[CONTRIBUTION FROM THE MALLINCKRODT LABORATORY, HARVARD UNIVERSITY]

A System of Bond Refractions for Tin Compounds

BY ROBERT WEST AND EUGENE G. ROCHOW

By analysis of the refraction data for ninety-three liquid tin compounds, a system of bond refractions for tin has been devised. Using the organic bond refractions established by Denbigh, this system makes possible a more accurate calculation of molecular refraction for organotin compounds.

The system of bond refractions for organosilicon compounds, proposed by Sauer[1] in 1946 and improved by Warrick,[2] has become generally accepted as a useful tool for studying the structure and identity of these compounds. This paper is an extension of this method of calculating molecular refraction to organotin compounds.

The bond refractions given below for tin compounds were obtained, as were those of Warrick for similar silicon compounds, by making use of the system of bond refractions devised by Denbigh.[3] Criteria established for compounds from the literature used in obtaining bond refractivities were that the refractive index and density had been measured at the same temperature, between 12 and 35°; that the structure of the compound was established beyond reasonable doubt, and that there was no evidence of impurity.

The Lorentz–Lorenz equation,

$$R = \frac{n^2 - 1}{n^2 + 2}\,\frac{M}{d}$$

was used to obtain the observed values for molecular refraction. By subtracting the appropriate amounts obtained from Denbigh's list,[4] the refractivity due to the bonds to tin remained. Evaluation of the Sn–C bond refraction, from the many tin tetraalkyls, allowed values for the other tin bonds to be established from other organotin compounds. The arithmetic mean for the bonds in all compounds meeting the above criteria was used to evaluate the refraction of the tin bonds.

TABLE I

TIN BOND REFRACTIONS

Bond	Refraction, ml.	No. compounds used	Standard deviation
Sn–C (primary)	4.09	19	0.063
Sn–C (secondary)	4.24	12	.127
Sn–C (aryl)	3.54	3	.25
Sn–Cl	8.81	6	.28
Sn–Br	12.02	14	.54
Sn–I	17.95	15	.44
Sn–Sn	10.96	3	.61
Sn–O	3.84	4	.30

All of the values given in Table I must be regarded as tentative and subject to improvement as new data appear in the literature. However, the bond refractions based on data from only three or four compounds are particularly doubtful. The standard deviation, σ, gives some measure of the statistical reliability of the bond refraction value among the compounds from which it was calculated.

