of the exchange capacity, sorption approaches the exchange capacity of 200 meq. per 100 grams. Washing removed and sorbed material absorbed at low concentrations indicating, probably, adsorption on the surface. At higher concentrations, the structure is apparently forced apart, allowing interlamellar adsorption.

This observation is supported somewhat by x-ray analysis on the low concentration range amine-contracted clay, the intermediate, and the high concentration range. The low concentration range indicates the structure to be all sodium vermiculite, the high range indicates the structure to be saturated with amine, and intermediate which shows vermiculite either containing no amine (the Na-vermiculite structure) or completely saturated. In no case was it indicated that partial saturation of the structure was obtained.

X-ray study of the washed samples showed the ΔC-axis spacing to be 5.4 A. when saturated. From the area per unit change, 75 sq. A., and the area of the butylamine, 44 to 40 sq. A., over 50% of the area is covered. Therefore, the possibility of stacking is indicated.

Sorption data for dodecylamine are given in Table II. Vermiculite sorbs almost all of the organic ions for concentrations below 200 meq. per 100 grams. At higher concentrations, the constant value of about 300 meq. per 100 grams is reached. This is about 50% in excess of the exchange capacity compared to about 110% for montmorillonite. This is logically based upon the larger area per unit change for montmorillonite. Washing removes amine in excess of the exchange capacity indicating again the excess is held in place by much weaker forces than those for the material held by ion exchange.

X-ray diffraction studies indicated vermiculite to have a Δ C-axis spacing of 13.5 A. when the exchange sites were saturated. This would require that ions be adsorbed at some angle to the C-axis or that there was a distortion of the organic molecule.

CONCLUSIONS

Sodium montmorillonite and sodium vermiculite will sorb the butylamine molecule, butylammonium ion, or butylammonium acetate in quantities slightly less than the exchange capacity.

Both clay forms will sorb in some form the dodecylamine molecule, ion, or salt in quantities in excess of their exchange capacities.

LITERATURE CITED

(1) Cowan, C.T., White, D., *Trans. Faraday Soc.* **54**, 691-7 (1958).
(2) Grim, R.E., "Clay Minerology," pp. 43-77. McGraw-Hill, New York, 1953.
(3) *Ibid.*, 11. 128-34.
(4) Grim, R.E., Allaway, W.H., Cuthbert, F.L., *J. Am. Ceramic Soc.* **30**, 137-42 (1947).
(5) Hendricks, S.B., *J. Phys. Chem.* **45**, 65-81 (1941).
(6) Jordan, J.W., *J. Phys. & Colloid, Chem.* **53**, 294-306 (1949).
(7) Myers, H.E., *Soil Sci.* **44**, 331-59 (1937).
(8) Smith, C.R., *J. Am. Chem. Soc.* **56**, 1561-3 (1934).
(9) Tamamushi, B., Tamaki, K., *Trans. Faraday Soc.* **55**, 1013-16 (1959).

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Molar Refraction

The Extension of the Eisenlohr-Denbigh System of Correlation to Liquid Organotin Compounds

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THE DENBIGH (*3, 24*) system of bond refractivities, based on the classical Lorenz-Lorentz equation

$$MR_L = \frac{n^2 - 1}{n^2 + 2} \times \frac{M}{d}$$

has been successfully employed in the field of organotin compounds by West and Rochow (*30*) and by Vogel, Cresswell, and Leicester (*27*). The subject is treated briefly in a recent review by Gillis (*5*). Because of the demonstrated superiority of the combined Eisenlohr and Denbigh concepts in providing a useful tool for research on liquid organophosphorus compounds (*21*), the present investigation was undertaken primarily to evaluate the merits, in their application to liquid organotin compounds, of each of four systems of correlation—*viz.*, two using refractivities (atomic and bond) based on the Lorenz-Lorentz equation, and two using refraction constants (atomic and bond) based on the empirical Eisenlohr molar refraction product, $MR_E = Mn^{20}D$ (*4*).

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Table I. Calculated Parameters

Atomic Refractivities		Bond Refractivities				Atomic Refraction Constants		Bond Refraction Constants	
		Bond	West & Rochow (*30*)	Vogel, others (*27*)	Present work				
Sn	14.156	Sn-C_{al}	4.09 (prim.) 4.24 (sec.)	4.16	4.170	Sn	197.90	Sn-C_{al}	54.09
—CH	3.791	Sn-C_{ar}	3.54	3.78	4.548	—CH	22.00	Sn-C_{ar}	64.14
		Sn-Cl	8.81	8.91	8.664			Sn-Cl	100.75
		Sn-Br	12.02	12.00	11.971			Sn-Br	179.65
—C—	2.981	Sn-I	17.95	17.92	17.407	—C—	23.41	Sn-I	259.40
		Sn-O	3.84	3.84	2.928			Sn-O	61.81
		Sn-S			7.631			Sn-S	84.46
		Sn-Sn	10.96	10.77	10.683			Sn-Sn	114.81

