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The Proton Nuclear Magnetic Resonance Spectra of Silicon Analogs of Simple Ethyl Compounds[1a]

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The proton chemical shifts, vicinal (H,H′), and directly bound ^{29}Si–H coupling constants of thirteen compounds containing the disilanyl, SiH_3SiH_2–, group have been measured. Similar data have also been obtained for $SiH_3SiH[N(CH_3)_2]_2$ and for SiH_3OCH_3. The data for analogous disilanyl, ethyl, and methylsilyl (CH_3SiH_2–) compounds are compared. Within the halides, the low-field shifts of the β-protons with decreasing electronegativity of attached halogen may be related to a "Si–Si bond shift," Δ^{X}_{Si-Si}. Certain chemical shift and $J_{^{29}Si-H}$ measurements suggest that there may be an interaction between the substituent, X, and the SiH_3 group in SiH_3SiH_2X compounds of a type not found in analogous ethyl or methylsilyl compounds.

Since the advent of nuclear magnetic resonance spectroscopy, considerable interest has been shown in the measurement and interpretation of proton chemical shift values in a wide variety of methyl and ethyl compounds. The spin–spin interactions between vicinal protons in ethyl compounds have also been studied extensively. Somewhat less work has been carried out in the measurement and interpretation of ^{13}C–proton spin–spin interactions in methyl and ethyl compounds. Since silicon lies immediately below carbon in the periodic table it is of particular interest to study the analogous magnetic resonance phenomena in those silicon compounds which could be regarded as silicon analogs of methyl and ethyl compounds.

Ebsworth and Turner[2,3] have examined the proton magnetic resonance spectra of almost all compounds which contain a silyl (SiH_3–) group. Such compounds may be formally considered to be the silicon counterparts of methyl compounds. The present investigation was therefore undertaken in order to study the proton magnetic resonance spectra of all known compounds which contain the disilanyl (SiH_3SiH_2–) group. Such species may be regarded as the silicon analogs of ethyl compounds. In particular it was considered desirable to ascertain whether a "silicon–silicon bond effect" similar to the well-known "carbon–carbon bond effect"[4] and the more recently discovered "silicon–carbon bond effect"[5] could be observed.

Results and Discussion

The proton nuclear magnetic resonance spectra of thirteen compounds of general formula SiH_3SiH_2R have been studied and have been found to be qualitatively similar to those of their ethyl analogs with the exception of SiH_3SiH_2I and $SiH_3SiH_2CH_3$. Where R is magnetically inactive the spectra were analyzed as first order A_2X_3 with the exception of SiH_3SiH_2I which is A_3X_2. In the case of SiH_3SiH_2F the spectrum was of the A_2X_3P type while that of $SiH_3SiH_2CH_3$ was $A_2X_3P_3$.[6] The effective symmetry is increased by rapid rotation about the silicon–silicon bond.

Two additional compounds, $SiH_3SiH[N(CH_3)_2]_2$ and SiH_3OCH_3, which are not of the above SiH_3SiH_2R type have also been studied in this investigation.

For all compounds, satellites arising from the directly bound ^{29}Si isotope of spin $^1/_2$ were observed. In some cases all the expected satellites could not be detected since they were masked by the SiH_3 triplet,

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(2) E. A. V. Ebsworth and J. J. Turner, *J. Phys. Chem.*, **67**, 805 (1963).

(3) E. A. V. Ebsworth and J. J. Turner, *J. Chem. Phys.*, **36**, 2628 (1962).

(4) J. R. Cavanaugh and B. P. Dailey, *ibid.*, **34**, 1099 (1961).

(5) E. A. V. Ebsworth and S. G. Frankiss, *Trans. Faraday Soc.*, **59**, 1518 (1963).

(6) J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High Resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co., New York, N. Y., 1959.

