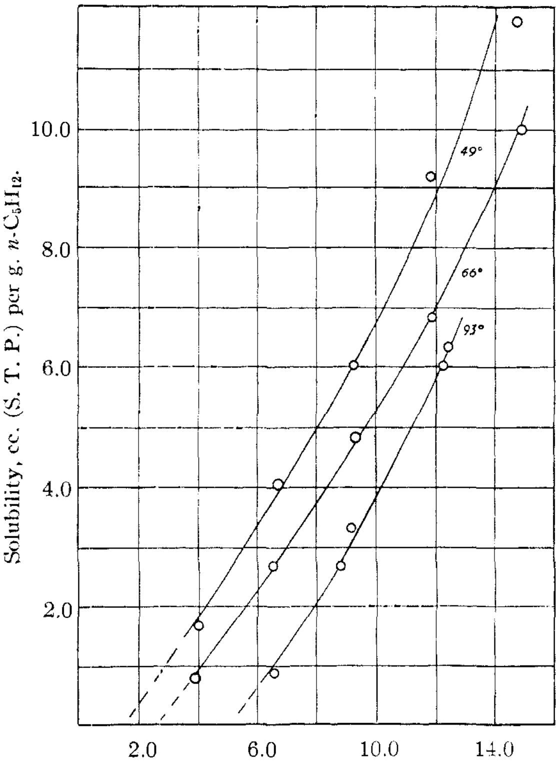

Fig. 1.—Solubility of boron fluoride in *n*-pentane at constant temperature.

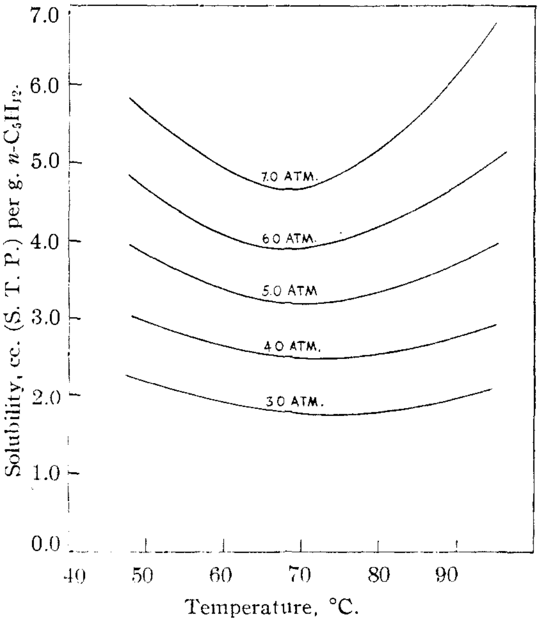

Fig. 2.—Solubility of boron fluoride in *n*-pentane at constant partial pressure of boron fluoride.

however, clearly shown. Similar minima were reported by Wiebe, Gaddy and Heins[3] for the solubility in nitrogen in water.

Summary

The solubility of boron fluoride in *n*-pentane was determined, with an average error of about ±5%, at 49, 66 and 93° and total absolute pressures ranging from 3.8 to 14.8 atmospheres and was found to be of the order of 1 to 12 cc. (STP) of boron fluoride per gram of normal pentane.

At constant partial pressure of boron fluoride, the solubility is a minimum at about 70°.

BARTLESVILLE, OKLAHOMA RECEIVED AUGUST 1, 1946

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[3] Wiebe, Gaddy and Heins, THIS JOURNAL, **55**, 947-953 (1933).

[CONTRIBUTION FROM THE MULTIPLE FELLOWSHIP SUSTAINED BY THE CORNING GLASS WORKS AT MELLON INSTITUTE OF INDUSTRIAL RESEARCH]

The Application of Bond Refractions to Organo-silicon Chemistry

BY E. L. WARRICK

A recent publication by R. O. Sauer[1] proposes a mixed system of group and bond refractions for application in the field of organo-silicon chemistry. It is the purpose of this work to present a simplified and more easily applied uniform system of bond refractions of wider utility.

These bond refractions are complementary to the work of Dr. Sauer, which represented a considerable step forward from the use of atomic refractions in organosilicon chemistry. A still greater simplification and wider utility is possible if we follow the work of Denbigh,[2] who established a rather complete uniform system of organic bond refractions. Denbigh's work was not used in the course of deriving the more cumbersome mixed system of group and bond refractions. Many of the required organic group refractions are not initially provided and have to be specially derived in Dr. Sauer's system.

