theory requires (V. Schomaker, private communication).

No new measurements have been taken, but the new results should be of interest both in boron chemistry and in computational crystallography – the former because the bond lengths are easily corrected for the errors introduced by the molecular rotation (Cruickshank, 1956*b*), giving bonds related by the molecular symmetry generally with improved agreement.

The computational advantages are encouraging. The least-squares cycles are shorter, owing to a decrease in the number of parameters necessary, and fewer cycles are required to complete refinement, which cannot then be significantly improved by removing the constraints. This last fact is a result of the careful choice of rigid molecule structures. Another advantage is that unreasonable results in the thermal motion are more obvious than they are with individual anisotropic temperature factors. This point is exemplified by the structures in § 2.

The program used was a modification of Busing & Levy's (1962) ORGLS, a full-matrix general least-squares program. The scattering factors used were from *International Tables for X-ray Crystallography* (1962). All the calculations were done on the Harvard IBM 7090 computer.

The results tabulated for each structure are in two different coordinate systems. The atomic positions and temperature factors are in the crystal fractional coordinate system as used in the appropriate original paper. Some of the atom coordinates have been transformed by a symmetry operation so that atoms in the same structure belong all to one molecule. The temperature factor is

$$\exp\left[-10^{-4}(h^2\beta_{11}+k^2\beta_{22}+l^2\beta_{33}+2kl\beta_{23}+2lh\beta_{31}+2hk\beta_{12})\right].$$

The mean-square displacement tensors **T** and **ω** are in an Å orthogonal system (X, Y, Z) related to the crystal system (x, y, z) by having $\mathbf{X}\parallel\mathbf{x}$ and $\mathbf{Y}\parallel\mathbf{y}^*$; then for any column vector **r**,

$$\mathbf{R}=\begin{pmatrix} a & b\cos\gamma & c\cos\beta \\ 0 & b\sin\gamma & c(\cos\alpha-\cos\beta\cos\gamma)\ \operatorname{cosec}\gamma \\ 0 & 0 & cd\operatorname{cosec}\gamma \end{pmatrix}\cdot\mathbf{r}$$

where $d^2=1-\cos^2\alpha-\cos^2\beta-\cos^2\gamma+2\cos\alpha\cos\beta\cos\gamma$.

The molecular centre of gravity (CG) and the origin of **ω**, (ξ, η, ζ), are also in this system.

The weighting scheme used in every refinement was

$$\sigma^2(F_o)=1 \quad \text{for } F_o<F_w,$$
$$=F_o/F_w \quad \text{for } F_o>F_w,$$

unobserveds or zeros excluded.

The value of F_w was always chosen so that there was very little variation of $|F_o-F_c|/\sigma(F_o)$ with F_o. The values of F_w quoted are on the same scales as the F_o's in the original papers.

Drops in R indices were tested for significance assuming $(R_{\text{initial}}/R_{\text{final}})^2$ is F-distributed, and as

$$R=\Sigma\,|F_o-F_c|/\,\Sigma\,F_o$$

the influence of different weighting schemes is avoided.

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* Present address: Department of Natural Philosophy, Drummond Street, Edinburgh 8, Scotland.

2. Unsuccessful structures

Three structures are discussed under this heading, all of which reached a lower R index than heretofore. Most of the atoms had positive definite temperature ellipsoids, yet the values taken on by **T**, **ω** and (ξ, η, ζ) were physically implausible. Common to all of these structures was the fact that only a small proportion of the reflections within the limiting sphere were observed, a situation which is known to give rise to temperature factor difficulties.

B_9H_{15}

This structure was solved by Dickerson, Wheatley, Howell & Lipscomb (1957) and refined to $R=0·155$. The present refinement reached $R=0·14$ after four cycles, and it was evident that (ξ, η, ζ) was moving with increasing steps away from the original value, which was always taken to be the centre of gravity. In fact the shift on the fourth cycle was larger than the total of previous shifts, as indicated in Table 1, and the error was becoming far too large. Refinement was stopped at this point, and little emphasis can be given to the results.

Table 1. *The course of* (ξ, η, ζ) *during refinement, for* B_9H_{15}

R dropped from 0·16 to 0·14
There were 374 observations

C.G.	shift 1	shift 2	shift 3	shift 4	error
4·88 Å	0·77	0·21	0·37	0·26	1·08
5·15	0·41	−0·20	−0·09	−1·07	0·88
2·72	−0·13	−0·61	−0·42	−1·13	1·36

Table 2. B_5H_{11}

299 observations
$F_w=8$

Final fractional coordinates

	x	y	z
B(1)	0·2890	0·1066	0·3202
B(2)	0·1326	0·1057	0·1762
B(3)	0·0234	0·0467	0·3171
B(4)	−0·1113*	0·1656	0·2076
B(5)	−0·1197*	0·2170	0·3773

	x	y	z
H(1)	0·412	0·012	0·327
H(2)	0·325	0·224	0·385
H(3)	0·147	0·031	0·103
H(4)	−0·034*	−0·064*	0·328
H(5)	−0·229*	0·111	0·151
H(6)	−0·020*	0·307	0·427
H(7)	−0·261*	0·169	0·415
H(8)	0·263	0·175	0·216
H(9)	0·027	0·207	0·142
H(10)	−0·149*	0·305	0·257
H(11)	0·068	0·103	0·401