TABLE I

PROTON CHEMICAL SHIFTS AND SPIN–SPIN COUPLING CONSTANTS IN DISILANYL AND RELATED COMPOUNDS

	Chemical shifts[a]				Spin–spin coupling constants		
Compound	Concn., vol. %	δ SiH_2,[b] p.p.m.	δ SiH_3,[b] p.p.m.	δ CH_3,[b] p.p.m.	$J_{H-H'}$, c.p.s.	$J_{^{29}Si-H}$ (SiH_2), c.p.s.	$J_{^{29}Si-H}$ (SiH_3), c.p.s.
Si_2H_6[c]	~25		−1.82[d]		4.0		196.2[e]
SiH_3SiH_2F[f,g,h]	11.5	−3.86	−1.83		2.7	217.0	*i*
SiH_3SiH_2Cl[j]	25	−3.42	−1.97		3.0	221.2	201.4
SiH_3SiH_2Br[k]	25	−2.86	−2.15		3.0	225.8	202.6
SiH_3SiH_2I[l]	25	−1.95	−2.42		3.0	224.4	204.6
$(SiH_3SiH_2)_2O$[l]	25	−3.68	−1.76		3.0	214.8	194.4
$SiH_3OSiH_2SiH_3$[m]	25	−3.69	−1.78[n]		2.5	210.6	192.8[o]
$CH_3OSiH_2SiH_3$[m]	20	−3.55	−1.73	−1.96	3.2	207.6	198.2
$(SiH_3SiH_2)_3N$[h,p]	27	−3.40	−1.84		2.7	205.2	*i*
$(SiH_3SiH_2)_2NCH_3$[h,q]	20	−3.34	−1.75	−1.18	2.3	203.0	*i*
$SiH_3SiH_2N(CH_3)_2$[f,h]	21	−3.30	−1.71	−1.07	2.7	199.8	*i*
$(SiH_3SiH_2)_2S$[p]	20	−3.11	−1.95		3.1	213.6	202.0
$CH_3SiH_2SiH_3$[h,q,r]	18	−2.23	−1.73	+1.20	2.5	189.0	191.0
$SiH_3SiH[N(CH_3)_2]_2$[f,h,s]	15	−3.56[t]	−1.86	−1.04	3.0	(SiH[i])	184.5
SiH_3OCH_3[u]	20		−3.08	−1.98			216.2

[a] Compounds were studied in cyclohexane solution. [b] Values reported relative to cyclohexane (internal standard). Error, ±0.01 p.p.m. A negative sign indicates a shift to low field of cyclohexane. [c] G. W. Bethke and M. K. Wilson, *J. Chem. Phys.*, **26**, 1107 (1957). [d] Previously reported value [J. E. Drake and W. L. Jolly, *ibid.*, **38**, 1033 (1963)], −1.78 p.p.m. (concentrated solution in tetramethylsilane solvent). [e] Previously reported value (see ref. *d*), 199 c.p.s. [f] M. Abedini and A. G. MacDiarmid, *Inorg. Chem.*, **2**, 608 (1963). [g] J_{F-H} is 43.2 c.p.s. for the SiH_2 protons and 6.6 c.p.s. for the SiH_3 protons. Reported J_{F-H} for SiH_3F is 45.8 c.p.s.[3] [h] N.m.r. data taken from Ph.D. Dissertation of Mansour Abedini, University of Pennsylvania, 1963. [i] Signal lost under main resonance signals of compound or solvent. [j] A. D. Craig, J. V. Urenovitch, and A. G. MacDiarmid, *J. Chem. Soc.*, 548 (1962). [k] M. Abedini, C. H. Van Dyke, and A. G. MacDiarmid, *J. Inorg. Nucl. Chem.*, **25**, 307 (1963). [l] L. G. L. Ward and A. G. MacDiarmid, *J. Am. Chem. Soc.*, **82**, 2151 (1960). [m] C. H. Van Dyke, Ph.D. Dissertation, University of Pennsylvania, 1964. [n] Value is for SiH_3 of $-SiH_2-SiH_3$ group. Chemical shift of the SiH_3O protons is −3.18 p.p.m. [o] Value given is for the SiH_3 of the SiH_3SiH_2- group. $J_{^{29}Si-H}$ for the SiH_3 of the SiH_3O- group is 219.2 c.p.s. [p] L. G. L. Ward and A. G. MacDiarmid, *J. Inorg. Nucl. Chem.*, **21**, 287 (1962). [q] M. Abedini, Ph.D. Dissertation, University of Pennsylvania, 1963. [r] $J_{H-H'}$ value given is for coupling between SiH_3 and SiH_2 protons. $J_{H-H'}$ of CH_3-SiH_2 protons, 4.2 c.p.s. [s] Chemical shift determined in benzene solution (δ benzene = −5.74 p.p.m. from cyclohexane). [t] Value given is for the SiH proton in the $H_3SiSiH{=}$ group. [u] B. Sternbach and A. G. MacDiarmid, *J. Am. Chem. Soc.*, **83**, 3384 (1961).

the SiH_2 quartet, or the solvent peaks. The measurements are given in Table I.

