SYDOW, E. VON (1956b). *Acta Chem. Scand.* **10**, 1.
VAINSHTEIN, B. K. & PINSKER, Z. G. (1950). *Dokl. Akad. Nauk. SSSR.* **72**, 53.
VAND, V. & BELL, I. P. (1951). *Acta Cryst.* **4**, 465.
VELICK, S. F. (1944). *J. Biol. Chem.* **156**, 101.
VELICK, S. F. (1947). *J. Amer. Chem. Soc.* **69**, 2317.

Acta Cryst. (1956). **9**, 668

The Crystal and Molecular Structure of $Cl_2BC_2H_4BCl_2$

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$Cl_2BC_2H_4BCl_2$ crystallizes in the monoclinic space group $C2/c$–C_{2h}^6. The lattice parameters are: $a = 10{\cdot}950 \pm 0{\cdot}006$, $b = 5{\cdot}723 \pm 0{\cdot}007$, $c = 12{\cdot}533 \pm 0{\cdot}014$ Å, $\beta = 100° \, 31' \pm 10'$. The four molecules per unit cell have the symmetry C_i and are nearly planar. X-ray diffraction data show the assignment of the formula $Cl_2BC_2H_4BCl_2$ to be correct.

Introduction

Recent interest and work in boron chemistry have resulted in new methods of organo-boron compound synthesis. Urry, Kerrigan, Parsons & Schlessinger (1954) have studied the addition product of B_2Cl_4 and C_2H_4 and have described its use as an intermediate. They have assigned the formula $Cl_2BC_2H_4BCl_2$ on the basis of chemical evidence. The purpose of this investigation is to determine by X-ray diffraction methods the molecular geometry of this compound.

Experimental

The sample of $Cl_2BC_2H_4BCl_2$ was distilled under vacuum into a trap and then into pyrex capillaries of less than one millimeter in diameter, one of which was then mounted in a goniometer. A single crystal was grown (m.p., $-28{\cdot}5°$ C.) and photographed, using modified low-temperature techniques of Reed & Lipscomb (1953). The crystals showed a tendency to grow with the unique monoclinic axis in the direction of the long capillary axis. Zero- and upper-level precession photographs and a zero-level ($h0l$ zone) Weissenberg photograph were taken at $-70°$ C., using Mo $K\alpha$ radiation ($\lambda = 0{\cdot}7107$ Å). The intensities were estimated visually with intensity scales prepared from single-crystal reflections. Lorentz and polarization correction factors (Waser, 1951; Lu, 1943) were applied, and the intensities were then put on a relative scale, using the Weissenberg and upper-level precession photographs and the 020, 040 and 060 reflections for correlating different precession films.

Crystal data

The presence only of reflections $h+k = 2n$ for all hkl data and $l = 2n$ for $h0l$ data leads to C centering and a c glide plane; i.e., the monoclinic space groups C_c or $C2/c$. The space group assumed and later shown to be correct is $C2/c$. The lattice parameters and their probable errors are:

$$a=10{\cdot}950\pm0{\cdot}006,\ b=5{\cdot}723\pm0{\cdot}007,\ c=12{\cdot}533\pm0{\cdot}014 \text{ Å},\ \beta = 100° \, 31'\pm10'.$$

The assumption of four molecules per unit cell leads to a calculated density of $1{\cdot}65$ g.cm.$^{-3}$, which seems reasonable in comparison with densities of compounds having somewhat similar formulas.

Determination of the structure

The structure was first attacked with the use of the $h0l$ Patterson projection in order to locate chlorine x and z parameters. Two interpretations seemed at first to be equally good but one soon gave way to the other after a few Fourier projections and structure-factor calculations. The carbon and boron atoms appeared in due course. The $0kl$ projection was also solved with the use of the Patterson projection. Its interpretation almost immediately yielded the y and z parameters of chlorine, carbon and boron. Finally, in order to make use of all the data, a least-squares treatment was carried out to complete the refinement of parameters. Hydrogen atoms were not included in the structure-factor calculations nor could they have been observed in the Fourier projections. Scattering curves were taken from the *Internationale Tabellen* (1935) for chlorine and from McWeeny (1951) for boron and carbon.

The Fourier calculations were done with the aid of Beevers–Lipson strips and the structure-factor and the least-squares calculations were done on International Business Machines, all by the usual methods.