The system of organo-silicon bond refractions herein developed when used with the organic bond system established by Denbigh[2] will expand the utility of refraction data to cover most of the probable organo-silicon compounds.

In organic chemistry the differences between the two systems of atomic or bond refraction constants are small. This may be the result of a nearly uniform character of bonding which is largely of a purely covalent type. In organo-silicon chemistry the differences between the two systems of

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[1] Sauer, THIS JOURNAL, **68**, 954 (1946).

[2] Denbigh, *Trans. Faraday Soc.*, **36**, 936 (1940).

constants are great and only a system of bond values can be used. This may be evidence for a more widely variable bond type as may be estimated from Pauling's values for the per cent. ionic character of bonds.[3]

Several attempts to develop a series of organic bond refractions have been made. Steiger,[4] Smyth,[5] and Fajans[6] all developed a type of bond refraction system. Each of these authors used the atomic values as a basis so that inherent in their work is the assumption that the atomic values remain constant irrespective of bonding. Likewise each of them retained some "group" refractions.

Denbigh[2] calculates bond refractions directly from molar refractions without any assumptions as to the additivity for atomic refractions. The bond refractions which he obtains are listed in Table I.

TABLE I

DENBIGH'S BOND REFRACTIONS

Bond	Bond refraction, ml./mole	Bond	Bond refraction, ml./mole
C–H	1.69	C–Br	9.37
N–H	1.81	C–I	14.55
O–H	1.73	C=C	4.16
C–C	1.25	C=O	3.38
C–N	1.54	C≡C	6.40
C–O	1.51	$C_{ar}=C_{ar}$	2.73
C–F	1.72	$C_{Na}=C_{Na}$	2.78
C–Cl	6.53		

Using these values Denbigh shows additivity for some 130 compounds with less than 0.7% error.

Development and Testing of Silicon Bond Refractions

The isolation of bond refractions in organosilicon chemistry is an easy task with the bond values of Denbigh as a basis of calculations. For example, silicon tetrachloride has a molar refraction of 28.71 ml., and if one divides this value by 4 the value for a Si–Cl bond appears to be 7.18 ml. Similarly, tetramethylsilane has a molar refraction of 30.02 ml., and if one takes Denbigh's value for C–H of 1.69, the residue after subtracting 12 C–H bonds is 9.74 ml. Dividing this by 4, one obtains an average value of 2.435 ml. for the bond refraction of Si–C. Tetramethoxysilane yields a value of 1.76 ml. for Si–O when subject to this same procedure. The values for Si–C and Si–O can be obtained by another independent method by using the data for the trimethyl end blocked polymers.[7a,b]

The first three members of this series will yield two simultaneous equations in Si–C and Si–O which when solved yield values of 2.50 for Si–C and 1.73 for Si–O. These methods were extended to many other compounds in order to obtain the bond refractions listed in Table II. The values obtained are averages from several compounds but will be improved in accuracy with the appearance of more literature data on organosilicon compounds from which bond refractions may be calculated. In particular, the value for Si–N is quite uncertain since it is based on only one or two compounds, and on the uncertain values for C=N and C≡N, which were not given by Denbigh but were taken from only a few compounds available in the literature.

TABLE II

SILICON BOND REFRACTIONS

Bond	Bond refraction, ml./mole	Bond	Bond refraction, ml./mole
Si–O	1.75	Si–F	1.50
$Si-C_{al}$	2.50	Si–Cl	7.20
$Si-C_{ar}$	2.56	Si–Br	10.20
Si–Si	5.65	Si–N	2.00
Si–H	3.20	Si–S	6.25

Of these bond refractions, the following are in substantial agreement with those of Sauer[1]

	Sauer	This research
Si–O	1.751	1.75
Si–Cl	7.18	7.20
Si–H	3.218	3.20

Inasmuch as no Si–C bond refractions are given in ref. (1), the only basis for comparison is the "group" values

	Sauer	This research
$Si-CH_3$	7.573	7.57
$Si-C_6H_5$	27.43	27.39

The five remaining bond values have no comparison in ref. 1 save that two values for Si–Si are discussed.

The application of these bond values to organosilicon compounds containing four substituents of the same type is illustrated by the examples of Table III.