(I) Proton Chemical Shifts and Electronegativity of Substituents.—The trend in the relative values of the proton chemical shifts of the $-SiH_3$ and $-SiH_2$ groups in traversing the series SiH_3SiH_2X (X = F, Cl, Br, I) is analogous to that observed in the ethyl halide series in that the SiH_2 resonance moves to higher fields and the SiH_3 resonance moves to lower fields as the electronegativity of the attached halogen decreases. However, the spectrum of SiH_3SiH_2I differs from that of CH_3CH_2I in that the MH_2 (M = C, Si) resonance in SiH_3SiH_2I falls at a higher field than the MH_3 resonance. In ethyl compounds, the value of (δ MH_3 − δ MH_2) is found to decrease as the value of the electronegativity of the attached element decreases and it has been calculated that the CH_2 resonance will fall at a higher field than the CH_3 resonance only when the electronegativity is less than 1.71.[7,8] For example, in a compound such as triethylaluminum[9] (Huggins electronegativity of Al = 1.5),[10] the resonance of the CH_2 group falls at a higher field than that of the CH_3 group. If it should be assumed that the relative anisotropic and related effects acting on the SiH_3 and SiH_2 groups in disilanyl compounds are comparable to those acting on the CH_3 and CH_2 groups in ethyl compounds, then the cross over of SiH_3 and SiH_2 resonance frequencies observed in the disilanyl halides suggests that the *effective* electronegativities of the halogens in these compounds are considerably less than their commonly accepted values. This conclusion is consistent with the fact that the dipole moments of those silyl halides which have been measured (SiH_3F, SiH_3Cl, and SiH_3Br) are smaller than those of the corresponding methyl halides,[11] even though silicon has a smaller electronegativity and larger radius than carbon. Hence dipole moment measurements of silyl halides also suggest that the halogens may have *effective* electronegativities which are less than the commonly accepted values. Such a reduction in electronegativity could arise through $(p \rightarrow d)\pi$ bonding[12] between halogen and silicon.

The methylsilyl halides are not strictly comparable to ethyl and disilanyl halides since there are already two different types of protons in the parent hydride, CH_3SiH_3. However, if the difference in chemical shifts between the CH_3 and SiH_3 groups in CH_3SiH_3 is subtracted from (δ CH_3 − δ SiH_2) in CH_3SiH_2X (X = F, Cl, Br, I) (Table II), then analogous results to those observed with the disilanyl halides are obtained.

Although it appears that SiHXYZ resonance chemical shifts are in general less sensitive than are CHXYZ

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[7] H. Spiesecke and W. G. Schneider, *J. Chem. Phys.*, **35**, 722 (1961).

[8] B. P. Dailey and J. N. Shoolery, *J. Am. Chem. Soc.*, **77**, 3977 (1955).

[9] E. B. Baker, *J. Chem. Phys.*, **26**, 960 (1957).

[10] M. L. Huggins, *J. Am. Chem. Soc.*, **75**, 4123 (1953).

[11] E. A. V. Ebsworth, "Volatile Silicon Compounds," Pergamon Press, New York, N. Y., 1963, p. 58.

[12] D. P. Craig, A. Maccoll, R. S. Nyholm, L. E. Orgel, and L. E. Sutton, *J. Chem. Soc.*, 332 (1954).

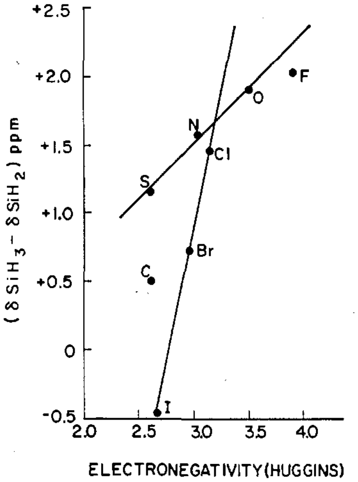

Fig. 1.—Relationship between internal chemical shift values in disilanyl compounds and the electronegativity of the substituent.