Average errors

B	0·0017	0·0012	0·0011
H	0·014	0·011	0·009

$$\mathbf{T}=\begin{bmatrix} 3{\cdot}42 & -0{\cdot}51 & 0{\cdot}63 \\ & 3{\cdot}79 & -0{\cdot}09 \\ & & 2{\cdot}89 \end{bmatrix} \quad \sigma(\mathbf{T})=\begin{bmatrix} 0{\cdot}26 & 0{\cdot}31 & 0{\cdot}18 \\ & 0{\cdot}40 & 0{\cdot}33 \\ & & 0{\cdot}31 \end{bmatrix} \text{Å}^2\,.\,10^{-2}$$

$$\boldsymbol{\omega}=\begin{bmatrix} -32{\cdot}0 & 16{\cdot}7 & 11{\cdot}7 \\ & 16{\cdot}1 & 1{\cdot}2 \\ & & 12{\cdot}5 \end{bmatrix} \quad \sigma(\boldsymbol{\omega})=\begin{bmatrix} 16{\cdot}7 & 9{\cdot}0 & 6{\cdot}6 \\ & 8{\cdot}1 & 6{\cdot}5 \\ & & 9{\cdot}0 \end{bmatrix} \text{deg}^2$$

C.G. = (0·09, 1·11, 2·83) (ξ, η, ζ) = (0·08, 0·88, 2·98) Å, error 0·27.

* Transformed coordinate.

Table 3. B_6H_{10}

234 observations
$F_w=6$

Final fractional coordinates

	x	y	z
B(1)	0	0·2455	0·3233
B(2)	0·1069	0·0699	0·3270
B(3)	0·1875	0·2084	0·2065
B(4)	0	0·3010	0·1255

	x	y	z
H(1)	0	0·344	0·416
H(2)	0·225	0·010	0·388
H(3)	0·329	0·260	0·237
H(4)	0	0·411	0·096
H(5)	0·104	0·229	0·054
H(6)	0·179	0·074	0·194

Average errors

B	0·0008	0·0009	0·0015
H	0·011	0·011	0·011

$$\mathbf{T}=\begin{bmatrix} 2{\cdot}42 & 0 & 0 \\ & 1{\cdot}81 & 0{\cdot}30 \\ & & 2{\cdot}58 \end{bmatrix} \quad \sigma(\mathbf{T})=\begin{bmatrix} 0{\cdot}26 & — & — \\ & 0{\cdot}21 & 0{\cdot}27 \\ & & 0{\cdot}25 \end{bmatrix} \text{Å}^2\,.\,10^{-2}$$

$$\boldsymbol{\omega}=\begin{bmatrix} -0{\cdot}4 & 0 & 0 \\ & 8{\cdot}9 & 0{\cdot}6 \\ & & 17{\cdot}0 \end{bmatrix} \quad \sigma(\boldsymbol{\omega})=\begin{bmatrix} 4{\cdot}2 & — & — \\ & 7{\cdot}2 & 5{\cdot}5 \\ & & 6{\cdot}9 \end{bmatrix} \text{deg.}^2$$

C.G. = (0, 1·70, 2·12) (ξ, η, ζ) = (0, 2·12, 2·81) Å, error 0·52.

B_5H_{11}

Lavine & Lipscomb (1954) solved this structure, and refinement to $R=0{\cdot}106$ was done by Moore, Dickerson & Lipscomb (1957). The present refinement reduced R to 0·093, a significant improvement on the 2% level, and the new coordinates are given in Table 2. No temperature factors or bond lengths are given however, as the mean-square rotational tensor is physically impossible, having a large negative ω_{11}, and thus rotational correction of bond lengths is meaningless.

B_6H_{10}

This is the best of the unsuccessful refinements, in which R was reduced to 0·078 from the 0·099 of Hirshfeld, Eriks, Dickerson, Lippert & Lipscomb (1958). Both effects of the previous two structures were present to a much smaller degree; in fact ω_{11} was only just negative (see Table 3). The error for (ξ, η, ζ) was perhaps the best indication of trouble with the origin of $\boldsymbol{\omega}$. It is of added interest that Hirshfeld *et al.* tried unsuccessfully to account for atomic vibrations in terms of a 'reasonable scheme of rigid-molecule vibrations'. They suggested that the boron atomic scattering factor employed might introduce error, but it seems most likely that lack of data was the prime reason, giving rise to anisotropic temperature factors with no physical meaning.

