began to separate in a few minutes. After the mixture had stood at room temperature for about 20 hr. with occasional aeration, filtration afforded 0.30 g. (93% yield from 2-methylthio-2-thiazoline) of fine white crystals, m.p. 144–145.5°. Recrystallization from 1:1 aqueous ethanol gave glistening plates, m.p. 145–146.5°. The infrared spectra of this product and of the disulfide from the rearrangement were identical; there was no mixed melting point depression.

The dihydroiodide of the disulfide, m.p. 244.5–246°, was isolated from an attempted preparation of the mercaptan (III) from 2-methylthio-2-thiazoline hydroiodide[4] and 2-mercaptoethylamine in refluxing methanol. The same compound was obtained from IV and hydrogen iodide.

Anal. Calcd. for $C_{10}H_{20}I_2N_4S_4$: C, 20.76; H, 3.49; S, 22.17. Found: C, 20.88; H, 3.57; S, 22.41.

Acknowledgment. The authors are indebted to Mr. C. DiPietro and Mr. W. A. Sassaman for the microanalyses and to Mr. F. H. Bissett for the infrared spectra.

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The Molecular Weights of Some Simple Borolanes and Borinanes[1]

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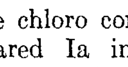
Only a few simple derivatives of the six-membered dioxaborinane ring (I) have been reported in the literature,[2–5] and none of the materials described has been characterized by molecular weight determinations. 2-Chloro-1,3,2-dioxaborinane (Ia) was prepared from equivalent amounts of trimethylene glycol and boron trichloride. Conklin and Morris[2] originally described this reaction but did not characterize the chloro compound. Finch, *et al.*,[5] who have prepared Ia independently by a similar method, described it as a viscous liquid, whereas the product obtained in the present work was not a viscous material at room temperature. Reaction of Ia with *n*-butyl alcohol gave 2-*n*-butoxy-1,3,2-dioxaborinane (Ib), a reaction which was also noted by Finch. The experimental molecular weights of these borinanes given in Table I show that they are monomeric in benzene solution in the concentration range studied.

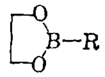


I

Ia. R = Cl–
Ib. R = n-C_4H_9O-

A number of related organoboron compounds containing the five-membered dioxaborolane ring (II) have been reported in the literature, and their physical properties have been described in some detail. Although they have generally been assumed to be monomeric in the liquid state, the only simple dioxaborolane for which an experimental molecular weight has been reported is 2-*n*-butoxy-1,3,2-dioxaborolane (IIc), which was found to be monomeric in cyclohexane solution.[6] The concentration used in this molecular weight determination was not specified.

IIa. R = Cl—
IIb. R = C_2H_5O—
IIc. R = n-C_4H_9O—
IId. R = $(CH_3)_2N$—



II

Recently 2-chloro- (IIa); 2-*n*-butoxy-(IIc), and 2-dimethylamino-1,3,2-dioxaborolanes (IId) have been prepared in this laboratory, and their physical properties agreed with those reported by previous workers.[2,6,7] It was noted, however, that the chloroborolane, IIa, is an extremely viscous compound with a boiling point which suggests a high degree of association in the liquid state. For example, chlorodimethoxyborane, $(CH_3O)_2BCl$, which has a molecular weight of 108.3 compared to 106.3 for IIa, has a vapor pressure of 1 mm. at $-47°$[8] while IIa boiled at 74° at 1 mm. Cryoscopic molecular weights of the borolanes, IIa, IIc and IId, were determined in benzene solution, and the results are shown in Table I.

The chloro compound (IIa) apparently exists in the dimeric form in benzene solution[9] in the concentration range studied. The only other examples of alkoxyhaloboranes which were reported to be strongly associated in the liquid state are difluoromethoxyborane[10,11,13] and *n*-butoxydifluoroborane[12] which were originally reported to be dimeric. Later McCusker[13] suggested that these compounds were complexes having the general formula, $(RO)_3B.2BF_3$. However, recent studies

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[1] The research reported in this document was supported in part by Wright Air Development Division of the U. S. Air Force under Contract AF 33(616)-5931.

[2] G. W. Conklin and R. C. Morris, Brit. Patent **790,090** (1958).

[3] P. J. Garner, Brit. Patent **722,538** (1955).

[4] P. J. Garner, U. S. Patent **2,839,564** (1958).

[5] A. Finch, J. C. Lockhart, and J. Pearn, *Chem. & Ind.*, 471 (1960).

[6] J. A. Blau, W. Gerrard, and M. F. Lappert, *J. Chem. Soc.*, 4116 (1957).

[7] R. L. Letsinger and I. H. Skoog, *J. Am. Chem. Soc.*, **76**, 4174 (1954).

[8] E. Wiberg and W. Sutterlin, *Z. anorg. Chem.*, **202**, 1 (1931).

[9] The extremely viscous nature of 2-chloro-1,3,2-dioxaborolane suggests that it is even more highly associated in the pure liquid state.

[10] J. Goubeau and K. E. Lucke, *Ann.*, **575**, 37 (1952).

[11] E. C. Allen and S. Sugden, *J. Chem. Soc.*, 760 (1932).

[12] M. F. Lappert, *J. Chem. Soc.*, 784 (1955).

[13] P. A. McCusker and S. M. Laeticia Kilzer, *J. Am. Chem. Soc.*, **82**, 372 (1960).