TABLE II

CHEMICAL SHIFT DIFFERENCE BETWEEN THE α AND β PROTON RESONANCES IN ETHYL, DISILANYL, AND METHYLSILYL HALIDES

	Ethyl halides (δ CH_3 − δ CH_2),[8] p.p.m.	Disilanyl halides (δ SiH_3 − δ SiH_2), p.p.m.	Methylsilyl halides (δ CH_3 − δ SiH_2),[a] p.p.m.	Methylsilyl halides [(δ CH_3 − δ SiH_2) − $\Delta_{CH_3SiH_3}$],[b] p.p.m.
F	3.20	2.03	4.42	0.99
Cl	2.13	1.45	4.21	0.78
Br	1.77	0.71	3.81	0.38
I	1.40	−0.47	3.15	−0.28

[a] Values calculated from ref. 5. [b] $\Delta_{CH_3SiH_3}$ = (δ CH_3 − δ SiH_3) in CH_3SiH_3. This has a value of 3.43 p.p.m.[5] The analogous quantities, $\Delta_{CH_3CH_3}$ and $\Delta_{SiH_3SiH_3}$, which could be applied to ethyl and disilanyl halides, respectively, are, of course, equal to zero.

shifts to changes in the rest of the molecule,[13] it is interesting to note that the smaller value of (δ MH_3 − δ MH_2) observed in disilanyl halides as compared to ethyl halides (Table II) is exactly what might have been expected in view of the dipole moment data mentioned above. It would appear that the effective electronegativity of any element having at least one pair of electrons which can undergo (p → d)π bonding with silicon might be considered as being reduced below its usual value when it is linked directly to a silicon atom.

It has been well established that an approximately linear relationship exists between the internal chemical shift (δ CH_3 − δ CH_2) in ethyl compounds and the electronegativity of the substituent.[8] However, no such simple relationship exists in disilanyl compounds as is shown by Fig. 1. No simple explanation for the relationship observed can be offered at the present time. However, if the electronegativity values of the attached elements are modified to varying extents by (p → d)π bonding to the silicon, no linear relationship between internal chemical shift values and electronegativity should necessarily be expected.

It has been shown that, in methyl compounds, there is an over-all general shift of the resonance signal to

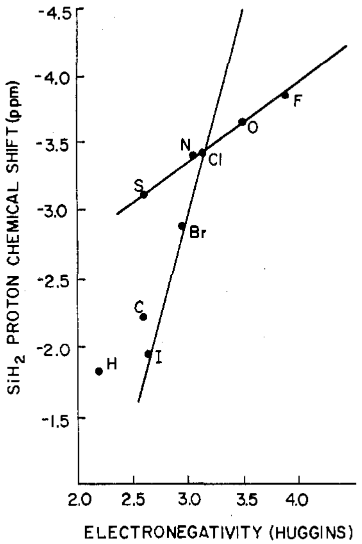

Fig. 2.—Relationship between α-proton chemical shift values in disilanyl compounds and the electronegativity of the substituent.

lower fields as the electronegativity of the attached substituent is increased.[7,14] A similar effect has been noted with the CH_2 protons in ethyl compounds.[7] For methyl compounds and for the α protons of ethyl compounds, the signals for F, N, O, and H lie on a straight line when plotted against their respective electronegativity values and the signals for F, Cl, Br, I, and S lie on a second straight line.[7] Silyl compounds differ from methyl compounds in that the signals for F, N, and O fall on one straight line and those for Cl, Br, and I fall on a second line, which does not include F. H and S fall on neither line.[2] The present investigation shows (Fig. 2) that the α proton shifts in disilanyl compounds are very much more similar to those observed in silyl compounds than to those in ethyl compounds. This is not surprising in view of the fact that (p → d)π bonding which is not present in the linkages between carbon and the substituent atom is present in the analogous linkages in the silyl compounds and also, presumably, in the disilanyl compounds. Other, as yet undetermined, factors will undoubtedly contribute to the differences observed between analogous carbon and silicon compounds.

