solutions of boron trichloride at 25° C., using dioxane and acetic acid as solvents. There were no indications of reaction. Analysis of the reaction mixtures indicated the presence of unreacted boron trichloride.

All the products of the new reactions were similar to those obtained by known reactions, and in no case analyzed properly for the structure $B(OOCCH_3)_3$. Although boron triacetate was never isolated, it may have been formed as an intermediate; but it was unstable and decomposed to yield acetic anhydride and pyroboron tetraacetate:

$$2B(OAc)_3 \rightarrow (AcO)_2B\text{-}O\text{-}B(OAc)_2 + Ac_2O$$

Boron and acetate content were determined by a titrimetric method similar to the one reported by Gerrard and Wheelans (*4*).

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Physical Properties of Organoboron Compounds

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IN A PREVIOUS publication (*5*) the Lorentz-Lorenz molar refraction, R_L, was evaluated for a number of organoboron compounds using literature data (*12*) for density and refractive index. A plot of the observed molar refraction, $R_{\text{obsd.}}$, *vs.* the number of carbon atoms in a single alkyl group, n, for six homologous series of compounds showed a linear relationship, and equations of the type $R_{\text{obsd.}} = a\ n + b$ were derived for the six series reported. It now becomes necessary to correct the equations previously reported, in view of the fact that some of the densities and refractive indices were incorrectly given in the review article (*12*). The corrected equations are listed below in Table I (numbers 1 to 6) along with some new equations (numbers 7 to 16) for other homologous series not previously reported. All equations were derived by the method of least-squares. The numbers in parentheses following the general formulas for series 7 to 16 give reference to the original articles from which representative compounds were selected. The n in Equations 8, 9, and 10 refer to the number of CH_2 groups in the compounds concerned, rather than to the number of carbon atoms in a single alkyl group. An estimation of the contribution by a CH_2 group to molar refraction may be found by dividing the slope of each equation by the number of alkyl groups given in the general formula. The mean value from the 16 series listed is 4.64 cc. per mole, which is the accepted value for R_{CH_2} as evaluated for long homologous series. The molar refraction, or electronic polarization, is taken as some measure of the deformation of the valence electron clouds in the presence of external electrical fields or to fields which result from the presence of strongly polar groups within the molecule. The loosening up of the electron sheaths is demonstrated in going from a cyclic to an open structure—i.e., from series 15 to 16—the value of R_{CH_2} increasing accordingly from 4.60 to 4.72 cc. per mole.

The molar volumes at temperature t, V_m^t, were evaluated for members of the series listed in Table I. The plot of V_m^t *vs.* the number of carbon atoms in a single alkyl group, n, also shows linearity, and equations of the type $V_m^t = c\ n + d$ can be derived. V_m^t among isomeric compounds differed at most by only a few per cent, thus the average value of this property was used in derivations. The resulting equations are given in Table II for the corresponding series listed in Table I. The last equation, 17, is for the series RBF_2. This series was not included in Table I, since refractive indices for representative compounds were not reported (*12*). An estimation of the contribution by the CH_2 group to V_m^t is given in the last column.

Table I. Equations for Molar Refractions

	Series	$R_{\text{obsd.}} = an + b$
1	$B(OR)_3$	$= 13.87n + 10.74$
2	$ClB(OR)_2$	$= 9.22n + 14.05$
3	$ROBCl_2$	$= 4.57n + 17.47$
4	BR_3	$= 13.97n + 6.73$
5	$C_6H_5B(OR)_2$	$= 9.29n + 34.29$
6	$C_6H_4CH_3B(OR)_2$	$= 9.36n + 39.09$
7	$(C_6H_5)_2BOR$ (*1*)	$= 4.67n + 57.85$
8	$B[O(CH_2)_nCl]_3$ (*2*)	$= 13.96n + 24.98$
9	$ClB[O(CH_2)_nCl]_2$ (*2*)	$= 9.71n + 22.06$
10	$Cl(CH_2)_nOBCl_2$ (*2*)	$= 4.42n + 22.83$
11	$C_6H_5B(OR)Cl$ (*8*)	$= 4.61n + 38.16$
12	$C_6H_4O_2BOR$ (*9*)	$= 4.65n + 33.01$
13	$(ROBO)_3$ (*13*)	$= 13.90n + 20.38$
14	$(RBO)_3$ (*15*)	$= 14.01n + 16.92$
15	$(BNHRNR)_3$ (*4*)	$= 27.61n + 34.39$
16	$B(NHR)_3$ (*4*)	$= 14.15n + 16.54$