3. Successful structures

B_8Cl_8

Full three-dimensional data were collected by Atoji & Lipscomb (1959) and the structure was solved and refined to $R=0{\cdot}17$ by Jacobson & Lipscomb (1959). Two cycles of refinement were sufficient to reduce R to 0·11, after which no significant improvement occurred.

The refinement results are given in Table 4 and the corrected bond lengths are shown in Fig. 1. The bonds

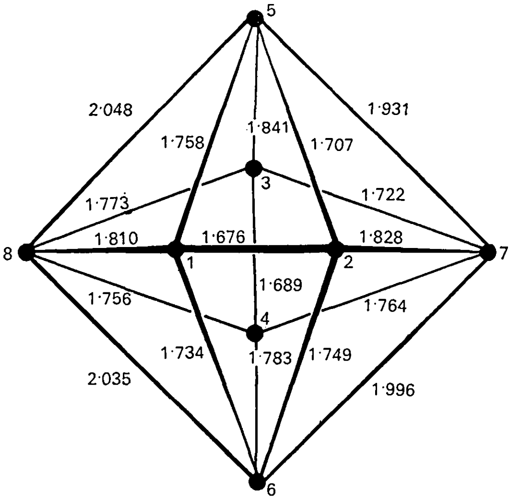

Fig. 1. Bonds in the boron framework of B_8Cl_8. The bonds to the chlorine atoms are, in numerical order: 1·739, 1·722, 1·720, 1·721, 1·772, 1·748, 1·746, 1·721 Å.

Table 4. B_8Cl_8

1168 observations
$F_w=15$

Final fractional coordinates and temperature factors

	x	y	z	β_{11}	β_{22}	β_{33}	β_{23}	β_{31}	β_{12}
Cl(1)	0·2993	0·3079	0·1292	90	162	57	31	8	−31
Cl(2)	0·4912	0·6423	0·2260	84	235	34	−7	−19	−5
Cl(3)*	0·4899	0·6219	−0·2361	82	230	33	1	14	−7
Cl(4)*	0·2769	0·9159	−0·1397	91	168	65	30	−16	32
Cl(5)*	0·5564	0·3610	−0·0254	65	170	66	−7	−2	34
Cl(6)	0·2325	0·8155	0·1193	70	205	61	−25	12	27
Cl(7)	0·5315	0·9230	0·0186	78	149	69	−8	−4	−42
Cl(8)*	0·2465	0·3984	−0·1278	68	184	55	−20	−14	−29
B(1)	0·3510	0·4825	0·0667	56	113	31	7	0	−8
B(2)	0·4342	0·6241	0·1075	56	128	27	−2	−6	−3
B(3)*	0·4326	0·6342	−0·1177	55	125	27	2	1	−4
B(4)*	0·3396	0·7577	−0·0755	58	113	35	7	−6	6
B(5)*	0·4615	0·5096	−0·0010	50	108	32	0	−3	4
B(6)	0·3233	0·6972	0·0564	52	119	32	−5	1	3
B(7)*	0·4520	0·7544	−0·0082	54	105	34	0	−2	−10
B(8)*	0·3260	0·5360	−0·0669	50	115	31	−3	−5	−6

Average errors

Cl	0·0004	0·0007	0·0004
B	0·0016	0·0026	0·0015

$$\mathbf{T}=\begin{bmatrix} 4{\cdot}42 & -0{\cdot}12 & -0{\cdot}20 \\ & 2{\cdot}99 & 0{\cdot}00 \\ & & 2{\cdot}14 \end{bmatrix} \qquad \sigma(\mathbf{T})=\begin{bmatrix} 0{\cdot}12 & 0{\cdot}10 & 0{\cdot}11 \\ & 0{\cdot}11 & 0{\cdot}09 \\ & & 0{\cdot}11 \end{bmatrix} \text{Å}^2 . 10^{-2}$$

$$\boldsymbol{\omega}=\begin{bmatrix} 12{\cdot}7 & 0{\cdot}3 & 0{\cdot}2 \\ & 12{\cdot}7 & 1{\cdot}0 \\ & & 15{\cdot}4 \end{bmatrix} \qquad \sigma(\boldsymbol{\omega})=\begin{bmatrix} 0{\cdot}8 & 0{\cdot}4 & 0{\cdot}5 \\ & 0{\cdot}8 & 0{\cdot}6 \\ & & 0{\cdot}8 \end{bmatrix} \text{deg}^2$$

C.G. = (5·33, 4·89, −0·06) (ξ, η, ζ) = (5·38, 4·75, −0·12) Å, error 0·04.

* Transformed coordinates

show a much closer agreement with the D_{2d} symmetry of an isolated molecule than in the earlier refinement; the boron–boron distances have all decreased whereas the boron–chlorine distances have increased, with the result that the chlorine–chlorine distances are unaltered. The origin of ω is very close to the centre of gravity which we would expect for such a highly symmetrical molecule.