Table II. Molar Values for Organotin Compounds

No.	Compound	Lit. Ref.	M	t	n'_D	d'_4	$n^{20}D$	Lorenz-Lorentz Molar Refractivity[a]			Eisenlohr Molar Refraction Product[b]		
								Obsd.	Calcd., atomic	Calcd., bond	Obsd.	Calcd., atomic	Calcd., bond
1	$(CH_3)_4Sn$	(*11*)	178.840	25	1.4386	1.2905	1.4406[c]	36.422	36.768	36.791	257.64	270.42	262.80
2	$(CH_3)_3(C_2H_5)Sn$	(*14*)	192.867				1.4527				280.18	291.01	283.40
3	$(CH_3)_2Sn(CH_2)_5$	(*8*)	218.905	23.1	1.5024	1.3357	1.5036[c]	48.398	48.697	48.679	329.15	337.11	329.72
4	$(CH_3)(C_2H_5)_3Sn$	(*14*)	220.921	20	1.5024	1.2160	1.4656	50.281	50.709	50.735	323.78	332.19	324.60
5	$(CH_3)_3(C_4H_9)Sn$	(*14*)	220.921	20		1.1830	1.4560	50.764	50.709	50.735	321.66	332.19	324.60
6	$(CH_3)[(CH_3)_2CHCH_2]Sn$	(*14*)	220.921	21.5	1.4544	1.1804	1.4550[c]	50.722	50.859	50.735	321.44	331.14	324.60
7	$(C_2H_5)_4Sn$	(*11*)	234.948	25	1.4693	1.1916	1.4713[c]	54.941	55.356	55.383	341.68	352.78	345.20
8	$(CH_3)_3(C_5H_{11})Sn$	(*14*)	234.948	15.6	1.4559	1.1586	1.4541[c]	55.114	55.356	55.383	341.64	352.78	345.20
9	$(CH_3)_3[(CH_3)_2CHCH_2CH_2]Sn$	(*14*)	234.948	21	1.4470	1.1305	1.4474[c]	55.528	55.506	55.383	340.06	351.73	345.20
10	$(C_2H_5)_2Sn(CH_2)_5$	(*8*)	246.959	19.9		1.2693	1.5067	57.872	57.991	57.975	372.09	378.29	370.92
11	$(C_2H_5)_3(C_3H_7)Sn$	(*12*)	248.975	20.6	1.4727	1.1673	1.4729[c]	59.802	60.003	60.031	366.72	373.37	365.80
12	$(C_2H_5)_3[(CH_3)_2CH]Sn$	(*14*)	248.975	12	1.4772	1.1733	1.4740[c]	59.981	60.153	60.031	366.99	372.32	365.80
13	$(CH_3)_2[(CH_3)_2CHCH_2]_2Sn$	(*7*)	263.002	20.1		1.1179	1.4635	64.858	64.950	64.679	384.90	391.86	386.40
14	$(CH_3)_2[(CH_3)_3C]_2Sn$	(*31*)	263.002	25	1.4662	1.1043	1.4682[c]	65.986	65.342	64.679	386.14	389.77	386.40
15	$(C_2H_5)_3(C_4H_9)Sn$	(*14*)	263.002	20		1.1457	1.4736	64.467	64.650	64.679	387.56	393.96	386.40
16	$(C_2H_5)_3[(CH_3)_2CHCH_2]Sn$	(*7*)	263.002	20.3	1.4730	1.1390	1.4731[c]	64.776	64.800	64.679	387.43	392.91	386.40
17	$(CH_3)_3(C_8H_{17})Sn$	(*15*)	277.029	25	1.4587	1.0802	1.4607[c]	70.071	69.297	69.327	404.66	414.55	407.00
18	$(C_2H_5)(C_3H_7)_3Sn$	(*7*)	277.029	21.8	1.4737	1.1225	1.4744[c]	69.321	69.297	69.327	408.45	414.55	407.00
19	$(C_2H_5)_3(C_5H_{11})Sn$	(*8*)	277.029	20		1.1258	1.4740	69.156	69.297	69.327	408.34	414.55	407.00
20	$(C_2H_5)_3[(CH_3)_2CHCH_2CH_2]Sn$	(*7*)	277.029	20.1		1.1203	1.4724	69.294	69.447	69.327	407.90	413.50	407.00
21	$(C_3H_7)_4Sn$	(*7*)	291.056	20.2	1.4745	1.1065	1.4746[c]	73.991	73.944	73.975	429.19	435.14	427.60
22	$(C_2H_5)_2[(CH_3)_2CHCH_2]_2Sn$	(*7*)	291.056	20.4	1.4736	1.1030	1.4738[c]	74.105	74.244	73.975	428.96	433.04	427.60
23	$(CH_3)_2[(CH_3)_3C]_2Sn$	(*31*)	291.056	25	1.4870	1.1229	1.4890[c]	74.548	74.636	73.975	433.38	430.95	427.60
24	$(CH_3)(C_4H_9)_3Sn$	(*10*)	305.083	20		1.0898	1.4735	78.603	78.591	78.623	449.54	455.73	448.20