The β proton shieldings in the series of compounds CH_3SiH_2X decrease along the series X = H, N, O, F (which is consistent with increasing inductive deshielding) but increase along the series X = I, Br, Cl, F.[13] A similar effect has been observed in ethyl, isopropyl, *t*-butyl, cyclohexyl, dimethylsilyl, and trimethylsilyl halides.[13] Although the disilanyl halides follow the above trend, the chemical shifts of the compounds where X = H, N, F are identical to within experimental error and fall at a somewhat lower field than when X = O. This suggests that when X = H, N, O, F there is an additional interaction across the Si–Si bond or across space between X and the SiH_3 group, besides the inductive effect. This could also be interpreted as indicating an increasing interaction involving only

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(13) E. A. V. Ebsworth and S. G. Frankiss, *J. Am. Chem. Soc.*, **85**, 3516 (1963).

(14) A. L. Allred and E. G. Rochow, *ibid.*, **79**, 5361 (1957).

the N, O, and F, which acts so as to compensate their increasing electronegativity and thus makes their net effect approximately equivalent to that of H. This might well be related in some way to an increase in $(p \rightarrow d)\pi$ bonding between X and the α silicon.

(II) The "Silicon–Silicon Bond Shift."—It has been found that the signal of the protons attached to a silicon atom which is linked directly to an electronegative substituent falls to a lower field when one of the protons is replaced by a silyl group. Thus, with the exception of SiH_3SiH_2I, the α proton signals of disilanyl compounds lie at a lower field than the proton signals of the analogous silyl compounds. An identical phenomenon has been observed for methyl and ethyl compounds[4] and for silyl and methylsilyl (CH_3SiH_2–) compounds[5] except that with these series the iodide is not exceptional.

The effect of the carbon–carbon bond in causing the signal of the α protons in ethyl compounds to fall at a lower field than the signal in the corresponding methyl compounds has been termed the "carbon–carbon bond shift."[4] The analogous phenomenon in methylsilyl compounds has been called the "carbon–silicon bond shift"[5] and hence this phenomenon in a disilanyl compound, SiH_3SiH_2X, can be described as the "silicon–silicon bond shift," $\Delta^X{}_{Si-Si}$. The carbon–carbon and silicon–silicon bond shifts could be referred to as "catenation shifts" and for the sake of convenience the carbon–silicon bond shift will also be referred to as a catenation shift in the following discussion. The magnitude of the carbon–carbon bond shift varies according to the nature of the attached substituent[4] as do also the magnitudes of the carbon–silicon[5] and silicon–silicon bond shifts. The values obtained for disilanyl compounds are given in Table III.

TABLE III

THE SILICON–SILICON BOND SHIFTS, $\Delta^X{}_{Si-Si}$, IN DISILANYL COMPOUNDS[a,b]

X	δ SiH_3X[c] in SiH_3X	δ SiH_2X in SiH_3SiH_2X	$\Delta^X{}_{Si-Si}$	δ β-(SiH_3SiH_2X) − $\Delta^X{}_{Si-Si}$
F	−3.32	−3.86	0.54	−2.37
SiH_3O–	−3.17	−3.69	0.52	−2.30
–O–	−3.17	−3.68	0.51	−2.27
CH_3O–	−3.08	−3.55	0.47	−2.20
–N<	−3.00	−3.40	0.40	−2.24
$(CH_3)_2N$–	−2.90	−3.30	0.40	−2.11
CH_3N<	−3.00	−3.34	0.34	−2.09
Cl	−3.15	−3.42	0.27	−2.24
–S–	−2.91	−3.11	0.20	−2.15
Br	−2.73	−2.86	0.13	−2.28
CH_3	−2.11	−2.23	0.12	−1.85
H	−1.76	−1.82	0.06	−1.88
I	−2.05	−1.95	−0.10	−2.32

[a] $\Delta^X{}_{Si-Si} = \delta\ SiH_3X - \delta\ SiH_2X$. [b] Values listed are in p.p.m. relative to cyclohexane. (A negative sign indicates a downfield shift from cyclohexane.) [c] Data for compounds not described in this study are from ref. 2.