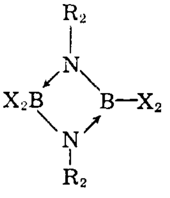
TABLE I

Molecular Weights of Some Dioxaborinanes and Dioxaborolanes

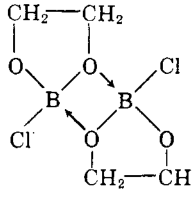
Compound	Moles/L.[a]	Molecular Weight			Degree of Polymerization
			Calcd.		
		Exptl.	Monomer	Dimer	
(Ia) 2-Chloro-1,3,2-dioxaborinane	0.27	124.8	120.8	241.6	1.03
(Ib) 2-*n*-Butoxy-1,3,2-dioxaborinane	0.14	162.7	158.0	316.0	1.03
(IIa) 2-Chloro-1,3,2-dioxaborolane	0.36	208.9	106.8	212.6	1.96
(IIc) 2-*n*-Butoxy-1,3,2-dioxaborolane	0.17	182.4	143.8	287.6	1.27
(IId) 2-Dimethylamino-1,3,2-dioxaborolane	0.33	113.6	114.8	229.6	1.01

[a] Moles/l. in benzene solution, moles based on monomer.

by Landesman and Williams[14] have proven that all boron atoms present in these compounds are equivalent and have postulated a cyclic trimeric structure with coordinate boron-oxygen bonds for these materials. The related aminohaloborane dimers with the empirical formula R_2NBX_2 have been assigned Structure (III) with coordinate boron-nitrogen bonds.[15-17] A comparable structure for the dimer, IIa, is represented by (IV) but on the basis of present evidence it is only possible to speculate on the structures of this dimeric derivative.



III



IV

2-Dimethylamino-1,3,2-dioxaborolane, IId, was found to be monomeric in the liquid state. However, 2-*n*-butoxy-1,3,2-dioxaborolane, IIc, which was previously reported[6] to be monomeric in cyclohexane solution, has now been found to have an intermediate degree of association in benzene at least in the concentration range indicated. The molecular weight of 2-ethoxy-1,3,2-borolane (IIb) was not determined, but on the basis of its reported boiling point[6] it is probably dimeric or highly associated also.

The striking differences in the molecular weights of these five and six-ring derivatives are difficult to explain, and more information is needed concerning both the nature and the absolute configurations of the five and six-membered boron-oxygen-carbon ring systems.

EXPERIMENTAL

Borolanes. The preparations of 2-chloro-1,3,2-dioxaborolane[2,6] and 2-dimethylamino-1,3,2-dioxaborolane[2] were as described in the literature. 2-*n*-Butoxy-1,3,2-dioxoborolane was prepared by Letsinger's method[7] from ethylene glycol and *n*-butyl borate and also by the reaction of 2-chloro-1,3,2-dioxaborolane with *n*-butyl alcohol as described by Gerrard and Lappert.[6] The products from both methods exhibited identical physical properties and molecular weights.

2-Chloro-1,3,2-dioxaborinane. Boron trichloride (71.70 g., 0.613 mole) was added slowly to a solution of 46.64 g. (0.613 mole) of trimethylene glycol in 200 ml. of pentane at $-10°$ in a dry-nitrogen atmosphere. The reaction mixture was warmed to room temperature, the hydrogen chloride and pentane removed by distillation at reduced pressure, and the residue distilled to give 55.0 g. (74.3% yield) of 2-chloro-1,3,2-dioxaborinane, b.p. 28–31°/0.5 mm., n_D^{24} 1.4361.

Anal. Calcd. for $C_3H_6O_2ClB$: C, 29.83; H, 5.01; Cl, 29.4; B, 8.97. Found: C, 29.90; H, 5.40; Cl, 29.04; B, 8.84.

2-n-Butoxy-1,3,2-dioxaborinane. A solution of 3.77 g. (0.051 mole) of *n*-butyl alcohol in 10 ml. of pentane was added slowly to 6.14 g. (0.051 mole) of 2-chloro-1,3,2-dioxaborinane in 15 ml. of pentane at 25° in a dry-nitrogen atmosphere. The solution was stirred for 3 hr. at this temperature, the pentane removed under vacuum, and the residue distilled to give 6.34 g. (79% yield) of 2-*n*-butoxy-1,3,2-dioxaborinane, b.p. 75–80°/1–2 mm., $n_D^{21.5}$ 1.4270.

Anal. Calcd. for $C_7H_{15}O_3B$: C, 53.21; H, 9.57; B, 6.84. Found: C, 53.80; H, 9.59; B, 6.95.

Molecular weight determinations. Molecular weights (Table I) were obtained in benzene using samples of about 0.5 g. in *ca.* 20 ml. of solvent (concentrations given in Table I) and standard cryoscopic techniques. The samples were handled and the determinations made in an atmosphere of dry, oxygen-free nitrogen. Molecular weight measurements were reproducible within 2–3% and the values given are the averages of two to four separate determinations in each case.

Acknowledgment. The authors wish to thank Mr. H. Goldsmith for the sample of 2-dimethylamino-1,3,2-dioxaborolane.

U. S. Borax Research Corporation
Anaheim, Calif.

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(14) H. Landesman and R. E. Williams, Abstracts of Papers presented at the 138th Meeting of the American Chemical Society, September 11–16, 1960, page 39N.

(15) E. Wiberg and K. Schuster, *Z. anorg. Chem.*, **213**, 89 (1933).

(16) E. Wiberg, A. Bolz, and P. Buchheit, *Z. anorg. Chem.*, **256**, 285 (1948).

(17) C. A. Brown and R. C. Osthoff, *J. Am. Chem. Soc.*, **74**, 2340 (1952).

Some New Orthoboric Acid Esters[1]

D. M. Young and C. D. Anderson

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During the course of work on the chemical properties and hydrolytic stability of organic