25	$(CH_3)_3(C_{10}H_{21})Sn$	(*15*)	305.083	25	1.4602	1.0487	1.4622[c]	79.708	78.591	78.623	446.09	445.73	448.20
26	$(C_3H_7)_3(C_4H_9)Sn$	(*14*)	305.083	20		1.0917	1.4741	78.552	78.591	78.623	449.72	455.73	448.20
27	$(C_3H_7)_3[(CH_3)_2CHCH_2]Sn$	(*7*)	305.083	24.1	1.4724	1.0841	1.4740[c]	78.859	78.741	78.623	449.69	454.68	448.20
28	$(C_2H_5)(C_4H_9)_3Sn$	(*10*)	319.110	20		1.0783	1.4732	83.049	83.238	83.271	470.11	476.32	468.80
29	$(C_2H_5)[(CH_3)_2CHCH_2]_3Sn$	(*7*)	319.110	21	1.4737	1.0779	1.4741[c]	83.155	83.688	83.271	470.40	473.17	468.80
30	$(C_2H_5)_2(\text{iso-}C_5H_{11})_2Sn$	(*7*)	319.110	19	1.4727	1.0725	1.4723[c]	83.423	83.538	83.271	469.83	474.22	468.80
31	$(CH_3)_3(C_{12}H_{25})Sn$	(*15*)	333.137	25	1.4610	1.0285	1.4650[c]	88.880	87.885	87.919	487.38	496.91	489.40
32	$(C_2H_5)(C_3H_7)(\text{iso-}C_5H_{11})_2Sn$	(*7*)	333.137	21.9	1.4721	1.0654	1.4729[c]	87.575	88.185	87.919	490.68	494.81	489.40
33	$(C_4H_9)_4Sn$	(*10*)	347.164	20		1.0572	1.4730	92.120	92.532	92.567	511.37	517.50	510.00
34	$[(CH_3)_2CHCH_2]_4Sn$	(*7*)	347.164	23	1.4742	1.0540	1.4754[c]	92.601	93.132	92.567	512.21	513.30	510.00
35	$(C_4H_9)_3]C_2H_5CH(CH_3)]Sn$	(*14*)	347.164	15	1.4796	0.9485	1.4776[c]	103.902	92.682	92.567	512.97	516.45	510.00
36	$(C_4H_9)_2[(CH_3)_3C]_2Sn$	(*31*)	347.164	25	1.4809	1.0527	1.4829[c]	93.834	93.224	92.567	514.81	513.31	510.00
37	$(CH_3)[(CH_3)_2CHCH_2CH_2]_3Sn$	(*14*)	347.164	15	1.4700	1.0519	1.4680[c]	92.081	92.982	92.567	509.64	514.35	510.00
38	$(C_4H_9)_3(\text{iso-}C_5H_{11})Sn$	(*14*)	361.191	20		1.0409	1.4715	97.078	97.329	97.215	531.49	537.04	530.60
39	$(\text{iso-}C_4H_9)_3(\text{iso-}C_5H_{11})Sn$	(*7*)	361.191	26.8	1.4717	1.0356	1.4744[c]	97.611	97.779	97.215	532.54	533.89	530.60
40	$(CH_3)_2[C_4H_9CH(C_2H_5)CH_2]_2Sn$	(*15*)	375.218	25	1.4715	1.0307	1.4735[c]	101.847	102.126	101.863	552.88	556.58	551.20
41	$(C_3H_7)(C_5H_{11})_3Sn$	(*10*)	375.218	20		1.0368	1.4732	101.560	101.826	101.863	552.77	558.68	551.20
42	$(C_4H_9)_3(C_6H_{13})Sn$	(*14*)	375.218	17	1.4762	1.0350	1.4750[c]	102.289	101.826	101.863	553.45	558.68	551.20
43	$(C_5H_{11})_4Sn$	(*10*)	403.272	20		1.0206	1.4720	110.645	111.120	111.159	593.62	599.86	592.40
44	$[(CH_3)_2CHCH_2CH_2]_4Sn$	(*12*)	403.272	19.6	1.4709	1.0353	1.4707[c]	108.856	111.720	111.159	593.09	595.66	592.40
45	$[d,l\text{-}C_2H_5CH(CH_3)CH_2]_4Sn$	(*10*)	403.272	20		1.0222	1.4730	110.672	111.720	111.159	594.02	595.66	592.40
46	$(\text{iso-}C_5H_{11})_3(C_7H_{15})Sn$	(*14*)	431.326	20		1.0030	1.4696	119.893	120.864	119.455	633.88	637.89	633.60
47	$(C_6H_{13})_4Sn$	(*10*)	459.380	20		0.9959	1.4706	128.837	129.708	129.751	675.56	682.22	674.80
48	$(C_7H_{15})_4Sn$	(*10*)	515.488	20		0.9748	1.4698	147.486	148.296	148.343	757.66	764.58	757.20
49	$(C_8H_{17})_4Sn$	(*10*)	571.596	20		0.9605	1.4691	165.762	166.884	166.935	839.73	846.94	839.60