It can be seen that $\Delta^X{}_{Si-Si}$ decreases along the series $X = F > O > N > Cl > S > CH_3 \sim Br > H > I$ which roughly follows an order of decreasing electronegativity. It is particularly interesting to note that this order is exactly the *reverse* of that observed for methylsilyl compounds[5] and is approximately the reverse order of that found for $\Delta^X{}_{C-C}$ in ethyl compounds.[5]

Various explanations have been offered to account for the carbon–carbon bond shift. For example, it has been suggested that if ethyl compounds are regarded as being derived from methyl compounds by substituting a proton by a methyl group, then the greater electronegativity of carbon (2.5) as compared to hydrogen (2.1) would cause the α proton signal to move to lower fields.[7] Although this argument could also be applied to methylsilyl compounds, it cannot be applied to disilanyl compounds, since silicon has a smaller electronegativity (1.8) than hydrogen and hence the α proton signal would be expected to move to higher fields, which is contrary to what is observed. At the present time the origin of the catenation shifts is not completely understood but there is evidence to suggest that the carbon–carbon shift is due neither to anisotropic effects of the substituent nor to magnetic anisotropy of the carbon–carbon bond.[4] Likewise in methylsilyl halides, it appears that the carbon–silicon shift is not caused by anisotropies of the halogens.[5] In disilanyl halides it is most unlikely that the silicon–silicon bond shift is caused by anisotropic effects of the halogens since the shift is smallest in the case of SiH_3SiH_2I, where anisotropic effects of the halogen would be expected to be greatest. In the case of SiH_3SiH_2F, where anisotropic effects would be considerably less, the largest shift is obtained.

In ethyl compounds it appears that the carbon–carbon bond effect acts equally on the protons present in both the CH_3 and CH_2 groups and decreases the shielding about them. This is suggested by the fact that if the carbon-carbon bond shift, $\Delta^X{}_{C-C}$ for a substituent X, is added to the proton chemical shift of the methyl group, δ CH_3, then a value is obtained which is approximately constant for all ethyl compounds. Moreover, this value lies close to the proton chemical shift of ethane. The value is always somewhat downfield from δ C_2H_6 (at least with electronegative substituents), and it may be regarded, at least in part, as the residual electronegativity effect of the substituent on the CH_3 group after correcting for the carbon–carbon bond effect.[4,5] This relationship[4] is shown diagrammatically in Fig. 3 for a few selected ethyl compounds.

An analogous effect has been observed in methylsilyl compounds.[5] However, in the case of disilanyl compounds (with the exception of SiH_3SiH_2I) a different effect is observed. Although the Si–Si bond effect causes the shielding of the protons on the SiH_2 groups to be decreased (relative to the shielding in the silyl analog), it apparently increases the shielding about the SiH_3 protons. This is suggested by the fact that δ SiH_3 for several disilanyl compounds actually falls at a higher field than δ Si_2H_6 (see Table I). In addition, if $\Delta^X{}_{Si-Si}$ is added to δ SiH_3 no constant value results, but if it is subtracted from δ SiH_3 then a constant is obtained. The variation in the "constant" values for

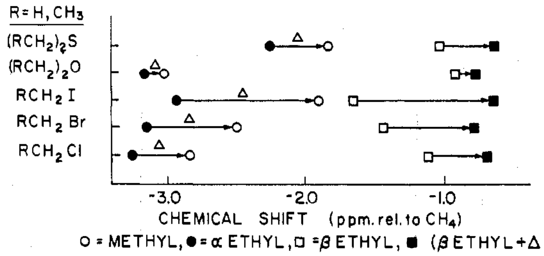

Fig. 3.—Modification of δ CH_3 in selected ethyl compounds by the carbon–carbon bond shifts.

disilanyl compounds is actually less than the variation observed either for ethyl or for methylsilyl compounds.[5] The data are summarized in Table III and illustrated in Fig. 4. It should be noted that as expected, all the $[\delta\ \beta\text{-}(SiH_3SiH_2X) - \Delta^{X}_{Si-Si}]$ values fall at a lower field than δ Si_2H_6. If it is assumed that, similarly to ethyl compounds, anisotropic effects of neither the substituent nor the Si–Si bond contribute appreciably to the above phenomena, then it appears possible that there might be an electronic interaction across the Si–Si bond from the SiH_2 group to the SiH_3 group. Although the same factors which cause the carbon–carbon and the carbon–silicon bond shifts in ethyl and methylsilyl compounds, respectively, may operate in disilanyl compounds, it appears that they are less important than some other unknown effect which is more specific to the silicon–silicon bond.