Table II. Equations for Molar Volumes

Series	$V_m^t = cn + d$	V_m for CH_2 group
1	$V_m^{20} = 50.02n + 68.53$	$50.02/3 = 16.67$
2	$V_m^{20} = 33.37n + 73.44$	$33.37/2 = 16.69$
3	$V_m^{20} = 16.45n + 77.95$	$16.45/1 = 16.45$
4	$V_m^{22\text{-}25} = 50.20n + 43.85$	$50.20/3 = 16.73$
5	$V_m^{20} = 34.13n + 118.6$	$34.13/2 = 17.07$
6	$V_m^{25} = 35.01n + 133.2$	$35.01/2 = 17.51$
7	$V_m^{20} = 17.25n + 174.6$	$17.25/1 = 17.25$
8	$V_m^{20} = 49.84n + 95.40$	$49.84/3 = 16.61$
9	$V_m^{20} = 34.30n + 84.90$	$34.30/2 = 17.15$
10	$V_m^{20} = 15.00n + 90.73$	$15.00/1 = 15.00$
11	$V_m^{20} = 16.82n + 126.6$	$16.82/1 = 16.82$
12	$V_m^{20} = 16.76n + 111.3$	$16.76/1 = 16.76$
13	$V_m^{20} = 53.62n + 87.50$	$53.62/3 = 17.87$
14	$V_m^{25} = 49.87n + 90.20$	$49.87/3 = 16.62$
15	$V_m^{20} = 105.0\ n + 104.7$	$105.0\ /6 = 17.50$
16	$V_m^{20} = 55.32n + 60.50$	$55.32/3 = 18.44$
17	$V_m^{25} = 15.75n + 61.98$	$15.75/1 = 15.75$

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V_m^{20-25} for the CH_2 group shows a large range of values—15.00 to 18.44 cc. per mole. This is not unexpected in view of the fact that it was evaluated from data at room temperature; a more correct estimation of this measurement should be made from compounds that are at some corresponding state—viz., the boiling point. The accepted value for V_{CH_2} of 22.0 cc. per mole was found by Kopp (*3*) at the boiling point. The mean value for V_m^{20-25} for the CH_2 group from the results presented in Table II is 16.9 cc. per mole. The equations, however, may be used for the calculation of the density of any member of the series for which equations were derived, by the following formula,

$$d_4^t = M/V_m^t = M/(c\,n + d) \qquad (1)$$

The refractive index may also be calculated by substituting the corresponding equations for $R_{\text{obsd.}}$ and V_m^t in the Lorentz-Lorenz equation.

The internal pressure of a liquid, P_i, often serves as an indication of the presence of intermolecular association. With organoboron compounds, such an indication might be attributed to the tendency for boron to become tetracoordinated. Sufficient data for the calculation of P_i were available for only a limited number of compounds; these are listed in Table III. The normal boiling points, T_b, and the latent heats of vaporization, ΔH_v, were taken from a number of sources (*11, 12, 18, 19*). The heats of vaporization not found in the literature, but listed in Table III, were evaluated by the author using a simplified form of the Clausius-Clapeyron equation

$$\log_{10} p = A - B/T \qquad (2)$$

The entropy of vaporization, Trouton's constant, ΔS_b, is also reported. P_i was calculated by means of the approximate form of Hällten's equation (*22*),

$$P_i = \Delta H_i/V_m^b = (\Delta H_v - RT_b)/V_m^b \qquad (3)$$

where ΔH_i is the internal molar heat of vaporization, ΔH_v the total molar heat of vaporization, and T_b the normal boiling point. The molar volume at the boiling point, V_m^b, was estimated by means of the following approximation,

$$V_m^b = (22.0/16.9)\,V_m^t = 1.3\,V_m^t \qquad (4)$$

In the light of the discussion following Table II, the use of Equation 4 is not unwarrented for approximate calculations of P_i. Values for V_m^t and $R_{\text{obsd.}}$ are also listed.

The high Trouton's constants and internal pressures indicate a large amount of intermolecular association to be present for the compounds listed. Since a great many tetracoordinated compounds have already been characterized in which the electron-deficient boron compounds readily react with ammonia, amines, and other Lewis bases (as well as with alkali metal alkyls), the possibility of autocoordination in the liquid state—i.e., intermolecular association—is not unexpected.