The range of atomic refraction for silicon as calculated from the observed molar refraction is from 3.87 to 8.12. The error in calculating molar refraction from the given bond values is less than 1.0% in all cases.

A correction has been applied by Sauer[1] which accounts for the difference between the bonds to an alpha carbon and all other carbons in a chain attached to silicon. His value of −0.12 ml. is also obtained if one uses all of the compounds given in the above reference (10). This amounts to a maximum correction of 0.4%.

The application of bond refractions to organosilicon compounds containing mixed substituents is illustrated by the samples of Table IV.

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(3) Linus Pauling "Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1939.

(4) Steiger, *Ber.*, **44**, 1381 (1921).

(5) Smyth, *Phil. Mag.*, **50**, 361 (1925).

(6) Fajans, *Ber.*, **59**, 249 (1926).

(7) (a) Hunter, Warrick, Hyde and Currie, THIS JOURNAL, **68**, 2284 (1946); (b) Patnode and Wilcock, *ibid.*, **68**, 358 (1946)

TABLE III

SYMMETRICALLY BONDED ORGANO-SILICON COMPOUNDS

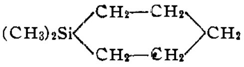
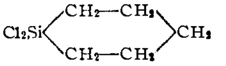
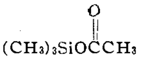
Compound	Obs. molar refr.	Atomic refr. Si	Calcd. molar refr. (from bond values)	% Error	Ref.
$SiCl_4$	28.71	4.84	28.80	+0.3	8
$SiBr_4$	40.74	5.28	40.80	+0.15	8
$Si(OCH_3)_4$	33.32	3.88	33.32	0	8
	33.49	4.05	33.32	−0.5	9
$Si(OC_2H_5)_4$	52.05	4.14	51.84	−0.4	8
$Si(OC_3H_7)_4$	70.25	3.87	70.36	+0.15	8
$Si(CH_3)_4$	30.02	7.15	30.28	+0.9	8
$Si(C_2H_5)_4$	48.42	7.07	48.80	+0.75	8
	48.34	6.98	48.80	+0.95	10
$(CH_3)_3SiC_2H_5$	34.90	7.41	34.91	+0.025	8
	34.73	7.23	34.91	+0.6	10
$(CH_3)_2Si(C_2H_5)_2$	39.40	7 30	39.54	+0 35	8
$(CH_3)_3SiC_6H_5$	50 10	7 74	50.10	0	8
$(CH_3)_3SiCH_2C_6H_5$	55.10	8.12	54.67	−0.8	8
	42.04	7.51	42.04	0	8
$(CH_3)_3SiC_{10}H_{21}$	72.04	7.58	71.95	−0.13	10
$(CH_3)_3SiC_3H_7$	39.49	7.37	39.54	+0.12	10

TABLE IV

UNSYMMETRICALLY BONDED ORGANO-SILICON COMPOUNDS

Compound	Obs. molar refr.	Atomic refr. Si	Calcd. molar refr. (from bond values)	% Error	Ref.
$C_6H_5CH_2SiCl_3$	53 76	6.03	53.56	−0.38	8
$C_2H_5SiCl_3$	33.85	5.61	33.80	−0.15	8
$C_6H_5SiCl_3$	48.94	5.83	48.99	+0.1	8
$(C_2H_5)_3SiF$	38.09		38.10	+0.03	12
$(C_3H_7)_3SiF$	51.58		51.99	+0.8	12
$(C_4H_9)_3SiF$	66.70		65.88	−1.23	12
	40.83	5.81	41.30	+1.4	8
$(CH_3)_3SiOC_2H_5$	35.67	7.44	35.67	0	11[1]
$(CH_3)_2Si(OC_2H_5)_2$	41.05	5.67	41.06	+0.025	11[2]
$CH_3Si(OC_2H_5)_3$	46.97	5.38	46.57	−0.89	11[3]
$(C_6H_5)(C_2H_5)Si(OC_2H_5)_2$	65.46	5.92	65.59	+0.2	11[4]
$(C_6H_5)_2Si(OC_2H_5)_2$	80.30	6.34	80.78	+0.6	11[5]
 $(CH_3)_3SiO\overset{\overset{O}{\|}}{C}CH_3$	35.51	6.37	35.67	+0.4	11[6]
$(CH_3)_2Si(OC_4H_9\text{-}n)_2$	59.45	5.58	59.58	+0.25	13
$(CH_3)Si(OC_4H_9\text{-}n)_3$	74.19	4.83	74.23	+0.05	13
$HSiCH_3Cl_2$	24.82	6.00	25.17	+1.4	11[7]