B_4H_{10}

This structure was solved and refined 'isotropically' by Nordman & Lipscomb (1953), and later the *R* index was reduced to 0·09 by Moore, Dickerson & Lipscomb (1957) using anisotropic temperature factors. The present refinement reached 0·076 (Table 5), a significant improvement on the 0·1% level. There were no significant changes in bond lengths in this small molecule, but the bonds are given in Fig. 2 because of the increased internal agreement obtained.

$B_{18}H_{22}$

This is the most highly refined structure on which improvement was attempted. Refined 'anisotropically' (except for hydrogen atoms) by Simpson & Lipscomb (1963), the structure reached an *R* index of 0·127, but as this includes more reflections than in the present refinement, namely the unobservable reflections and some outer reflections unnecessary for positioning hydrogen atoms, comparison with the present *R* value of 0·099 is not possible. Of special interest here is the high accuracy which can be obtained for **T** and ω given good intensity measurements. This enables the errors of bond lengths due to librations to be eliminated with considerable accuracy, the resulting bond lengths being shown in Fig. 3. Here the B–H bonds should be somewhat more accurate than previously, especially as in the earlier refinement the isotropic temperature factors for the hydrogen atoms ranged from 0·0 to 3·0.

B_8H_{12} and $B_4C_2H_8$

These were the first structures refined by the present method, and the author is grateful to Enrione, Boer & Lipscomb (1964) and Boer, Streib & Lipscomb (1964)

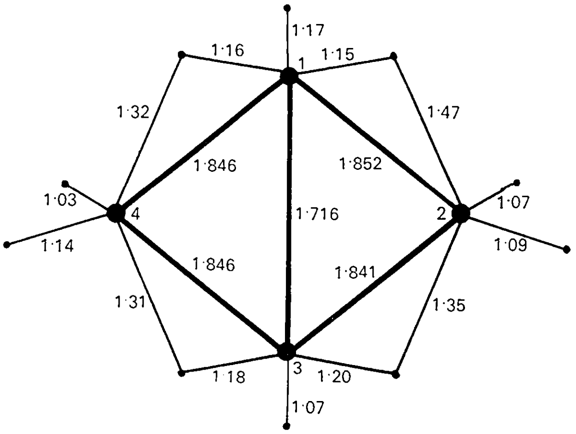

Fig. 2. Bond lengths in B_4H_{10}.

Table 5. B_4H_{10}

616 Observations
$F_w = 5$

Final fractional coordinates and temperature factors

	x	*y*	*z*	β_{11}	β_{22}	β_{33}	β_{23}	β_{31}	β_{12}
B(1)	0·2775	0·4142	0·1731	101	58	192	−11	37	3
B(2)	0·1155	0·2963	0·1755	110	64	234	−10	67	1
B(3)	0·2680	0·2709	0·0132	96	57	197	−8	42	6
B(4)	0·2435	0·4276	−0·1553*	134	66	200	6	50	0
H(1)	0·397	0·440	0·318	120	72	234	−19	14	−5
H(2)	0·167	0·432	0·242	124	65	247	−24	75	2
H(3)	0·138	0·242	0·345	169	79	243	−2	99	−10
H(4)	−0·001	0·318	0·064	98	71	355	−16	69	3
H(5)	0·144	0·217	0·005*	99	58	210	−9	39	2
H(6)	0·368	0·207	0·080	101	61	301	−8	48	12
H(7)	0·228	0·300	−0·192*	135	69	188	−13	56	−2
H(8)	0·357	0·457	−0·205*	175	80	284	1	115	−14
H(9)	0·130	0·449	−0·261*	158	76	222	23	10	3
H(10)	0·243	0·500	0·034	110	56	238	−2	44	5

Average errors

	x	*y*	*z*
B	0·0004	0·0003	0·0006
H	0·005	0·004	0·007

$$\mathbf{T} = \begin{bmatrix} 3{\cdot}24 & 0{\cdot}32 & 0{\cdot}07 \\ & 2{\cdot}89 & -0{\cdot}15 \\ & & 2{\cdot}78 \end{bmatrix} \quad \sigma(\mathbf{T}) = \begin{bmatrix} 0{\cdot}12 & 0{\cdot}09 & 0{\cdot}08 \\ & 0{\cdot}10 & 0{\cdot}08 \\ & & 0{\cdot}10 \end{bmatrix} \text{Å}^2 \,.\, 10^{-2}$$

$$\boldsymbol{\omega} = \begin{bmatrix} 11{\cdot}1 & 4{\cdot}8 & 0{\cdot}5 \\ & 23{\cdot}6 & 2{\cdot}5 \\ & & 6{\cdot}6 \end{bmatrix} \quad \sigma(\boldsymbol{\omega}) = \begin{bmatrix} 3{\cdot}9 & 3{\cdot}3 & 3{\cdot}6 \\ & 5{\cdot}4 & 2{\cdot}6 \\ & & 5{\cdot}1 \end{bmatrix} \text{deg}^2$$

C.G. = (1·87, 3·58, 0·28) (ξ, η, ζ) = (1·88, 3·33, 0·34) Å, error 0·09.