(III) Vicinal Spin–Spin Coupling of Protons.—Whereas the vicinal spin–spin coupling of the α and β protons in most ethyl compounds is in the order of 7 c.p.s.,[6] that of the α and β protons in disilanyl compounds is approximately 2–3 c.p.s. The lower value is probably due principally to the fact that in disilanyl compounds coupling occurs across a greater distance (R_C = 0.77 Å.; R_{Si} = 1.17 Å.). In methylsilyl compounds, where the Si–C distance is intermediate between the C–C and Si–Si distances, the coupling constants have intermediate values.[5]

No apparent relationship such as that observed in ethyl[15] and methylsilyl compounds[5] between $J_{H-H'}$ and the electronegativity of the substituent could be found in the disilanyl compounds investigated. It appears likely that the larger distance over which coupling occurs may make the $J_{H-H'}$ values less sensitive to changes in electronegativity of the substituent.

(IV) Spin–Spin Coupling between α and β Protons and Fluorine.—The fluorine in SiH_3SiH_2F was found to couple effectively with both the SiH_2 and SiH_3 protons although the values observed (J_{H-F} (SiH_2) = 43.2 c.p.s. and J_{H-F} (SiH_3) = 6.6 c.p.s.) were considerably less than the analogous values for C_2H_5F (J_{H-F} (CH_2) = 60 c.p.s. and J_{H-F} (CH_3) = 20 c.p.s.).[16] The coupling was attenuated to a greater extent over the Si–Si bond (84.7%) than across the C–C bond (66.6%). This is probably related, at least in part, to the greater bond distance in the silicon compound.

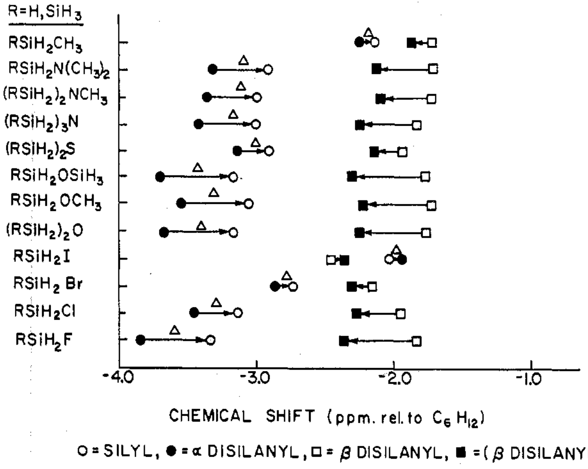

Fig. 4.—Modification of δ SiH_3 in disilanyl compounds by the silicon–silicon bond shifts.

(V) Spin–Spin Coupling between Protons and ^{29}Si.—Spin–spin coupling was found to occur between protons and a ^{29}Si atom to which they were directly attached. Attenuation across the Si–Si bond is apparently so great that no coupling could be observed between a proton and a ^{29}Si atom to which it was not directly bonded. However, in the case of Si_2H_6 it was interesting to observe that the satellites of disilane consisted of well-defined quartets (the higher field satellite was partly obscured by the solvent resonance signal). The small natural abundance of the ^{29}Si isotope (4.7%)[6] makes it unlikely that many molecules of Si_2H_6 will contain more than one ^{29}Si atom. Hence, the protons bound to this isotope will be magnetically nonequivalent to those bound to the ^{28}Si isotope, and hence spin–spin coupling between the protons will occur. The $J_{H-H'}$ value observed was 4.0 c.p.s. A similar effect has been reported for $(SiH_3)_2S$,[3] but in this case $J_{H-H'}$ was only 0.70 c.p.s., which is not surprising since coupling occurred over a distance of four bonds.

Where comparable data are available it is found that $J_{^{29}Si-H}$ (SiH_3) is smaller than $J_{^{29}Si-H}$ (SiH_2) in a given disilanyl compound with the exception of $CH_3SiH_2SiH_3$, for which it is slightly larger. In general, the values of $J_{^{29}Si-H}$ (SiH_3) are closer to the $J_{^{29}Si-H}$ (Si_2H_6) value than are the $J_{^{29}Si-H}$ (SiH_2) values.