TABLE II

MOLECULAR REFRACTIONS OF TIN COMPOUNDS

	MR, found	Temp., °C.	MR, calcd.	Error, %	References
Section A. Tin Tetraalkyls					
$(CH_3)_4Sn$	36.43	25	36.64	+0.6	a
$(CH_3)_3Sn(n\text{-}C_4H_9)$	50.76	20	50.53	− .5	b
$(CH_3)_3Sn(i\text{-}C_4H_9)$	50.72	21.5	50.68	− .1	b
$(CH_3)_3Sn(i\text{-}C_5H_{11})$	55.53	21	55.31	− .4	b
$(CH_3)_2Sn(i\text{-}C_4H_9)_2$	64.85	20.1	64.72	− .2	c
$(CH_3)_2Sn(CH_2)_5$	48.39	23.1	48.30	− .2	h
$CH_3Sn(C_2H_5)_3$	50.27	20	50.53	+ .5	b
$CH_3Sn(n\text{-}C_4H_9)_3$	78.85	20	78.31	− .7	d
$CH_3Sn(i\text{-}C_5H_{11})_3$	92.08	15	92.65	+ .3	b
$(C_2H_5)_4Sn$	54.94	25	55.16	− .4	a,e
$(C_2H_5)_3Sn(n\text{-}C_3H_7)$	59.77	20.6	59.79	...	f
$(C_2H_5)_3Sn(i\text{-}C_3H_7)$	59.98	12	59.94	− .1	g
$(C_2H_5)_3Sn(i\text{-}C_4H_9)$	64.77	20.3	64.57	− .3	c
$(C_2H_5)_3Sn(n\text{-}C_5H_{11})$	69.16	20	69.05	− .2	h
$(C_2H_5)_3Sn(i\text{-}C_5H_{11})$	69.36	20.1	69.20	− .2	c
$(C_2H_5)_2Sn(i\text{-}C_4H_9)_2$	74.10	20.4	74.00	− .1	c
$(C_2H_5)_2Sn(CH_2)_5$	57.87	19.9	57.66	− .3	h
$(C_2H_5)_2Sn(i\text{-}C_5H_{11})_2$	83.42	19.0	83.24	− .2	c
$C_2H_5Sn(n\text{-}C_3H_7)_3$	69.32	21.8	69.05	− .4	c
$C_2H_5Sn(n\text{-}C_4H_9)_3$	83.05	20	82.94	− .1	d
$C_2H_5Sn(i\text{-}C_4H_9)_3$	83.15	21.0	83.09	− .1	c
$C_2H_5Sn(n\text{-}C_3H_7)(i\text{-}C_5H_{11})_2$	87.57	21.9	87.87	+ .3	c
$(n\text{-}C_3H_7)_4Sn$	73.99	20.2	73.68	− .4	c
$(n\text{-}C_3H_7)_3Sn(n\text{-}C_4H_9)$	78.55	20	78.31	− .3	b
$(n\text{-}C_3H_7)_3Sn(i\text{-}C_4H_9)$	78.86	24.1	78.46	− .4	c
$(n\text{-}C_3H_7)Sn(n\text{-}C_5H_{11})_3$	101.56	20	101.46	− .1	d
$(n\text{-}C_4H_9)_4Sn$	92.11	20	92.20	+ .1	d
$(i\text{-}C_4H_9)_4Sn$	92.60	23.0	92.80	+ .2	c
$(n\text{-}C_4H_9)_3Sn(i\text{-}C_5H_{11})$	97.07	20	96.98	− .1	b
$(i\text{-}C_4H_9)_3Sn(i\text{-}C_5H_{11})$	97.61	26.8	97.43	− .2	c
$(n\text{-}C_4H_9)_3Sn(n\text{-}C_5H_{11})$	102.73	17	101.46	−1.2	g
$(n\text{-}C_5H_{11})_4Sn$	110.64	20	110.72	+0.1	d
$(i\text{-}C_5H_{11})_4Sn$	111.32	19.6	111.32	...	f
$(d,l\text{-}C_5H_{11})_4Sn$	110.66	20	110.72	+0.1	d
$(i\text{-}C_5H_{11})_3Sn(n\text{-}C_7H_{15})$	119.88	20	120.43	+ .4	g
$(n\text{-}C_6H_{13})_4Sn$	128.83	20	129.43	+ .3	d
$(n\text{-}C_7H_{15})_4Sn$	147.48	20	147.76	+ .2	d,g
$(n\text{-}C_8H_{17})_4Sn$	165.75	20	166.28	+ .3	d
$(C_2H_5)_3Sn(CH_2)_5Sn(C_2H_5)_3$	113.00	20	112.82	− .2	h
$(C_2H_5)_3Sn(CH_2)_{10}Sn(C_2H_5)_3$	136.20	20.7	135.98	− .2	h
B. Tin-Chlorine Compounds					
$SnCl_4$	35.22	25.0	35.24	...	i
$(C_2H_5)_3SnCl$	50.14	23.3	50.20	+0.1	c
$(C_2H_5)_2(n\text{-}C_3H_7)SnCl$	54.77	15.7	54.81	+ .1	c
$(C_2H_5)_2(i\text{-}C_5H_{11})SnCl$	63.94	19.9	64.22	+ .4	c
$(n\text{-}C_3H_7)_3SnCl^p$	64.75	28.0	64.07	−1.0	c
$(n\text{-}C_4H_9)_3SnCl^p$	78.41	25	77.96	−0.6	j
$(i\text{-}C_4H_9)_3SnCl$	78.97	24.8	78.41	− .7	c
$(i\text{-}C_5H_{11})_3SnCl$	92.55	34.2	92.30	− .3	c
$(cis\text{-}ClCH{=}CH)_3SnCl^p$	62.59	20	63.29	+1.3	k
$(cis\text{-}ClCH{=}CH)_2SnCl_2^p$	53.93	20	53.94	....	l
$(trans\text{-}ClCH{=}CH)SnCl_3^p$	43.61	20	44.59	+2.2	k
C. Tin–Bromine Compounds					
$SnBr_4$	48.73	35.0	48.08	−1.3	i
$(C_2H_5)_3SnBr$	53.22	20	53.39	+0.3	c
$(C_2H_5)_2(n\text{-}C_3H_7)SnBr$	57.46	21	58.02	+1.0	c
$(C_2H_5)_2(i\text{-}C_4H_9)SnBr$	62.74	20.4	62.80	+0.1	c
$(C_2H_5)_2(n\text{-}C_5H_{11})SnBr$	68.12	22.3	67.28	−1.2	h
$(C_2H_5)_2(i\text{-}C_5H_{11})SnBr$	66.61	17.0	67.43	+1.2	c
$(C_2H_5)_2(Br(CH_2)_5)SnBr$	75.39	20.3	74.96	−0.6	h
$(C_2H_5)(i\text{-}C_4H_9)_2SnBr$	72.41	19.5	72.21	− .3	c
$(C_2H_5)(i\text{-}C_5H_{11})_2SnBr$	80.56	20.0	81.47	+1.1	c
$(n\text{-}C_3H_7)_3SnBr$	68.35	25.2	67.28	−1.6	c

---

(1) R. O. Sauer, THIS JOURNAL, **68**, 954 (1946).