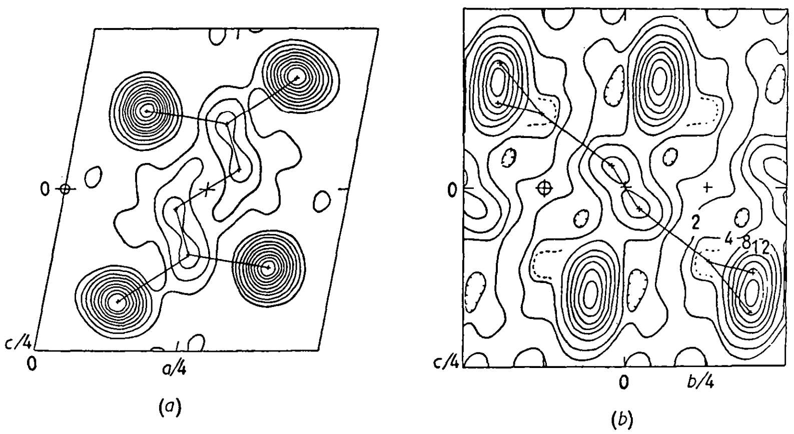

Fig. 1. (a) Fourier projection along the b axis. Contour interval is 2 e.Å^{-2} (b) Fourier projection along the a axis. Contours are 2, 4, 8, 12 etc. e.Å^{-2}. Broken contour is at 5 e.Å^{-2}.

Results and discussion

The atomic parameters, interatomic distances and angles from the Fourier series, least-squares and weighted-average treatments are listed in Tables 1 and 2. Structure factors are listed in Table 3. Figs. 1 and 2 show Fourier projections and a line drawing of the molecule.

Table 1. *Atomic parameters*

		Least squares	Fourier*	Weighted average
Cl_I	x	$0·382_5$	0·383	$0·382_5$
	y	$0·648_1$	0·647	$0·647_5$
	z	$0·121_1$	0·122	$0·121_5$
Cl_{II}	x	$0·127_0$	0·128	$0·127_5$
	y	$0·639_0$	0·639	0·639
	z	$0·175_0$	0·175	0·175
C	x	$0·204_6$	0·202	$0·203_5$
	y	$0·286_1$	0·298	0·290
	z	$0·028_4$	0·036	0·031
B	x	$0·238_6$	0·239	0·239
	y	$0·512_7$	0·514	0·513
	z	$0·105_4$	0·103	$0·104_5$

* Not corrected for termination of series. The constant $B = 3·0$ Å^2 in the isotropic temperature factor was found.

Table 2. *Interatomic distances and angles*

	Least squares*	Fourier	Weighted average
Cl_I–Cl_{II}	3·00±0·01 Å	2·99 Å	2·99 Å
Cl_I–B	1·73±0·04	1·73	1·73
Cl_{II}–B	1·78±0·04	1·79	1·78
C–B	1·62±0·05	1·51	1·58
C–C	1·39±0·06	1·60	1·46
Cl_I–B–Cl_{II}	117·0°	116·2°	116·6°
B–C–C	115·9	117·2	116·2
Cl_I–B–C	122·1	125·7	123·6
Cl_{II}–B–C	120·9	118·1	119·8

* Standard deviations are included.

The photographs covered 60% of the permitted reciprocal-lattice points out to the outermost observed reflection, but we observed only 25% of the total reflections permitted by the space group in this volume of reciprocal space. These data were sufficiently good to locate the chlorine atoms accurately, but boron and carbon are not accurately known. Hence, an average molecule is listed, weighted two-to-one in favor of the least-squares treatment since the Fourier series was not corrected for termination. Owing to the large calculated standard deviations in the positions of the carbon and boron and to the symmetry, the bond distances cannot be considered reliable. However, the C–C distance of 1·46±0·06 Å may be compared to the C–C distance of 1·49±0·04 Å in $ClCH_2CH_2Cl$ (Reed & Lipscomb, 1953), and the B–C distance of 1·58±0·05 Å may be compared to the rather uncertain value of 1·52±0·07 Å in $C_6H_5BCl_2$ (Coffin & Bauer, 1955), and the average B–Cl distance of $1·75_5$±0·04 Å may be compared to the published values of B–Cl = 1·73±0·02 Å in BCl_3 (Levy & Brockway, 1937), 1·72±0·02 Å in B_2Cl_4 (Atoji & Lipscomb, 1955) and 1·70±0·03 Å in B_4Cl_4 (Atoji & Lipscomb, 1953). The good agreement of the closest Cl · · · Cl distance of 2·99±0·01 Å with that of 3·00±0·01 Å in B_2Cl_4 suggests that the chlorine atoms are located in this

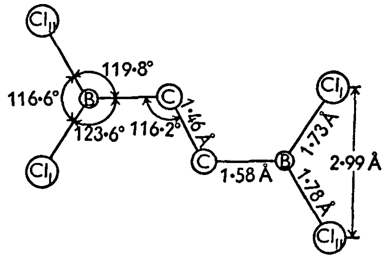

Fig. 2. The $Cl_2BC_2H_4BCl_2$ molecule, hydrogens omitted. The distances and angles are not to be considered abnormal in view of the large standard deviations.