A search of the literature failed to disclose any investigations concerning the evaluation (either theoretical or experimental) of critical data for organoboron compounds. The calculation of complete critical data for the 17 compounds listed in Table III may be made with the help of the following two relationships, deduced by the author, after an examination of some current critical data (*10, 16*).

$$V_c = 13\,R_L \qquad (5)$$

$$V_c = 12\,R_L \qquad (6)$$

where R_L is the Lorentz-Lorenz molar refraction, Equation 5 is applicable to nonhalogenated compounds, and Equation 6 for chlorine-containing compounds. The calculated data are presented in Table IV, where the numbers in the first column refer to the compounds listed in Table III. T_c was evaluated from the expression

$$T_c = 2t\,V_m^t/(4\,V_m^t - V_c) \qquad (7)$$

which is a slightly modified form of the equation derived by Mathias on the basis of the law of the rectilinear diameter (*6*). p_c was calculated from the relationship

$$p_c = 11.4\,T_c^2/(2\,T_c - t)\,V_m^t \qquad (8)$$

which is a combination of the equations of Mathias (*6*) and Berthelot (*7*). The critical ratio is seen to be close to 3.6; this value being in accordance with the demands of the Berthelot relationship (*7*). The data also show that, with the exception of compounds 13, 15, 16, and 17, the ratio T_c/T_b follows Guldberg's rule (*21*), viz.,

$$T_c = 3\,T_b/2 \qquad (9)$$

The van der Waals correction factors, a and b, were evaluated from

$$a = 27R^2T_c^2/64p_c \qquad (10)$$

and

$$b = RT_c/8p_c \qquad (11)$$

On the assumption of spherically-shaped molecules, the molecular radii were calculated from the covolume term, b, by the relationship

$$r = (9.908 \times 10^{-26}\,b)^{1/3} \qquad (12)$$

The ratio V_c/b = 2.222; that V_c should be approximately $2b$ is more in harmony with experimental data, since the van der Waals relationship $V_c = 3b$ does not agree with facts. Shortly after deducing this equation of state, van der Waals published a paper (*17*) in which he gave reasons for taking $V_c = 2.13b$. The correction factor a is in some way related to the cohesive forces of attraction between the molecules of a van der Waals fluid. That the a values listed in Table IV are rather large is in accord with the high internal pressures (Table III) found for these compounds. The critical data calculated in the present investigation must be regarded only as approximations and subject to the limitations imposed by Equations 5 and 6. The results, however, may be used as a guide for any future experimental investigations.