* Transformed coordinate.

for access to their data before publication. The results in Tables 7 and 8 and in Figs. 3 and 4 correspond to *R* values of 0·096 and 0·079 for the respective structures. For both of these structures unreasonable corrections for molecular libration were made to the bond lengths 'on the assumption that each second atom rides on each first atom'. Difficulty arises here in awarding atomic priority, but the authors avoid this by emphasizing the uncorrected bonds, suggesting that the quoted corrections are much greater than they would be on assuming that the molecule moves as a rigid body. However it would seem that this assumption is implicit in the method of correction they use.

The bond lengths of Fig. 4 now agree internally with a molecular plane of symmetry without any significant deviations.

$B_{10}C_2H_4Cl_8$ and $B_{10}H_{10}(CCH_2Br)_2$

The present method was used extensively in the refinements of these structures by Potenza & Lipscomb

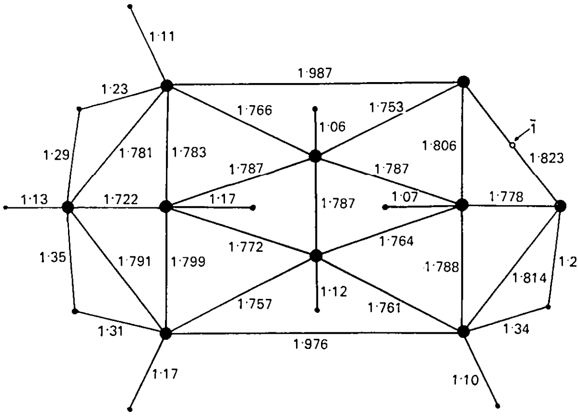

Fig. 3. Bond lengths in $B_{18}H_{22}$.

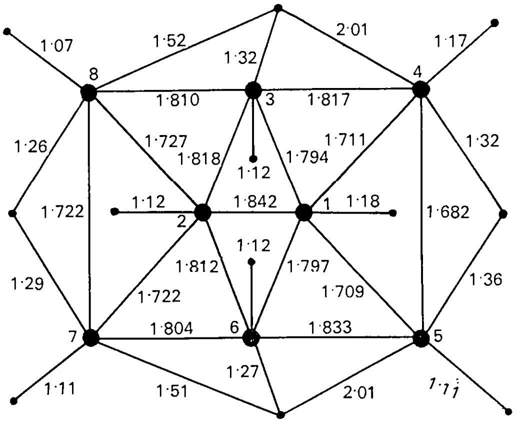

Fig. 4. Bond lengths in B_8H_{12}.

Table 6. $B_{18}H_{22}$

1120 observations
$F_w = 5$

Final fractional coordinates and temperature factors

	x	*y*	*z*	β_{11}	β_{22}	β_{33}	β_{23}	β_{31}	β_{12}
B(1)	0·1787	0·0532	0·0870	41	46	55	−4	−6	−1
B(2)	0·1541	0·0617	0·2502	56	59	53	−4	−11	−5
B(3)	0·0882	0·1623	0·1513	50	45	58	−9	−3	−3
B(4)	0·0580	0·1163	−0·0005	43	38	53	−2	−3	−1
B(5)	0·1441	−0·0675	0·1718	52	49	59	4	−14	2
B(6)	0·0458	−0·0331	0·2980	69	64	49	4	−9	−9
B(7)	−0·0030	0·1059	0·2699	59	60	53	−13	2	−7
B(8)	−0·0659	0·1448	0·1039	46	42	62	−10	−1	3
B(9)	−0·0759	0·0318	−0·0059	39	39	50	−2	−3	2
H(1)	0·2693	0·0583	0·0516	40	54	67	−7	−5	−2
H(2)	0·2315	0·0911	0·3175	67	75	61	−7	−19	−10
H(3)	0·1210	0·2492	0·1638	61	47	73	−15	−4	−7
H(4)	0·0872	0·1641	−0·0788	53	42	58	3	−3	−5
H(5)	0·2125	−0·1355	0·1768	60	54	80	7	−23	8
H(6)	0·0394	−0·0762	0·3903	95	84	51	12	−13	−19
H(7)	−0·0408	0·1594	0·3519	74	78	63	−27	9	−11
H(8)	−0·1306	0·2138	0·0880	54	45	85	−14	−3	9
H(9)	−0·1302	0·0504	0·0981	41	46	54	−7	1	1
H(19)	0·0452	−0·1038	0·2092	61	51	55	8	−11	−4
H(20)	−0·0629	0·0117	0·2638	59	62	49	−6	3	−9