Table II (*Continued*)

No.	Compound	Lit. Ref.	M	t	n'_D	d'_4	n^{20}_D	Lorenz-Lorentz Molar Refractivity[a]			Eisenlohr Molar Refraction Product[b]		
								Obsd.	Calcd., atomic	Calcd., bond	Obsd.	Calcd., atomic	Calcd., bond
50	$(C_2H_5)_3Sn(CH_2)_5Sn(C_2H_5)_3$	(*8*)	481.907	20		1.2654	1.5053	113.014	113.347	113.358	725.41	731.07	716.13
51	$(C_2H_5)_3Sn(CH_2)_{10}Sn(C_2H_5)_3$	(*8*)	552.042	20.7	1.4983	1.1887	1.4986[c]	136.197	136.582	136.598	827.29	834.02	819.13
52	$(CH_3)_3(CH_2=CH)Sn$	(*23*)	190.851	25	1.4544	1.265	1.4564[c]	40.887	40.988	40.961	277.96	289.30	282.19
53	$(CH_3)(C_2H_5)_2(CH_2=CH)Sn$	(*23*)	218.905	25	1.4697	1.222	1.4717[c]	49.952	50.282	50.257	322.16	330.48	323.39
54	$(C_2H_5)_3(CH_2=CH)Sn$	(*23*)	232.932	25	1.4738	1.198	1.4758[c]	54.623	54.929	54.905	343.76	351.07	343.99
55	$(C_4H_9)_3(CH_2=CH)Sn$	(*17*)	317.094	25	1.4761	1.085	1.4781[c]	82.445	82.811	82.793	468.70	474.61	467.59
56	$(CH_3)_2(CH_2=CH)_2Sn$	(*17*)	202.862	25	1.4720	1.284	1.4740[c]	44.241	45.208	45.131	299.02	308.18	301.58
57	$(C_4H_9)_2(CH_2=CH)_2Sn$	(*17*)	287.024	25	1.4824	1.127	1.4844[c]	72.658	73.090	73.019	426.06	431.72	425.18
58	$(C_4H_9)(CH_2=CH)_3Sn$	(*23*)	256.954	25	1.4851	1.174	1.4871[c]	62.740	63.369	63.245	382.12	388.83	382.77
59	$(C_8H_{13})(CH_2=CH)_3Sn$	(*15*)	285.008	25	1.485	1.1266	1.4871[c]	72.517	72.663	72.541	432.84	430.01	423.97
60	$(C_8H_{17})(CH_2=CH)_3Sn$	(*15*)	313.062	25	1.4819	1.0865	1.4839[c]	82.130	81.957	81.837	464.55	471.19	465.17
61	$(C_{10}H_{21})(CH_2=CH)_3Sn$	(*15*)	341.116	25	1.4820	1.0672	1.4840[c]	91.125	91.251	91.133	506.22	512.37	506.37
62	$(CH_2=CH)_4Sn$	(*17*)	226.884	25	1.4993	1.267	1.5013[c]	52.606	53.648	53.471	340.62	345.94	340.36
63	$(CH_3)_3(CH_2=CHCH_2)Sn$	(*23*)	204.878	25	1.4741	1.248	1.4761[c]	46.145	45.635	45.609	302.42	309.89	302.79
64	$(C_4H_9)_2(CH_2=CHCH_2)_2Sn$	(*15*)	315.078	25	1.4986	1.0999	1.5006[c]	84.053	82.384	82.315	472.81	472.90	466.38
65	$(C_4H_9)(CH_2=CHCH_2)_3Sn$	(*15*)	299.035	25	1.5162	1.1335	1.5182[c]	79.710	77.310	77.189	453.99	450.60	444.57
66	$(C_2H_5)_3(o\text{-}C_6H_4OH)Sn$	(*2*)	298.992	25	1.5379	1.3150	1.5399[c]	71.107	71.866	72.177	460.42	451.51	463.15
67	$(C_6H_5)(CH_2=CH)_3Sn$	(*23*)	276.944	25	1.5478	1.282	1.5498[c]	68.591	69.134	69.159	429.21	430.96	432.78
68	$(C_6H_5)_2(CH_2=CH)_2Sn$	(*17*)	327.004	25	1.5949	1.3195	1.5969[c]	84.197	84.620	84.847	522.19	515.98	525.21
69	$(C_6H_5)_2(CH_2=CHCH_2)_2Sn$	(*15*)	355.058	25	1.6013	1.2688	1.6033[c]	95.902	93.914	94.143	569.26	557.16	566.41
70	$SnCl_4$	(*9*)	260.528	25	1.5094	2.2091	1.5114[c]	35.237	37.532	34.655	393.76	399.54	403.00
71	$(CH_2=CH)SnCl_3$	(*16*)	252.117	25	1.5361	1.9981	1.5381[c]	39.350	41.561	39.359	387.78	386.14	387.34
72	$C_6H_5SnCl_3$	(*13*)	302.177	23	1.5844	1.8347	1.5844[c]	55.152	57.047	55.047	479.13	471.16	479.76
73	$(CH_2=CH)_2SnCl_2$	(*16*)	243.706	20		1.7645	1.5510[c]	44.066	45.590	44.063	377.99	372.74	371.68