Table 3. *Structure factors*

Calculated from the least-squares parameters, observed reflections only.

hkl	F_o	F_c	*hkl*	F_o	F_c	*hkl*	F_o	F_c
004	100	−117	246	43	40	$\bar{2},0,10$	71	−79
006	55	55	310	26	20	$\bar{2}21$	34	−28
008	11	17	311	70	68	$\bar{2}22$	24	22
0,0,14	22	−35	312	31	29	$\bar{2}23$	48	−38
020	51	−45	319	22	28	$\bar{2}24$	34	35
021	124	−132	332	64	−58	$\bar{2}25$	86	85
022	18	−11	333	30	−24	$\bar{2}27$	34	−22
023	46	−41	353	18	21	$\bar{2}28$	36	−18
025	87	89	400	135	−137	$\bar{2}29$	70	−73
026	17	−22	402	84	83	$\bar{2}41$	30	20
040	71	−69	404	77	87	$\bar{2}44$	52	50
041	25	29	406	48	−45	$\bar{2}46$	40	−35
042	34	33	420	41	37	$\bar{2},4,10$	43	40
043	12	9	421	96	100	$\bar{3}11$	88	−94
044	44	45	424	40	−36	$\bar{3}12$	78	−72
045	26	−28	440	82	82	$\bar{3}13$	110	110
046	32	−30	441	31	−25	$\bar{3}16$	44	45
047	11	−7	442	21	−19	$\bar{3}31$	28	−22
060	37	35	444	38	−38	$\bar{3}32$	90	94
061	28	30	461	36	−33	$\bar{3}33$	49	40
064	21	−25	510	22	−15	$\bar{3}36$	67	−70
065	17	−17	511	36	−41	$\bar{3}51$	31	35
111	39	42	512	46	−54	$\bar{3}53$	58	−56
112	115	135	515	16	−17	$\bar{4}02$	14	29
113	137	−162	530	16	14	$\bar{4}04$	75	75
114	49	−44	532	74	75	$\bar{4}06$	66	−55
115	26	−23	600	27	−21	$\bar{4}21$	97	99
116	52	−54	602	32	−22	$\bar{4}24$	28	−29
117	61	69	606	51	54	$\bar{4}28$	24	19
118	32	41	620	15	−8	$\bar{4}41$	40	−34
131	45	46	646	26	−27	$\bar{4}44$	54	−52
132	76	−81	711	29	−26	$\bar{5}11$	40	39
133	36	−32	712	31	−30	$\bar{5}32$	44	−34
134	48	57	800	79	86	$\bar{5}51$	31	−22
136	34	40	802	42	−36	$\bar{6}02$	26	16
138	50	−62	804	45	−46	$\bar{6}04$	104	97
151	25	−31	808	11	7	$\bar{6}06$	54	−42
153	48	53	821	67	−70	$\bar{6}08$	52	−43
157	34	−44	840	34	−43	$\bar{6},0,10$	62	65
200	71	−60	844	21	20	$\bar{6}46$	34	35
202	33	−24	12,0,0	45	−42	$\bar{7}11$	66	58
204	63	68	12,0,6	26	−23	$\bar{7}12$	72	71
206	74	−87	$\bar{1}11$	33	−31	$\bar{7}17$	69	64
208	42	−44	$\bar{1}12$	72	−86	$\bar{7}32$	62	−61
2,0,10	56	61	$\bar{1}13$	62	58	$\bar{7}51$	28	−26
221	31	22	$\bar{1}17$	30	37	$\bar{7}57$	30	−29
223	26	23	$\bar{1}18$	31	36	$\bar{8}04$	75	−72
225	85	−84	$\bar{1}31$	33	−28	$\bar{8}21$	44	−46
226	36	36	$\bar{1}32$	44	40	$\bar{9}11$	31	−29
229	56	55	$\bar{1}51$	29	26	$\overline{10},0,10$	37	−40
2,2,11	42	−40	$\bar{2}02$	52	−45	$\overline{11},1,1$	31	−25
240	22	−17	$\bar{2}04$	87	−89	$\overline{11},1,2$	36	−27
242	17	−14	$\bar{2}06$	103	96	$\overline{11},3,2$	49	41
244	26	−35	$\bar{2}08$	47	45	$\overline{12},2,1$	18	19

study with reasonable certainty. The molecule is nearly planar, carbon and boron being only 0·05 Å and 0·01 Å respectively out of the plane of Cl_I and Cl_{II} and the center of the molecule. The value of $R = \Sigma\|F_o\|-\|F_c\|\div\Sigma\|F_o\|$ for the least-squares molecule is 0·105. It is to be noted that R is greater by 0·02 when carbon is exchanged for boron. In addition we found that when Cl is substracted from the Fourier series the remaining peak for carbon is higher than that for boron.