(2) E. L. Warrick, *ibid.*, **68**, 2455 (1946).

(3) K. G. Denbigh, *Trans. Faraday Soc.*, **36**, 936 (1940).

(4) Reprinted in Warrick's paper, reference 2.

TABLE II (*Continued*)

	MR, found	Temp., °C.	*MR*, calcd.	Error, %	References
$(n\text{-}C_4H_9)_3SnBr$	81.41	20	81.37	...	*d*
$(i\text{-}C_4H_9)_3SnBr$	81.09	20	81.62	+0.6	*e*
$(n\text{-}C_5H_{11})_3SnBr$	94.99	20	95.07	+0.1	*d*
$(i\text{-}C_5H_{11})_3SnBr$	95.72	20.7	95.51	−0.2	*e*
D. Tin–Iodine Compounds					
$(CH_3)_2SnI_2$[p]	53.88	39.3	54.02	+0.3	*c*
$(CH_3)_3SnI$	45.11	28	45.43	+ .8	*c*
$(CH_3)_2(n\text{-}C_4H_9)SnI$	59.31	20	59.32	...	*b*
$(CH_3)_2(i\text{-}C_4H_9)SnI$	59.33	20	59.46	+0.2	*b*
$(CH_3)_2(n\text{-}C_5H_{11})SnI$	63.69	18	63.95	+ .4	*b*
$(CH_3)_2(i\text{-}C_5H_{11})SnI$	64.01	21	64.10	+ .1	*b*
$(C_2H_5)_3SnI$	59.37	17.5	59.32	− .1	*c*
$(C_2H_5)_2(n\text{-}C_3H_7)SnI$	63.09	20	63.95	+1.3	*b*
$(C_2H_5)_2(n\text{-}C_4H_9)SnI$	69.31	20	68.58	−1.0	*b*
$(n\text{-}C_3H_7)_3SnI$	73.32	30.4	73.21	−0.1	*c*
$(n\text{-}C_3H_7)_2(n\text{-}C_4H_9)SnI$	77.13	20	77.84	+ .9	*b*
$(i\text{-}C_4H_9)_3SnI$	88.47	22.2	87.55	− .9	*c*
$(n\text{-}C_4H_9)_2(i\text{-}C_5H_{11})SnI$	92.36	20	91.88	− .5	*b*
$(n\text{-}C_4H_9)_2(n\text{-}C_6H_{13})SnI$	97.14	18	96.36	− .8	*g*
$(i\text{-}C_5H_{11})_3SnI$	100.92	26.5	101.44	+ .5	*c*
$(n\ C_8H_{17})_3SnI$[p]	134.32	20	142.67	+6.2	*g*
E. Distannanes					
$[(C_2H_5)_3Sn]_2$	93.28	17.8	93.70	+0.4	*m*
$[(C_2H_5)_2n\text{-}C_3H_7Sn]_2$	102.56	15.3	102.96	+0.4	*m*
$[(C_2H_5)_2i\text{-}C_4H_9Sn]_2$[p]	118.17	19.8	112.60	−4.7	*m*
$[(n\text{-}C_3H_7)_3Sn]_2$	122.36	19.5	121.56	−0.7	*m*
$[(i\text{-}C_4H_9)_3Sn]_2$[p]	150.91	59	150.16	−0.5	*m*
F. Aryltin compounds					
$(C_2H_5)_3Sn(o\text{-}HOC_6H_4)$	71.10	25	71.29	−0.6	*n*
$C_6H_5SnCl_3$	64.28	23	64.43	+ .2	*o*
$C_6H_5SnBr_3$	55.15	23	54.80	+ .3	*o*
G. Tin–oxygen compounds					
$(C_2H_5)_3SnOC_2H_5$	56.02	23.3	56.42	+0.7	*c*
$(n\text{-}C_4H_9)_3SnOH$	75.25	25	74.72	− .7	*j*
$(n\text{-}C_4H_9)_2Sn(OOCCH_3)_2$	76.50	25	76.26	− .3	*j*
$(n\text{-}C_4H_9)_2Sn(OOCC_{11}H_{23})_2$	168.29	25	168.76	+ .3	*j*