	$N^{20}{}_D$	$d^{20}{}_4$		$N^{20}{}_D$	$d^{20}{}_4$
(1)	1.3743	0.7573	(5)	1.5250	1.0303
(2)	1.3815	.8393	(6)	1.3860	0.8742
(3)	1.3850	.8899	(7)	1.3982	1.119
(4)	1.4720	.9597			

Here the range of atomic refraction for silicon as calculated from the observed molar refraction is 4.83 to 7.44, while the error in calculating molar refraction from bond values is less than ± 1.5%. The agreement within a series such as the methylethoxysilanes indicates the absence of any progressive change with type of substituent.

The application of bond refraction values to a series of organo-silicon polymers and hydroxyl containing compounds is illustrated by the examples of Table V.

TABLE V

HYDROXYL AND POLYMERIC ORGANO-SILICON COMPOUNDS

Polymer	Obs. molar refr.	Atomic refr. Si	Calcd. molar refr. (from bond values)	% Error	Refs.
$(CH_3)_3SiOH$	26.23	6.45	26.19	−0.2	14
$(C_2H_5)_3SiOH$	40.02	6.39	40.08	+0.15	15
$O[Si(OC_3H_7)_3]_2$	107.68	3.23	109.04	+1.27	8
$(CH_3)_3Si\text{-}Si(CH_3)_3$	51.39	8.54	51.07	−0.6	8
Si_2Cl_6	48.71	6.45	48.77	+0.12	8
$Si_2Cl_5OC_2H_5$	54.41	6.30	54.61	+0.36	8
$Si_2Cl_4(OC_2H_5)_2$	59.94	6.06	60.37	+0.7	8
$Si_2Cl_3(OC_2H_5)_3$	66.28	6.22	66.13	−0.22	8
$Si_2Cl(OC_2H_5)_5$	73.38	3.76	77.65	+6.0	8
$Si_2(OC_2H_5)_6$	83.65	5.89	83.41	−0.3	8
Si_3Cl_8	68.81	7.02	68.90	+0.13	8
$[n\text{-}(C_4H_9O)(CH_3)_2Si]_2\text{-}O$	41.33	3.52	40.86	−1.1	13
Cyclic dimethylsiloxanes					
Tetramer	74.60	5.53	74.56	−0.05	16
Pentamer	93.40	5.57	93.20	− .22	16
Hexamer	112.08	5.57	111.84	− .20	16
Heptamer	130.66	5.57	130.48	− .15	16
Trimethyl end blocked dimethylsiloxanes					
Dimer	48.89	6.518	48.92	+ .06	7(a)
Trimer	67.48	6.25	67.56	+ .12	7(a)
Tetramer	86.15	6.10	86.20	+ .05	7(a)
Pentamer	105.06	6.05	104.84	− .2	7(a)
Hexamer	123.56	5.96	123.48	− .07	7(a)
Heptamer	142.98	5.83	142.12	− .5	7(a)
Octamer	160.88	5.79	160.76	− .07	7(a)
$[CH_3SiHO]_4$	57.10		57.08	− .04	1
$[CH_3SiHO]_5$	71.54		71.35	− .25	1
$[CH_3SiHO]_6$	85.82		85.62	− .25	1
$(CH_3)_3SiOSiH(CH_3)OSi\text{-}(CH_3)_3$	63.14		63.19	+ .08	1
$(CH_3)_3Si[OSiH(CH_3)]_2\text{-}OSi(CH_3)_3$	77.42		77.46	+ .06	1
$(CH_3)_3Si[OSiH(CH_3)]_3\text{-}OSi(CH_3)_3$	91.77		91.73	− .07	1

The range of atomic refraction for silicon here shown is from 3.23 to 8.54, while the error in calculating molar refraction from bond values is less than ± 1.2% with one exception which seems a matter of purity. In the series of chloroethoxydisilanes the agreement does not indicate any progressive change with type of substituent.

Organo-silicon compounds containing negative substituents on the organic portion of the molecule exhibit properties which are often quite different from the usual substituted organic compound. Some organo-silicon compounds of this type are presented in Table VI.