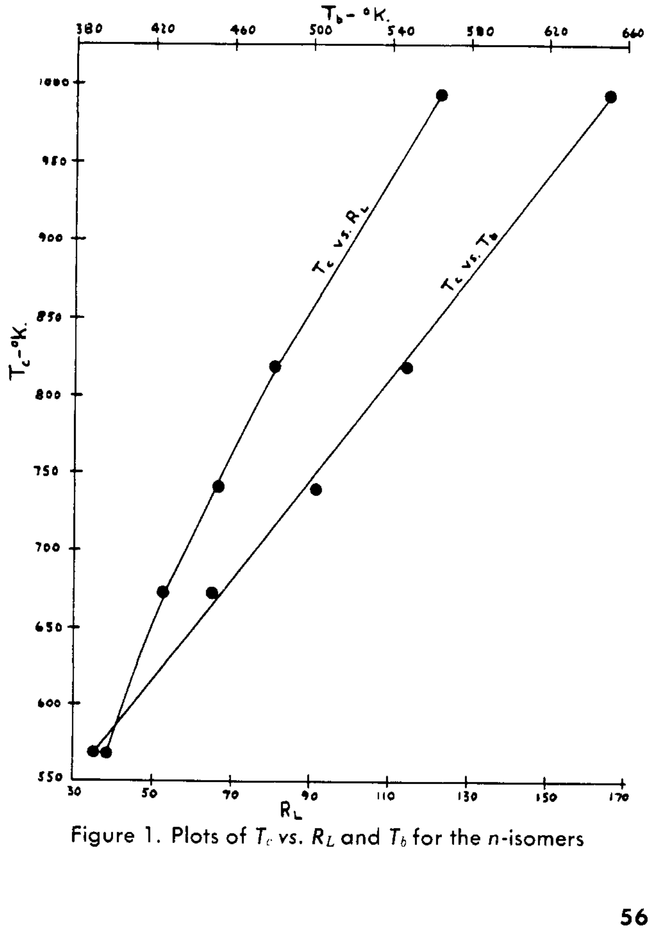

Figure 1. Plots of T_c vs. R_L and T_b for the *n*-isomers

Table III. Physical and Thermodynamic Constants

	Compound	$R_{\text{obsd.}}$, Cc./Mole	V_m^{20}, Cc./Mole	T_b, ° C.	ΔH_v, Cal./Mole	ΔS_b, Cal./Degree	P_i, Atm.
1	$B(OC_2H_5)_3$	38.62	169.1	117.3	9,579	24.53	1655
2	*n*-$B(OC_3H_7)_3$	52.60	218.4	177.0	11,720	26.04	1575
3	*n*-$B(OC_4H_9)_3$	66.42	268.9	230.5	13,200	26.21	1442
4	*iso*-$B(OC_4H_9)_3$	66.61	273.9^a	212.3	11,440	23.57	1216
5	*sec*-$B(OC_4H_9)_3$	66.44	277.6^a	195.6	11,300	24.11	1188
6	*tert*-$B(OC_4H_9)_3$	66.78	282.8	175.1	10,600	23.70	1091
7	*n*-$B(OC_5H_{11})_3$	80.41	318.4	275.3	13,780	25.13	1267
8	*iso*-$B(OC_5H_{11})_3$	80.16	319.7	256.1	14,260	26.94	1313
9	*n*-$B[OCH(CH_3)C_3H_7]_3$	80.09	325.1	237.3	12,680	24.82	1140
10	*iso*-$B[OCH(CH_3)C_3H_7]_3$	79.57	322.6	228.0	14,910	29.76	1371
11	*n*-$B(OC_8H_{17})_3$	122.3	466.2	378.5	20,400	31.30	1302
12	*n*-$B[OCH(CH_3)C_6H_{13}]_3$	118.9	461.1	344.5	19,280	31.21	1244
13	$B(OCH_2CH=CH_2)_3$	50.87	197.4	181.0	11,160	24.58	1652
14	$B(OCH_2CH_2Cl)_3$	52.99	195.1	271.2	13,780	25.32	2070
15	$B[OCH(CH_2Cl)_2]_3$	81.13	281.4	359.1	18,450	29.18	1942
16	*n*-$B(C_3H_7)_3$	48.41	193.9^b	156.0	10,770	25.09	1626
17	*n*-$B(C_4H_9)_3$	62.80	243.9^a	209.7	13,070	27.07	1578

[a] At 25° C. [b] At 22.6° C.

Table IV. Complete Critical Data Obtained from Calculations

	V_c, Cc./Mole	T_c, ° C.	p_c, Atm.	RT_c/p_cV_c	T_c/T_b	a, L.^{2} Atm./Mole^2	b, L./Mole	r, A.
1	502.0	295.5	25.83	3.599	1.456	35.57	0.2258	2.818
2	683.7	401.2	22.48	3.600	1.498	57.48	0.3077	3.124
3	863.4	470.0	19.63	3.598	1.475	79.93	0.3884	3.376
4	866.0	438.2	18.73	3.599	1.466	76.78	0.3896	3.380
5	863.8	398.2	17.72	3.599	1.432	72.28	0.3887	3.377
6	868.0	356.9	16.55	3.598	1.409	68.13	0.3904	3.383
7	1046	547.2	17.87	3.602	1.496	106.9	0.4708	3.599
8	1042	518.6	17.33	3.598	1.496	102.8	0.4687	3.594
9	1041	461.6	16.10	3.597	1.440	95.28	0.4681	3.593
10	1035	467.6	16.32	3.600	1.478	95.52	0.4656	3.587
11	1590	721.5	14.27	3.599	1.526	197.1	0.7153	4.138
12	1546	632.9	13.37	3.598	1.453	174.5	0.6953	4.100
13	661.3	629.2	31.10	3.600	1.986	74.39	0.2977	3.089
14	635.9	518.6	28.40	3.597	1.454	62.70	0.2860	3.049
15	973.6	812.8	25.42	3.599	1.717	131.7	0.4381	3.515
16	629.2	510.2	28.39	3.598	1.825	61.41	0.2830	3.038
17	816.4	640.3	25.52	3.598	1.892	92.90	0.3672	3.313

It has been shown (*20*) that T_c and R_L are related by the equation

$$T_c = BR_L + A \qquad (13)$$

where A and B are constants. A plot of this relationship is shown in Figure 1, for the *n*-isomers listed in Table III (compounds 1, 2, 3, 7, and 11). On the same graph, and for the same compounds, a plot of T_c *vs.* T_b is also shown. According to Livingston (*14*), the two temperatures are related in the following manner,

$$T_c = DT_b + C \qquad (14)$$

where C and D are constants. T_c is thus related to both R_L and T_b, and it was demonstrated (*14*) that R_L and T_b are also related by an equation of the type

$$R_L = FT_b + E \qquad (15)$$

in which case $F = D/B$, and $E = (C - A)/B$. Using the least-squares method of calculation, constants A and B, Equation 13, are 402.7 and 4.962, respectively. Constants C and D, Equation 14, are -60.80 and 1.613, respectively,

$$R_L = 0.3251\ T_b - 93.42 \qquad (16)$$

With the exception of the C_2 isomer, Equation 16 reproduces values of R_L to within 5% and better.

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