74	$(CH_3)_2(C_2H_5)SnCl$	(*14*)	213.289	20		1.6024	1.5082	39.691	41.606	40.905	321.68	323.29	318.45
75	$(C_2H_5)_3SnCl$	(*7*)	241.343	23.3	1.5055	1.4288	1.5068[c]	50.142	50.900	50.201	363.66	364.47	359.65
76	$(C_2H_5)_2(C_3H_7)SnCl$	(*7*)	255.370	15.7	1.5058	1.3848	1.5041[c]	54.770	55.547	54.849	384.10	385.06	380.25
77	$(C_3H_7)_3SnCl$	(*7*)	283.424	28	1.4910	1.2678	1.4942[c]	64.746	64.841	64.145	423.49	426.24	421.45
78	$(C_2H_5)_2(\text{iso-}C_5H_{11})SnCl$	(*7*)	283.424	19.9		1.2994	1.4980	63.935	64.991	64.145	424.57	425.19	421.45
79	$[(CH_3)_2CHCH_2]_3SnCl$	(*7*)	325.505	24.8	1.4856	1.1826	1.4875[c]	78.969	79.232	78.089	484.19	484.86	483.25
80	$[(CH_3)_2CHCH_2CH_2]_3SnCl$	(*7*)	367.586	34.2	1.4804	1.1290	1.4861[c]	92.557	93.173	92.033	546.27	546.63	545.05
81	$(CH_3)_2(CH_2=CH)SnCl$	(*22*)	211.273	25	1.5105	1.575	1.5125[c]	40.152	41.179	40.427	319.55	321.58	317.24
82	$(C_4H_9)_2(CH_2=CH)SnCl$	(*17*)	295.435	20		1.266	1.4987	68.484	69.061	68.315	442.77	445.12	440.84
83	$(C_4H_9)(CH_2=CH)_2SnCl$	(*17*)	265.365	25	1.4970	1.370	1.4990[c]	56.680	59.340	58.541	397.78	402.23	398.43
84	$(CH_2=CH)_3SnCl$	(*16*)	235.295	20		1.5139	1.5255[c]	47.669	49.619	48.767	358.94	359.34	356.02
85	$SnBr_4$	(*9*)	438.364	35	1.6601	3.3210	1.6661[c]	48.735	49.120	47.886	730.36	670.18	718.60
86	$C_6H_5SnBr_3$	(*13*)	435.554	23	1.6605	2.5028	1.6617[c]	64.283	65.738	64.970	723.76	674.14	716.46
87	$(C_2H_5)_3SnBr$	(*7*)	285.802	20		1.6539	1.5281	53.219	53.797	53.509	436.73	432.13	438.55
88	$(C_2H_5)_2(C_3H_7)SnBr$	(*7*)	299.829	21	1.5218	1.5910	1.5222[c]	57.458	58.444	58.157	456.40	452.72	459.15
89	$(C_2H_5)_2(\text{iso-}C_4H_9)SnBr$	(*7*)	313.856	20		1.5108	1.5159	62.737	63.241	62.805	475.77	472.26	479.75
90	$(C_3H_7)_3SnBr$	(*7*)	327.883	25.2	1.5065	1.4263	1.5086[c]	68.356	67.738	67.453	494.64	493.90	500.35
91	$(C_2H_5)_2(C_5H_{11})SnBr$	(*8*)	327.883	22.3	1.5087	1.4365	1.5096[c]	68.119	67.738	67.453	494.97	493.90	500.35
92	$(C_2H_5)_2(\text{iso-}C_5H_{11})SnBr$	(*7*)	327.883	17	1.5165	1.4881	1.5153[c]	66.605	67.888	67.453	496.84	492.85	500.35
93	$(C_2H_5)(\text{iso-}C_4H_9)_2SnBr$	(*7*)	341.910	19.5	1.5084	1.4085	1.5082[c]	72.409	72.685	72.101	515.67	512.39	520.95
94	$(C_4H_9)_3SnBr$	(*10*)	369.964	20		1.3365	1.5000	81.416	81.679	81.397	554.95	555.67	562.15
95	$(\text{iso-}C_4H_9)_3SnBr$	(*7*)	369.964	20		1.3523	1.5046	81.091	82.129	81.397	556.65	552.52	562.15
96	$(C_2H_5)(\text{iso-}C_5H_{11})_2SnBr$	(*7*)	369.964	20		1.3650	1.5603	80.565	81.979	81.397	557.28	553.57	562.15
97	$(C_5H_{11})_3SnBr$	(*10*)	412.045	20		1.2678	1.4963	94.991	95.620	95.341	616.54	617.44	623.95
98	$(\text{iso-}C_5H_{11})_3SnBr$	(*7*)	412.045	20.7	1.4978	1.2613	1.4981[c]	95.725	96.070	95.341	617.28	614.29	623.95
99	$(CH_3)_2(CH_2=CH)SnBr$	(*22*)	255.732	25	1.5350	1.838	1.5370[c]	43.317	44.076	43.735	393.06	389.24	396.14