The range of atomic refraction for silicon here shown is from 4.49 to 7.42 while the error in calculating molar refraction from bond values is less than ± 0.75%.

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(8) A. Bygden, *Z. physik. Chem.*, **90**, 243 (1915).

(9) Anderson, THIS JOURNAL, **66**, 1703 (1944).

(10) Whitmore, *ibid.*, **68**, 475 (1946).

(11) Unpublished data from the work of A. J. Barry, Dow Corning Corp. Laboratories.

(12) Gierut, THIS JOURNAL, **58**, 897 (1936).

(13) Sauer, *ibid.*, **68**, 138 (1946).

(14) Sauer, *ibid.*, **66**, 1707 (1944).

(15) Krause and Von Grosse, "Metalorganic Compounds," p. 273, Photo-Lithoprint, Edwards Brothers, Inc., Ann Arbor, Michigan.

(16) Hunter, Hyde, Warrick, Fletcher, THIS JOURNAL, **68**, 667 (1946).

TABLE VI

NEGATIVE SUBSTITUENTS ON ORGANO-SILICON COMPOUNDS

Compound	Obs. molar refr.	Atomic refr. Si	Calcd. molar refr. (from bond values)	% Error	Refs.
$CH_3CHClSi(CH_3)_3$	39.82	7.36	39.75	−0.18	17
$ClCH_2Si(CH_3)_3$	35.17	7.42	35.12	− .13	18
$ICH_2Si(CH_3)_3$	43.02	7.34	43.14	+ .3	18
$ClCH_2(CH_3)_2Si\text{-}O\text{-}$	53.62	6.27	53.76	+ .21	19
$Si(CH_3)_3$	53.90	6.55	53.76	− .26	11
$[ClCH_2(CH_3)_2Si]_2O$	58.18	6.05	58.60	+ .75	19
	58.58	6.45	58.60	+ .035	11
$Si(OCH_2CH_2Cl)_4$	71.07	4.49	71.20	+ .18	20
$HSi(OCH_2CH_2Cl)_3$	56.99	4.96	58.60	− .7	20
$CH_3Si(OCH_2CH_2Cl)_3$	60.92	5.27	60.97	+ .08	20
$(C_6H_5)_2Si(OCH_2CH_2Cl)_2$	90.54	6.84	90.38	− .11	20

Organo-silicon compounds containing sulfur and nitrogen have been purposely omitted from the above tables. Denbigh did not list C–S, C═N or C≡N in his values. It was necessary, therefore, to obtain a few examples of such bonding from the literature.

The data for C–S and also S–S were all taken from the work of Vogel and Cowan.[21]

Data from eight sulfides yielded an average value of 4.55 ml. for the bond refraction of C–S. Similarly five disulfides yielded an average bond refraction for S–S of 8.15 ml. When applied to organo-silicon compounds containing S, the value for Si–S was found to be 6.25 as was given in Table II.

The application to a few organo-silicon compounds containing sulfur is shown in Table VII.

TABLE VII

SULFUR-CONTAINING ORGANO-SILICON COMPOUNDS

Compound	Obs. molar refr.	Calcd. molar refr. (from bond values)	% Error	Ref.
$Si(SCH_3)_4$	62.12	63.48	+2.0	22
$Si(SC_2H_5)_4$	82.1	82.0	−0.12	22
$Si(SC_3H_7\text{-}n)_4$	100.25	100.52	+0.27	22
$Si(SC_4H_9\text{-}n)_4$	119.13	119.04	−0.09	22

The agreement is rather good and with one exception falls in the range of error found for most other compounds.

Data for C═N and C≡N were obtained from V. Auwers[23] and Bruhl,[24] but rather wide variation was noted in the C═N value and only one compound was available to evaluate C≡N.

Instead of averaging the C═N values an examination of the organo-silicon compounds containing C═N and Si–N was made and a value for C═N of 3.90 ml. was selected to give the greatest possible uniformity. The single value for C≡N was taken as 4.95 ml.

Realizing the limitations of the C═N and C≡N values of 3.90 ml. and 4.95 ml., respectively, we may apply them to organo-silicon compounds and determine Si–N which is listed in Table II as 2.00. When a greater number of these compounds are accurately characterized, it will be possible to get more reliable bond refraction data. The few nitrogen containing organo-silicon compounds available are listed in Table VIII.