[a] H. Korsching, *Z. Naturforschung*, 1, 219 (1945). [b] Z. M. Manulkin, *J. Gen. Chem.* (U.S.S.R.), **13**, 42 (1943). [c] G. Grüttner and E. Krause, *Ber.*, **50**, 1802 (1917). [d] W. J. Jones, D. P. Evans, T. Gulwell and D. C. Griffiths, *J. Chem. Soc.*, 39 (1935). [e] L. A. K. Stavely, H. P. Paget, B. B. Goalby and J. B. Warren, *ibid.*, 2290 (1950). [f] E. Krause, *Ber.*, **51**, 1447 (1918). [g] Z. M. Manulkin, *J. Gen. Chem.* (*U. S. S. R.*), **14**, 1047 (1944). [h] G. Grüttner, E. Krause and M. Wiernik, *Ber.*, **50**, 1594 (1917). [i] P. Hölemann, *Z. physik. Chem.*, **B32**, 353 (1936). [j] C. K. Banks, letter to E. G. Rochow. [k] A. N. Nesmeyanov, A. E. Borisov and A. N. Abramova, *Izvest. Akad. Nauk S. S. S. R. Otdel. Khim. Nauk.*, 570 (1949). [l] A. N. Nesmeyanov, A. E. Borisov and A. N. Abramova, *ibid.*, 647 (1946). [m] G. Grüttner, *Ber.*, **50** 1808 (1917). [n] C. E. Arntzen, *Iowa State Coll. J. Sci.*, **18**, 6 (1943). [o] E. Krause and A. von Grosse, "Die Chemie der Metall-organischen Verbindungen," Gebruder Borntraeger, Berlin, 1937, p. 352. [p] Compounds not used in calculation of bond refraction.

The tin bond refractions established in this study permitted the calculation of molecular refractions with an average error of only 0.55% for the 93 liquid tin compounds whose properties were found in the literature. Using either the Sauer or Warrick method for calculating bond refractions of organosilicon compounds, the average error among fifty-eight representative silicon compounds chosen by Sauer was about 0.8%.

In 1935 Jones, Evans, Gulwell and Griffiths[5] compiled values for the molecular refraction of seventeen tin tetraalkyls and five organotin bromides. By subtracting from these the values for the atomic refractions of carbon, hydrogen and bromine according to Eisenlohr's tables,[6] and taking the arithmetic mean of the remainders, they obtained a value of 13.87 ml. for the atomic refraction of tin attached to primary alkyl groups. Although the method of atomic refractions gives accurate values for the molecular refraction of most tin tetraalkyls, it is more noticeably in error for other classes of compounds. The average error for the 93 compounds used in this study was greater than 1% no matter what value was chosen for the atomic refraction of tin.

The errors are much smaller for tetraalkyls than for other organotin compounds, as might be expected since the tetraalkyls are stable and more easily obtainable pure. The higher value for Sn—C (secondary) was obtained by comparing the molecular refractions of twelve pairs of compounds of identical structure save for the isomerization of one or more groups from a primary to a secondary group (*i.e.*, triethyl *n*-propyltin, *MR* 59.79 ml. and triethyl *i*-propyltin, *MR* 59.98 ml.). A similar exaltation among secondary alkyl derivatives of mercury and lead was noted by Jones, Evans, Gulwell and Griffiths.[5] It is to be expected that tertiary alkyl tin compounds might have a still higher refractivity for the tin–carbon bond.

The use of bond refractivities for organosilicon and organotin compounds leads to speculation about the applicability of bond refraction methods in the study of the other fourth group, organometallic compounds. Bond refractivities would appear to have little advantage over atomic refractivities[7] for lead compounds, since the tetraalkyls, and a few mixed aryl-alkyls, are the only organolead compounds which are liquids at room temperature. Insufficient data have been recorded for a system of bond refractions for germanium compounds; but the information which is available[8] indicates that for germanium, as for silicon and tin, no single value for atomic refraction will be accurate for all types of compounds.

CAMBRIDGE, MASSACHUSETTS

RECEIVED DECEMBER 17, 1951

---

(5) W. J. Jones, D. P. Evans, T. Gulwell, D. C. Griffiths, *J. Chem. Soc.*, 39 (1935).

(6) F. Eisenlohr, *Z. physik. Chem.*, **75**, 585 (1911).

(7) G. Grüttner and E. Krause, *Ann.*, **415**, 338 (1918).

(8) O. H. Johnson, *Chem. Revs.*, **48**, 259 (1951).