Average errors

B	0·0003	0·0003	0·0004
H	0·0039	0·0037	0·0041

$$\mathbf{T}=\begin{bmatrix} 2{\cdot}28 & 0{\cdot}09 & -0{\cdot}15 \\ & 2{\cdot}77 & -0{\cdot}12 \\ & & 2{\cdot}79 \end{bmatrix} \quad \sigma(\mathbf{T})=\begin{bmatrix} 0{\cdot}08 & 0{\cdot}05 & 0{\cdot}05 \\ & 0{\cdot}08 & 0{\cdot}05 \\ & & 0{\cdot}14 \end{bmatrix} \text{Å}^2 . 10^{-2}$$

$$\boldsymbol{\omega}=\begin{bmatrix} 6{\cdot}63 & 2{\cdot}52 & 1{\cdot}07 \\ & 5{\cdot}30 & 1{\cdot}67 \\ & & 5{\cdot}04 \end{bmatrix} \quad \sigma(\boldsymbol{\omega})=\begin{bmatrix} 0{\cdot}47 & 0{\cdot}35 & 0{\cdot}50 \\ & 0{\cdot}42 & 0{\cdot}45 \\ & & 0{\cdot}92 \end{bmatrix} \text{deg}^2$$

C.G. is a symmetry cente.

Table 7. B_8H_{12}

1291 Observations
$F_w = 100$

Final fractional coordinates and temperature factors

	x*	y*	z	β_{11}	β_{22}	β_{33}	β_{23}	β_{31}	β_{12}
B(1)	0·1728	0·1969	0·2933	34	47	60	−2	2	0
B(2)	0·0613	0·0977	0·3034	30	59	69	−1	4	1
B(3)	0·1646	0·0713	0·4105	40	55	56	2	0	3
B(4)	0·2778	0·1142	0·3289	31	75	82	−2	−4	2
B(5)	0·2519	0·1497	0·1751	37	70	73	1	13	−2
B(6)	0·1196	0·1299	0·1505	40	58	57	0	−2	3
B(7)	0·0636	−0·0221	0·1895	45	64	79	−9	−6	−9
B(8)	0·0899	−0·0577	0·3472	49	54	78	5	6	−8
H(1)	0·160	0·305	0·323	52	47	77	−5	2	0
H(2)	−0·009	0·145	0·335	31	90	98	−3	10	7
H(3)	0·160	0·079	0·518	61	77	56	3	0	3
H(4)	0·349	0·126	0·391	36	119	121	−4	−19	0
H(5)	0·294	0·193	0·095	54	101	94	8	29	−9
H(6)	0·085	0·180	0·067	60	81	65	7	−12	8
H(7)	0·010	−0·066	0·122	62	95	108	−19	−20	−22
H(8)	0·052	−0·125	0·407	71	71	105	15	15	−21
H(9)	0·199	−0·042	0·376	48	55	72	7	−2	10
H(10)	0·152	0·021	0·114	51	63	60	−10	2	3
H(11)	0·298	0·046	0·225	34	85	94	−4	10	12
H(12)	0·120	−0·105	0·243	58	48	84	−6	1	−4

Average errors

B	0·0002	0·0003	0·0003
H	0·003	0·004	0·004

$$\mathbf{T} = \begin{bmatrix} 2\cdot77 & 0\cdot15 & 0\cdot14 \\ & 2\cdot52 & -0\cdot06 \\ & & 3\cdot03 \end{bmatrix} \qquad \sigma(\mathbf{T}) = \begin{bmatrix} 0\cdot07 & 0\cdot05 & 0\cdot04 \\ & 0\cdot08 & 0\cdot05 \\ & & 0\cdot07 \end{bmatrix} \text{Å}^2 \,.\, 10^{-2}$$

$$\boldsymbol{\omega} = \begin{bmatrix} 9\cdot6 & -0\cdot3 & -0\cdot1 \\ & 16\cdot5 & 0\cdot4 \\ & & 16\cdot6 \end{bmatrix} \qquad \sigma(\boldsymbol{\omega}) = \begin{bmatrix} 1\cdot3 & 1\cdot0 & 0\cdot7 \\ & 1\cdot1 & 0\cdot8 \\ & & 1\cdot1 \end{bmatrix} \text{deg}^2$$

C.G. = (2·04, 0·88, 2·86) (ξ, η, ζ) = (2·05, 1·17, 2·96) Å, error 0·04.

* Transformed coordinate.

Table 8. $B_4C_2H_8$

923 observations
$F_w = 200$

Final fractional coordinates and temperature factors

	x	y	z	β_{11}	β_{22}	β_{33}	β_{23}	β_{31}	β_{12}
B(1)	0·2904	0·1232	0·3629	84	59	155	−4	9	−9
B(2)	0·1696	0·1910	0·5372	120	72	235	−30	57	−15
B(3)	0·0952	0·1219	0·2704	84	76	214	10	7	−5
B(3′)	0·2927	0·0678	0·6507	120	109	160	17	0	−20
C(4)	0·1746	−0·0034	0·2696	99	64	200	−16	23	−17
C(4′)	0·2759	−0·0313	0·4650	105	68	247	28	26	−1
H(5)	0·180	−0·055	0·124	137	84	259	−53	50	−37
H(5′)	0·358	−0·106	0·445	132	75	443	60	64	17
H(6)	0·383	0·165	0·272	88	64	186	−4	17	−12
H(7)	0·157	0·291	0·604	180	83	416	−73	136	−26
H(8)	0·035	0·171	0·115	96	122	304	58	−16	1
H(8′)	0·378	0·082	0·801	160	188	177	33	−33	−43
H(9)	0·038	0·148	0·445	97	76	297	−1	52	−2
H(9′)	0·166	0·118	0·705	145	107	185	−24	54	−30