TABLE VIII

NITROGEN-CONTAINING ORGANO-SILICON COMPOUNDS

Compound	Obs. molar refr.	Calcd. molar refr. (from bond values)	% Error	Refs.
$Si(NCO)_4$	37.29	37.12	− 0.5	19
$Si(OCH_3)(NCO)_3$	36.33	36.17	− 0.4	19
$Si(OCH_3)_2(NCO)_2$	35.07	35.22	+ 0.4	19
$Si(OCH_3)_3NCO$	33.95	34.27	+ 0.9	19
$Si(OCN)_4$	38.31	32.84	−14.4	25
Cl_3SiNCO	31.11	30.88	− 0.8	26
$Cl_2Si(NCO)_2$	33.34	32.96	− 1.1	26
$ClSi(NCO)_3$	35.31	35.04	− 0.8	26
$[(CH_3)_3Si]_2NH$	51.38	51.23	− 0.3	27
$(CH_3)_3SiNHCH_3$	33.12	33.13	+ 0.03	27
$(C_2H_5)_2ClSiN(C_2H_5)_2$	56.79	56.08	− 1.4	11
$(C_2H_5)_2Si[N(C_2H_5)_2]_2$	72.38	73.36	+ 1.4	11
Cl_3SiSCN	39.40	37.35	− 5.1	28
$(CH_3O)_3SiSCN$	41.86	40.74	− 2.7	29

It is difficult to establish reliable values for C═N and C≡N because of the small number of compounds available and the wide variation apparent in even those few compounds. As a result, it is impossible to relate the variable error in molar refraction calculations to any true variation in Si–N. We may expect some variation in the polarizability of the carbon–nitrogen multiple bonds, depending upon the presence or absence of the highly polar Si–Cl or Si–O linkage.

TABLE IX

UNSATURATED ORGANO-SILICON COMPOUNDS

Compound	Obs. molar refr.	Atomic refr. Si	Calcd. molar refr. (from bond values)	% Error	Refs.
$H_2C{=}CH{-}SiCl_3$	33.41	5.65	33.33	−0.24	30, 11
$Si[OCH_2{-}CH{=}CH_2]_4$	67.92	3.41	68.48	+0.8	31
$C_3H_5Si(OC_2H_5)_3$	53.10	2.68	55.24	+4.0	32
$C_2H_3Si(C_2H_5)_3$	47.62	6.75	48.33	+1.4	33
$C_6H_5{-}C{\equiv}C{-}Si(OC_2H_5)_3$	77.49	9.12	73.86	−5.0	34

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(17) Sommer and Whitmore, THIS JOURNAL, **68**, 485 (1946).

(18) Sommer and Whitmore, *ibid.*, **68**, 481 (1946).

(19) Krieble and Elliott, *ibid.*, **67**, 1810 (1945).

(20) Sauer and Patnode, *ibid.*, **67**, 1548 (1945).

(21) Vogel and Cowan, *J. Chem. Soc.*, 16–24 (1943).

(22) Backer and Stienstra, *Rev. Trav. Chim.*, **51**, 1197 (1932).

(23) V. Auwers, *Ber.*, **61**, 1041 (1928).

(24) Bruhl, *Z. physik. Chem.*, **79**, 1 (1912).

(25) Anderson, THIS JOURNAL, **62**, 761 (1940).

(26) Anderson, *ibid.*, **66**, 934 (1944).

(27) Sauer and Hasek, *ibid.*, **68**, 241 (1946).

(28) Anderson, *ibid.*, **67**, 223 (1945).

(29) Anderson, *ibid.*, **67**, 2176 (1945).

(30) D. T. Hurd, *ibid.*, **67**, 1813 (1945).

(31) Helferich and Hausen, *Ber.*, **57**, 795 (1924).

(32) Andrianov and Kamenskaya, *J. Gen. Chem.*, *U. S. S. R.*, **8**, 10 969 (1938).

(33) Ushakov and Itenberg, *ibid.*, **7**, 2492 (1937).

(34) Vol'nov and Reutt, *ibid.*, **10**, 1600 (1940).

A few organo-silicon compounds with unsaturated substituents have data available for refraction calculations, as listed in Table XI.

Not enough data are available for compounds of this type to be certain of any regularities. Here as in the case of the carbon–nitrogen multiple bond systems above the influence of the Si–O and Si–Cl linkages of rather large percentage ionic character (Si–O = 51%; Si–Cl = 30%) may be altering the polarizabilities of double bond systems.