100	$(C_4H_9)_2(CH_2=CH)SnBr$	(22)	339.894	25	1.5102	1.416	1.5122[c]	71.815	71.958	71.623	513.99	512.78	519.74
101	$(CH_3)_2SnI_2$	(7)	402.590	39.3	1.6906	2.8282	1.6983[c]	53.874	53.370	53.209	683.72	626.70	650.20
102	$(CH_3)_3SnI$	(7)	290.715	28	1.5724	2.1216[d]	1.5756[c]	45.113	45.069	45.000	458.05	448.56	456.50
103	$(C_2H_5)_3SnI$	(7)	332.796	17.5	1.5649	1.8255	1.5639[c]	59.372	59.010	58.944	520.46	510.33	518.30
104	$(CH_3)_2(C_4H_9)SnI$	(14)	332.796	20		1.7817	1.5478	59.307	59.010	58.944	515.10	510.33	518.30
105	$(CH_3)_2(iso\text{-}C_4H_9)SnI$	(14)	332.796	20		1.7803	1.5475	59.326	59.160	58.944	515.00	509.28	518.30
106	$(CH_3)_2(C_5H_{11})SnI$	(14)	346.823	18	1.5440	1.7192	1.5432[c]	63.684	63.657	63.592	535.22	530.92	538.90
107	$(CH_3)_2(iso\text{-}C_5H_{11})SnI$	(14)	346.823	21	1.5410	1.7027	1.5414[c]	64.007	63.807	63.592	534.59	529.87	538.90
108	$(C_2H_5)_2(C_3H_7)SnI$	(14)	346.823	20		1.7730	1.5582	63.084	63.657	63.592	540.42	530.92	538.90
109	$(C_2H_5)_2(C_4H_9)SnI$	(14)	360.850	20		1.6485	1.5460	69.313	68.304	68.240	557.87	551.51	559.50
110	$(C_3H_7)_3SnI$	(7)	374.877	30.4	1.5367	1.5960	1.5409[c]	73.320	72.951	72.888	577.65	572.10	580.10
111	$(C_3H_7)_2(C_4H_9)SnI$	(14)	388.904	20		1.5624	1.5320	77.132	77.598	77.536	595.80	592.69	600.70
112	$(C_4H_9)_3SnI$	(14)	416.958				1.5345				639.82	633.87	641.90
113	$(iso\text{-}C_4H_9)_3SnI$	(7)	416.958	22.2	1.5222	1.4378	1.5231[c]	88.475	87.342	86.832	635.07	630.72	641.90
114	$(C_4H_9)_2(iso\text{-}C_5H_{11})SnI$	(14)	430.985	20		1.4310	1.5254	92.357	91.689	91.480	657.42	653.41	662.50
115	$(C_4H_9)_2(C_6H_{13})SnI$	(14)	445.012	18	1.5246	1.403	1.5238[c]	97.142	96.186	96.128	678.11	675.05	683.10
116	$(iso\text{-}C_5H_{11})_3SnI$	(7)	459.039	26.5	1.5177	1.3777	1.5203[c]	100.917	101.283	100.776	697.88	692.49	703.70
117	$(C_7H_{15})_3SnI$	(14)	543.201	30	1.4732		1.4772[c]				802.42	819.18	827.30
118	$(C_8H_{17})_3SnI$	(14)	585.282	20		1.3205	1.5181	134.331	142.656	142.608	888.52	880.95	889.10
119	$(CH_3)_2(CH_2=CH)SnI$	(22)	302.726	25	1.5762	2.033	1.5782[c]	49.290	49.289	49.170	477.76	467.44	475.89
120	$(C_4H_9)_2(CH_2=CH)SnI$	(22)	386.888	25	1.5384	1.556	1.5404[c]	77.820	77.171	77.058	595.96	590.98	599.49
121	$(CH_2=CH)_3SnI$	(22)	326.748	25	1.5828	1.898	1.5848[c]	57.519	57.729	57.510	517.83	505.20	514.67
122	$(C_2H_5)_3SnOC_2H_5$	(7)	250.948	23.3	1.4655	1.2394	1.4668[c]	56.026	56.963	55.601	368.09	375.19	370.38
123	$(C_2H_5)_3SnOC_6H_5$	(19)	298.992	20		1.315	1.5422	71.580	72.022	70.433	461.10	458.50	451.54
124	$(C_2H_5)_3SnOC_6H_4CH_3(p)$	(19)	313.019	20		1.283	1.5365	76.134	76.864	75.081	480.95	479.29	472.14
125	$(C_4H_9)_2Sn(OOCCH_3)_2$	(18)	351.024	26	1.475		1.4774[c]	76.50[e]	77.050	74.348	518.60	522.24	521.27
126	$(C_4H_9)_2Sn(OOCC_{11}H_{23})_2$	(18)	631.564	26	1.470		1.4724[c]	168.29[e]	169.990	167.308	929.91	934.04	933.27
127	$[(C_4H_9)_3Sn]_2O$	(18)	596.096	25	1.4848	1.2176	1.4868[c]	140.261	147.483	144.707	886.28	897.61	888.64
128	$(C_2H_5)_3SnSCH_3$	(1)	252.987	20		1.319	1.5290	59.154	58.630	58.807	386.82	385.05	387.81
129	$(C_2H_5)_3SnSC_2H_5$	(19)	267.014	20		1.278	1.5150	63.003	63.277	63.455	404.53	405.64	408.41
130	$(C_2H_5)_3SnSCH(CH_3)_2$	(19)	281.041	20		1.236	1.5132	68.364	68.074	68.103	425.27	425.18	429.01
131	$(C_2H_5)_3SnSC_4H_9$	(19)	295.068	20		1.234	1.5133	71.571	72.571	72.751	446.53	446.82	449.61
132	$(C_2H_5)_3SnSCH_2CH(CH_3)_2$	(19)	295.068	20		1.244	1.5122	71.198	72.721	72.751	446.20	445.77	449.61
133	$(C_2H_5)_3SnSC(CH_3)_3$	(19)	295.068	20		1.240	1.5051	70.591	72.917	72.751	444.11	444.72	449.61
134	$(C_2H_5)_3SnS(iso\text{-}C_5H_{11})$	(19)	309.095	20		1.188	1.5060	77.300	77.368	77.399	465.50	466.36	470.21
135	$(C_2H_5)_3SnSC_6H_5$	(20)	315.058	20		1.3163	1.5828	79.970	78.336	78.287	498.67	488.95	489.57
136	$(C_2H_5)_3SnSC_6H_{13}$	(20)	323.122	20		1.1668	1.5032	81.891	81.865	82.047	485.72	488.00	490.81
137	$(C_2H_5)_3SnSC_6H_4CH_3(o)$	(19)	329.085	20		1.295	1.5740	83.854	83.178	82.935	517.98	509.74	510.17
138	$(C_2H_5)_3SnSC_6H_4CH_3(m)$	(19)	329.085	20		1.283	1.5705	84.215	83.178	82.935	516.83	509.74	510.17
139	$(C_2H_5)_3SnSC_6H_4CH_3(p)$	(19)	329.085	20		1.288	1.5712	83.973	83.178	82.935	517.06	509.74	510.17
140	$(C_2H_5)_3SnSCH_2C_6H_5$	(19)	329.085	20		1.304	1.5682	82.585	82.983	82.935	516.07	509.54	510.17
141	$(C_2H_5)_3SnSC_7H_{15}$	(20)	337.149	20		1.1473	1.5006	86.518	86.512	86.695	505.95	508.59	511.41
142	$[(C_2H_5)_3Sn]_2S$	(19)	443.838	20		1.429	1.5468	98.468	98.033	98.337	686.53	680.98	686.73
143	$[(C_2H_5)_3Sn\text{-}]_2$	(6)	411.772	17.8	1.5374	1.3795	1.5365[c]	93.277	90.112	93.766	632.69	628.12	632.62
144	$[(C_2H_5)_2(C_3H_7)Sn\text{-}]_2$	(6)	439.826	15.3	1.5354	1.3346	1.5335[c]	102.665	99.406	103.062	674.47	669.30	673.82
145	$[(C_2H_5)_2(iso\text{-}C_4H_9)Sn\text{-}]_2$	(6)	467.880	19.8	1.5257	1.2919	1.5256[c]	111.112	109.000	112.358	713.80	708.38	715.02
146	$[(C_3H_7)_3Sn\text{-}]_2$	(6)	495.934	19.5	1.5258	1.2436	1.5256[c]	122.368	117.994	121.654	756.60	751.66	756.22
147	$[(iso\text{-}C_4H_9)_3Sn\text{-}]_2$	(6)	580.096	59	1.5013	1.1330	1.5169[c]	150.920	146.775	149.542	879.95	868.90	879.82