Average errors

B	0·0003	0·0003	0·0005
C	0·0003	0·0002	0·0005
H	0·004	0·004	0·006

$$\mathbf{T} = \begin{bmatrix} 3\cdot36 & -0\cdot35 & -0\cdot03 \\ & 3\cdot27 & -0\cdot09 \\ & & 2\cdot60 \end{bmatrix} \qquad \sigma(\mathbf{T}) = \begin{bmatrix} 0\cdot08 & 0\cdot06 & 0\cdot07 \\ & 0\cdot07 & 0\cdot05 \\ & & 0\cdot08 \end{bmatrix} \text{Å}^2 \,.\, 10^{-2}$$

$$\boldsymbol{\omega} = \begin{bmatrix} 25\cdot0 & 7\cdot8 & -9\cdot6 \\ & 14\cdot9 & -3\cdot2 \\ & & 12\cdot1 \end{bmatrix} \qquad \sigma(\boldsymbol{\omega}) = \begin{bmatrix} 1\cdot9 & 1\cdot1 & 1\cdot3 \\ & 2\cdot0 & 1\cdot2 \\ & & 1\cdot9 \end{bmatrix} \text{deg}^2$$

C.G. = (1·75, 0·76, 2·46) (ξ, η, ζ) = (2·10, 1·09, 1·87) Å, error 0·07.

(1964) and Voet & Lipscomb (1964) respectively, the latter structure being the first to be fully refined from the trial structure stage. This took four cycles, each of six minutes for about 1400 reflections and 72 parameters (see Table 10). The fact that for both these structures final twenty minute cycles with constraints lifted gave no significant improvements is indicative of considerable computational economy. As neither original paper quoted the thermal parameters they are listed in Tables 9 and 10, from which we see that the values for $B_{10}H_{10}(CCH_2Br)_2$ are considerably the less accurate. This is not surprising as we would expect the CH_2Br groups to have flexibility; what is surprising is that removal of constraints gave no improvement. Consequently the method might be more generally applicable than was first thought.

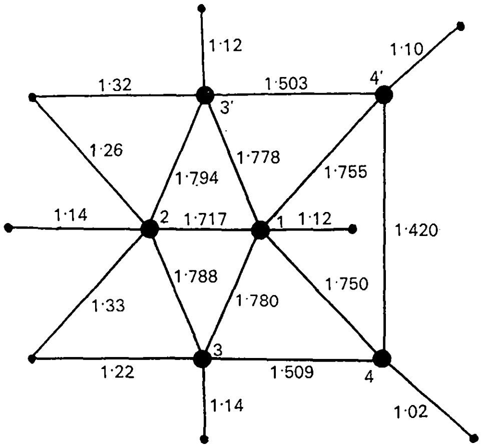

Fig. 5. Bond lengths in $B_4C_2H_8$.

4. Conclusions

This work casts some doubts on the physical meaning of anisotropic temperature factors and even of isotropic temperature factors for hydrogen atoms, except for structures with good intensity measurements. The refinement method does give the investigator a greater chance of finding systematic erroneous trends during refinement, and as **T**, **ω** and (ξ, η, ζ) are all in Å coordinates their errors as listed here for both good and bad refinements can serve as a yardstick for the reliability of the thermal parameters in later structure determinations. When these parameters have high or uneven standard deviations it would seem fruitless to apply librational corrections. Thus we could argue that in $B_{18}H_{22}$ the higher errors for T_{33} and ω_{33} are indicative of perhaps scaling errors which affect the thermal parameters. But comparison with the other structures leads one to conclude that the thermal tensors are exceptionally reliable and that the molecule is indeed rigid.

The computational advantages exemplified by $B_{10}H_{10}(CCH_2Br)_2$ and the increased reliability of bond lengths, often the prime reason for accurate structure work, should make the method very attractive to workers with sufficiently rigid molecules. The limit of applicability to flexible molecules has however not yet been investigated.