The chemical evidence (Urry *et al.*, 1954) for the formula $Cl_2BC_2H_4BCl_2$ may be summarized as follows: one mole of diboron tetrachloride reacts with one mole of ethylene at temperatures as low as −80° C.; the observed vapor tensions of the product agree with those calculated for $Cl_2BC_2H_4BCl_2$; treatment of $Cl_2BC_2H_4BCl_2$ with dimethyl zinc replaces each chlorine with a methyl group and treatment with methanol replaces each chlorine with a methoxy group. The basis for the assumption of the boron–boron bond severance is the fact that treatment of $Cl_2BC_2H_4BCl_2$ with aqueous sodium hydroxide generates no hydrogen gas, in contrast to the hydrolysis of diboron tetrachloride which yields hydrogen.

The X-ray diffraction data has thus established the molecular geometry and confirmed the formula of $Cl_2BC_2H_4BCl_2$.

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References

ATOJI, M. & LIPSCOMB, W. N. (1953). *Acta Cryst.* **6**, 547.
ATOJI, M. & LIPSCOMB, W. N. (1955). *J. Chem. Phys.* **23**, 1176.
COFFIN, K. P. & BAUER, S. H. (1955). *J. Phys. Chem.* **59**, 193.
Internationale Tabellen zur Bestimmung von Kristallstrukturen (1935), vol. 2, p. 571. Berlin: Borntraeger.
LEVY, H. A. & BROCKWAY, L. O. (1937). *J. Amer. Chem. Soc.* **59**, 2085.
LU, C.-S. (1943). *Rev. Sci. Instrum.* **14**, 331.
MCWEENY, R. (1951). *Acta Cryst.* **4**, 513.
REED, T. B. & LIPSCOMB, W. N. (1953). *Acta Cryst.* **6**, 45.
URRY, G., KERRIGAN, J., PARSONS, T. D. & SCHLESSINGER, H. I. (1954). *J. Amer. Chem. Soc.* **76**, 5299.
WASER, J. (1951). *Rev. Sci. Instrum.* **22**, 567.

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X-ray Study of the Alkali Metals at Low Temperatures

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Using a spectrometer having provision for cold working and X-raying specimens in a high vacuum at low temperatures, it is found that sodium partially transforms on cooling (below 36° K.) or on deforming (below 51° K.) to a close-packed hexagonal structure with stacking faults, having $a = 3{\cdot}767$, $c = 6{\cdot}154$ Å, $c/a = 1{\cdot}634$ at 5° K., this coexisting with body-centered cubic sodium of $a_0 = 4{\cdot}225$ Å. The body-centered cubic form at 78° K. has $a_0 = 4{\cdot}235$ Å. Severe cold work at 5° K. transforms about half of the material to the hexagonal form; subsequent reversion to cubic starts on heating to 60–75° K. and is completed at 100–110° K., or at lower temperatures if there has been no cold work. Reversion can be aided by cold work at 45–100° K. High purity severely deformed sodium recrystallizes at 98° K.

Patterns of lithium that has been cooled can be interpreted similarly, and indicate a phase of close-packed hexagonal structure with parameters $a = 3{\cdot}111$, $c = 5{\cdot}093$ Å, $c/a = 1{\cdot}637$ (which differ from the earlier, tentative ones). This phase coexists with the body-centered cubic phase of $a_0 = 3{\cdot}491$ Å, at 78° K. Confirming the earlier work, hexagonal lithium is converted to face-centered cubic by cold working.

Potassium, rubidium and cesium retain their body-centered cubic structure after cooling and cold working at 5° K., with $a_0 = 5{\cdot}225$, $5{\cdot}585$, and $6{\cdot}045$ Å respectively at 5° K. and with $a_0 = 5{\cdot}247$, $5{\cdot}605$ and $6{\cdot}067$ Å at 78° K.

Introduction

Microscopic tests involving cooling to 1·2° K. have recently shown that there is a martensitic-type transformation at low temperatures in sodium as well as in lithium, but have failed to reveal any in the other alkali metals (Barrett, 1955). Cold working at low temperature promotes a change of phase in lithium (Barrett, 1947; Barrett & Trautz, 1948) and is also suspected of doing so in sodium, judging by a single diffraction peak observed at 78° K. after deformation at 20·4° K. (Barrett, 1948). Diffraction data on the low-temperature phases are few and are complicated by the presence of stacking faults (Barrett, 1950), so that the crystal structure determinations must be regarded as tentative (Barrett, 1947, 1948).

To learn whether cold work at liquid-helium temperatures can induce transformations in the metals potassium, rubidium and cesium which do not transform on simple cooling, and to determine the low-temperature structures of lithium and sodium more reliably, we have performed a number of experiments using apparatus much improved over that used in the earlier work.

The apparatus, designed by E. Long, L. Meyer, C. B. Walker and the author, consists of a cryostat