It may be useful to compare the range of error and the average error (disregarding sign) for the compounds examined above, as in Table X.

TABLE X

AVERAGE ERROR OF CALCULATIONS

Table no.	No. of compd.	Range of error −	+	Average error + or − %	Type compounds
3	14	0.8	0.95	0.44	Tetra substituted
4	16	1.23	1.4	.49	Mixed substitution
5[a]	29	1.1	1.27	.26	Polymers
6	9	0.7	0.75	.27	Substituents on carbon
7	4	0.9	2.0	.62	S-containing
8	14	14.4	1.4	2.16	N-containing
9	5	5.0	4.0	2.36	Unsaturated substituents

[a] With one exception of doubtful purity.

It is apparent that for the 72 compounds represented in Tables III, IV, V, VI and VII, the average error is less than 0.62%. However, the introduction of nitrogen or unsaturation into the compound greatly increases the error. As has been indicated, this may be an influence of the highly ionic Si–O and Si–Cl bonds, but too few compounds are available at present to test this hypothesis.

It might be added that the 58 test compounds of Table III in reference (1) show about 0.8% error whether Sauer's method be used or the bond refractions herein developed.

Applications

The application of these bond values to problems of identification of new compounds in the field of organo-silicon chemistry is proving quite valuable in these laboratories. As an illustration of the greater ease of application of a uniform system of bond refractions it is interesting to compare the calculation of the molar refraction of a compound by Dr. Sauer's mixed method and by the bond refraction method. Trimethylsilanol is an example in Table III of reference (1) and bears this footnote, "Calculated as $MR_d = 0.75A + 0.25C + 0.5r(H_2O)$ in which $r(H_2O)$ was calculated from Eisenlohr's atomic values for alcoholic oxygen and hydrogen." On a bond refraction basis the molar refraction of trimethylsilanol is the sum of 9(C–H), 3(Si–C), 1(Si–O) and 1(O–H).

As a test of purity of materials, it may find considerable utility. Wilcock[35] has indicated that a method of specific refraction developed by Sauer was used to determine the purity of a series of trimethyl end blocked dimethylsiloxanes. Following Wilcock's specific refraction data and bond refraction values it is possible to duplicate his and Sauer's calculations of degree of methyl substitution almost exactly.

A further application of this type which may be of interest is to the determination of molecular weight of a high polymer siloxane fluid by refraction data alone. A polymer of the type $(CH_3)_xSiO_{(4-x)/2}$ has only one parameter and that may be found by an equation for molar refraction involving only refractive index and density. From the value of x it is possible to calculate a molecular weight if one assumes that only dimethyl and trimethyl siloxane units occur in the polymer. Several high polymer fluids were so examined and the results are listed in Table XI.

TABLE XI

MOLECULAR WEIGHT FROM REFRACTION

Fluid viscosity, c. s.	N	d	r	Molecular weight Refraction	Viscosity	Av. deg. of subst.
100	1.4030	0.9651	0.25285	6050	6700	2.0252
200	1.4031	.9681	.25214	12260	11300	2.0121
500	1.4033	.9691	.25197	16660	19000	2.0088
1000	1.4035	.9701	.25183	23060	26400	2.0064

The molecular weights by intrinsic viscosity measurements are from the work of A. J. Barry.[36]

Conclusions

1. A system of organo-silicon bond refractions has been developed of greater simplicity and easier application than a mixed system of group and bond refractions. Taken with the organic bond refractions developed by Denbigh, this system makes possible the analysis of refraction data for most of the probable organo-silicon compounds.

2. The principle of additivity of bond refractions is demonstrated for 72 compounds within an average error of 0.62% while for the same compounds a system of atomic constants would require a great many different values for the atomic refraction for silicon. With the appearance of more literature data it should be possible to revise the actual bond refractions to more accurate values.

3. Deviations for organo-silicon compounds containing N or unsaturation may be the result of dipole effects from the highly ionic Si–O or Si–Cl bonds, but more compounds are needed to test any hypothesis.

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[35] Wilcock, THIS JOURNAL, **68**, 691 (1946).

[36] A. J. Barry, "Viscometric Investigation of Dimethyl Siloxane Polymers," presented before the High Polymer Division of the American Physical Society, New York, N. Y., January 26, 1946.