The author would like to thank Professor W. N. Lipscomb for suggesting a number of most suitable structures and for making generously available the facilities of his laboratory, F.P. Boer for assistance

Table 9. *Vibration constants for* $B_{10}C_2H_4Cl_8$

$$\mathbf{T}=\begin{bmatrix} 2{\cdot}08 & -0{\cdot}07 & 0{\cdot}20 \\ & 2{\cdot}03 & 0{\cdot}04 \\ & & 5{\cdot}32 \end{bmatrix} \quad \sigma(\mathbf{T})=\begin{bmatrix} 0{\cdot}15 & 0{\cdot}11 & 0{\cdot}13 \\ & 0{\cdot}15 & 0{\cdot}13 \\ & & 0{\cdot}22 \end{bmatrix} \text{Å}^2 \,.\, 10^{-2}$$

$$\boldsymbol{\omega}=\begin{bmatrix} 6{\cdot}3 & -1{\cdot}1 & -0{\cdot}1 \\ & 10{\cdot}9 & 2{\cdot}4 \\ & & 14{\cdot}4 \end{bmatrix} \quad \sigma(\boldsymbol{\omega})=\begin{bmatrix} 0{\cdot}8 & 0{\cdot}6 & 0{\cdot}5 \\ & 1{\cdot}0 & 0{\cdot}7 \\ & & 0{\cdot}8 \end{bmatrix} \text{deg}^2$$

C.G. = (3·13, 6·39, 5·79) (ξ, η, ζ) = (2·94, 5·22, 6·30) Å, error 0·07.

Table 10. *Vibration constants for* $B_{10}H_{10}(CCH_2Br)_2$, *and the improvement of the R index*

$$\mathbf{T}=\begin{bmatrix} 7{\cdot}45 & -0{\cdot}05 & 0{\cdot}19 \\ & 5{\cdot}71 & -0{\cdot}39 \\ & & 2{\cdot}80 \end{bmatrix} \quad \sigma(\mathbf{T})=\begin{bmatrix} 2{\cdot}34 & 0{\cdot}27 & 0{\cdot}37 \\ & 0{\cdot}23 & 0{\cdot}36 \\ & & 0{\cdot}52 \end{bmatrix} \text{Å}^2 \,.\, 10^{-2}$$

$$\boldsymbol{\omega}=\begin{bmatrix} 8{\cdot}4 & -4{\cdot}1 & -2{\cdot}5 \\ & 17{\cdot}4 & 3{\cdot}3 \\ & & 8{\cdot}6 \end{bmatrix} \quad \sigma(\boldsymbol{\omega})=\begin{bmatrix} 1{\cdot}6 & 4{\cdot}0 & 1{\cdot}1 \\ & 3{\cdot}5 & 1{\cdot}3 \\ & & 1{\cdot}2 \end{bmatrix} \text{deg}^2$$

C.G. = (3·5, 5·6, 12·1) (ξ, η, ζ) = (3·1, 3·3, 11·5) Å, error 0·3.

	R	Parameters refined
Trial structure	0·590	All positional & thermal, one scale
After cycle 1	0·241	
2	0·187	All positional & thermal, nine scales
3	0·167	
4	0·165	

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Trioctahedral One-Layer Micas.
III. Crystal Structure of a Synthetic Lithium Fluormica[*]

By Hiroshi Takeda[†] and J. D. H. Donnay

The Johns Hopkins University, Baltimore, Maryland 21218, *U.S.A.*

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The crystal structure of a synthetic lithium fluormica, between $K(Mg_2Li)Si_4O_{10}F_2$ and $KMg_3(Si_3Al)O_{10}F_2$ in composition but potassium deficient, was determined and refined from three-dimensional photometer data and $0kl$ counter data. The site occupancies of octahedral and interlayer positions were also refined to establish the final chemical formula. In keeping with the small c/b of fluormicas, the structure shows flattening of the octahedral sheet, little ditrigonality in the basal oxygen rings of the tetrahedral sheets, and flattening of the oxygen octahedron around potassium. As to interatomic distances, F–F (2·629 Å) is shorter than O–O (2·804 Å), so that fluorine and oxygen ions are not coplanar. Inner and outer K–O distances average 2·995 and 3·278 Å respectively.

Introduction

It remains as important as ever to accumulate data on the crystal structures of micas, if we are to understand the polymorphism of this mineral group. Few mica structures have been refined. No refined structure is available either for a lithium mica or for a fluormica. The lepidolites, which contain both lithium and fluorine, are of special interest because of their many polymorphs. The synthetic polylithionite, which we had hoped to study, never yielded any single crystal suitable for X-ray work. We had also hoped to refine the structure of synthetic taeniolite, which would have had the advantage of having only silicon in the tetrahedra, as opposed to ferri-annite and ferriphlogopite, in which ferric iron substitutes for silicon (Donnay, Donnay, & Takeda, 1964), but our sample turned out not to be pure taeniolite: aluminum substitutes for silicon, less lithium is present, and potassium is deficient. The site occupancies were refined by least squares, along with the structural parameters.

Experimental

The sample, which Dr H. S. Yoder, Jr. kindly gave us for investigation, was synthesized by the Mycalex Corporation of America. The process used is briefly described in a letter from E. V. deVilleroy (private communication, 1963):

'A charge of blended raw materials is fed in an electric furnace. Large graphite electrodes produce the needed heat. Heat is applied at the center of the charge under

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[†] On leave of absence from the Mineralogical Institute, University of Tokyo, Hongo, Tokyo, Japan.