[a] $MR_L = \frac{n^2-1}{n^2+2} \times \frac{M}{d}$ [b] $MR_E = Mn^{20}D$. [c] Corrected by use of coefficient − 0.0004/° C.

[d] The value for d_4^{28} given by Grüttner and Krause (7) is 1.1216. This is so manifestly out of line with the values given by the same authors for other trialkyltin iodides that the inference of a typographical error is inescapable. The value here used (2.1216) is plausible in the light of published density of similar compounds; it gives the MR_L used by West and Rochow (30) and by Vogel and others (24). Furthermore, the density of trimethyltin iodide at 18° C. was reported as 2.155 by A. Cahours, *Ann.* **114**, 370 (1860) and as 2.1096 by A. Ladenburg, Ber. **3**, 358 (1870). [e] These values for MR_L were used by West and Rochow (30) and by Vogel and others (27).

Atomic, group, and bond values from Vogel's tables (*25*, *26*) have been used in this work for elements other than tin. Atomic and bond values for tin, as well as special group values for —CH and —C—, were computed by the least squares method from literature data on 147 representative tin compounds. The newly derived parameters are given in Table I. Table II shows literature data and observed molar values for each compound, together with molar values calculated in accordance with each of the four systems. Refractive indices measured at temperatures other than 20° C. have been corrected approximately by means of the coefficient −0.0004 per ° C. For an accurate evaluation of the four systems, the following coefficients of variation have been calculated:

Property	Refractivity (Lorenz-Lorentz)	Refraction Product (Eisenlohr)
Atomic	0.094	0.055
Bond	0.068	0.019

These coefficients are about as clear an indication of the superiority of the Eisenlohr-Denbigh system of correlation as were those obtained in the work on phosphorus compounds (*21*).

Most of the bond refractivities derived in the present work are in fairly close agreement with those previously calculated by West and Rochow (*30*) and by Vogel and others (*27*); there is, however, conspicuous disagreement in the relative magnitude of the values for Sn-C_{al} and Sn-C_{ar}, the earlier investigators assigning a higher value to the former, whereas present work indicates the reverse. While there seems to have been no general awareness of the need for differentiating between aliphatic and aromatic carbon atoms, Vogel's table (*26*) gives higher bond refractivity and bond refraction constants for C_{ar}-C_{ar} than for C-C, Warrick (*28*) and Vogel and others (*27*) reported a higher refractivity for Si-C_{ar} than for Si-C_{al}, and Weidmann and Zimmerman (*29*) have recently assigned a slightly higher refractivity to B-C_{ar} than to B-C_{al}.

The disagreement noted in the case of the Sn-C_{al} and Sn-C_{ar} refractivities has impelled a search for further evidence as to the consistency of the relative magnitude of values for the two varieties of carbon atoms. As a preliminary and partial test, rough calculations were made using literature data on 19 compounds containing the P-C_{ar} bond; a few of these compounds had been included in the phosphorus investigation cited above (*21*), but no distinction had been made between P-C_{al} and P-C_{ar}. Owing in part to the less rigorous method of calculation employed, but chiefly to serious discrepancies in some of the density measurements, no claim is made for the correctness of the calculated values for P-C_{ar}, R_L = 5.4 and R_E = 30.5; there can be no doubt, however, that the true values are substantially higher than the fairly reliable ones for P-C (3.575 and 25.57, respectively). Furthermore, least squares computations now in progress show that the refractivity of the B-C_{ar} bond exceeds that of the B-C_{al} bond by a considerably wider margin than that reported by Weidmann and Zimmerman (*29*). In the light of the literature cited in the preceding paragraph and of further evidence just adduced, it seems rather improbable that the refractivity of any aliphatic linkage will be found to exceed that of the corresponding aromatic linkage, and there are good reasons for believing that greater exactitude in refractive correlation may be achieved when separate values for C_{al} and C_{ar} linkages have been calculated for many of the other elements.

LITERATURE CITED

(1) Anderson, H.H., Vasta, J.A., *J. Org. Chem.* **19**, 1300 (1954).
(2) Arntzen, C.E., *Iowa State Coll. J. Sci.* **18**, 6 (1943).
(3) Denbigh, K.G., *Trans. Faraday Soc.* **36**, 936 (1940).
(4) Eisenlohr, F., "Spektrochemie Organischen Verbindungen," pp. 12-14, Enke, Stuttgart, 1912.
(5) Gillis, R.G., *Revs. Pure and Appl. Chem. (Australia)* **10**, 25 (1960).
(6) Grüttner, G., *Ber.* **50**, 1808 (1917).
(7) Grüttner, G., Krause, E., *Ibid.*, **50**, 1802 (1917).
(8) Grüttner, G., Krause, E., Wiernik, M., *Ibid.*, **50**, 1549 (1917).
(9) Hölemann, P., *Z. physik. Chem.* **B 32**, 358 (1936).
(10) Jones, W.J., Evans, D.P., Gulwell, T., Griffiths, D.C., *J. Chem. Soc.* **1935**, 39.
(11) Korsching, H., *Z. Naturforsch.* **1**, 219 (1946).
(12) Krause, E., *Ber.* **51**, 1447 (1918).
(13) Krause, E., Grosse, A., von, "Die Chemie der Metallorganischen Verbindungen," p. 352, Gebrüder Borntträger, Berlin, 1937.
(14) Manulkin, Z.M., *Zhur. Obshcheĭ Khim.* **13**, 42, 46 (1943); **14**, 1047 (1944); **16**, 235 (1946).
(15) Rosenberg, S.D., Debreczeni, E., Weinberg, E.L., *J. Am. Chem. Soc.* **81**, 973 (1959).
(16) Rosenberg, S.D., Gibbons, A.J., Jr., *Ibid.*, **79**, 2139 (1957).
(17) Rosenberg, S.D., Gibbons, A.J., Jr., Ramsden, H.E., *Ibid.*, **79**, 2138 (1957).
(18) Ross, Alexander, Metal & Thermit Corp., Rahway, N. J., private communication.
(19) Sasin, G.S., *J. Org. Chem.* **18**, 1142 (1953).
(20) Sasin, R., Sasin, G.S., *Ibid.*, **20**, 770 (1955).
(21) Sayre, Ralph, *J. Am. Chem. Soc.* **80**, 5438 (1958).
(22) Seyferth, D., *Ibid.*, **79**, 2134 (1957).
(23) Seyferth, D., Stone, F.G.A., *Ibid.*, **79**, 515 (1957).
(24) Vickery, B.C., Denbigh, K.G., *Trans. Faraday Soc.* **45**, 61 (1949).
(25) Vogel, A.I., *J. Chem. Soc.* **1948**, p. 1842.
(26) Vogel, A.I., Cresswell, W.T., Jeffery, G.H., Leicester, J., *Ibid.*, **1952**, 531.
(27) Vogel, A.I., Cresswell, W.T., Leicester, J., *J. Phys. Chem.* **58**, 174 (1954).
(28) Warrick, E.I., *J. Am. Chem. Soc.* **68**, 2455 (1946).
(29) Weidmann, H., Zimmerman, H.K., Jr., *J. Phys. Chem.* **64**, 182 (1960).
(30) West, R., Rochow, E.G., *J. Am. Chem. Soc.* **74**, 2490 (1952).
(31) West, R., Webster, M.H., Wilkinson, G., *Ibid.*, **74**, 5794 (1952).

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