The $J_{^{29}Si-H}$ (SiH_2) values of the disilanyl compounds are all smaller than the ^{29}Si–H coupling constants for the corresponding silyl[3] and methylsilyl[5] compounds with the exception of $(CH_3SiH_2)_2O$ and $(CH_3SiH_2)_3N$, which have values slightly smaller than the corresponding disilanyl compounds.

Considerable evidence relating the amount of s-character in a carbon hybrid orbital with the $J_{^{13}C-H}$ coupling constant has been presented.[17–20] As the amount of s-character and hence the bond angle in the C–H bonds increases, $J_{^{13}C-H}$ becomes larger. However, the relationship between $J_{^{29}Si-H}$ and the HSiH bond angles in silicon compounds is not yet well

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(20) C. S. Foote, *Tetrahedron Letters*, **9**, 579 (1963).

defined,[3,18] and further structural data on silyl and disilanyl compounds are needed in order to gain definite information concerning this relationship.

In the present investigation it has been found that within the limits of experimental error, and with the exception of $CH_3OSiH_2SiH_3$, δ SiH_3 moves to lower fields as the value of $J_{^{29}Si-H}$ (SiH_3) increases (see Table I). A similar relationship has been observed for the CH_3 group in ethyl and methylsilyl compounds.[5,21,22] If change of $J_{^{29}Si-H}$ should depend principally on the change in s-character of the silicon bonding orbital, then the decrease of δ SiH_3 with increasing $J_{^{29}Si-H}$ indicates that neither the anisotropy of the Si–Si bond nor that of the (Si-substituent) system significantly affects the shielding of the β protons. However, in the case of the α protons, a decrease in δ SiH_2 parallels an increase in $J_{^{29}Si-H}$ only for the first-row elements (see Table I). No such correlation is observed when I, Br, Cl, or S is the substituent. Hence, when these elements are present it appears that anisotropic effects do affect the extent of shielding of the α protons. A similar effect can be observed with the α protons of methylsilyl compounds and with silyl compounds.[2,3,5] Since, therefore, it seems possible that anisotropic effects do not significantly affect the shielding of the β protons, it appears that the apparently anomalous downfield trend of the SiH_3 proton chemical shift in disilanyl compounds with decreasing electronegativity of X is not primarily controlled by anisotropic effects. This is in agreement with the similar conclusions reached for ethyl and methylsilyl compounds.[5] Hence, it might be suggested that similarly to ethyl and methylsilyl compounds,[5] the electron releasing power of $-SiH_2X$ in disilanyl compounds increases in the order $X = I < Br < Cl < F$.

It has been found for ethyl compounds that $J_{^{13}C-H}$ (CH_2) is an additive property of the substituents which can be expressed by the equation[21]

$$J_{^{13}C-H}\,(CH_2) = J_{^{13}C-H}\,(CH_4) + \Delta J^{X} + \Delta J^{CH_3}$$

where by definition

$$\Delta J^{X} = J_{^{13}C-H}\,(CH_3X) - J_{^{13}C-H}\,(CH_4)$$

A similar effect has been noted in methylsilyl compounds.[5] In the case of each disilanyl compound the value of ΔJ^{SiH_3} may be calculated by an analogous equation using previously published data for silyl compounds[3] together with appropriate $J_{^{29}Si-H}$ values obtained in this investigation. The results are given in Table IV together with the corresponding values of ΔJ^{CH_3} for methylsilyl compounds. The ΔJ^{MH_3} values indicate, in effect, the contribution made by the MH_3 group in the compounds in reducing the $J_{^{29}Si-H}$ value found in SiH_4 to the $J_{^{29}Si-H}$ (SiH_2) value observed in the MH_3SiH_2X compounds.

It can be seen that in compounds having the general formula CH_3SiH_2X, the CH_3 group contributes in an additive manner to the $J_{^{29}Si-H}$ values, since the value of ΔJ^{CH_3} is essentially constant. However, in SiH_3-SiH_2X compounds no constant value of ΔJ^{SiH_3} is found and hence the contribution of an SiH_3 group to the value of $J_{^{29}Si-H}$ (SiH_2) varies considerably from one compound to another according to the nature of X. This observation is of particular interest since it implies that there is an interaction between X and the SiH_3 group either across the Si–Si bond or across space. It may be noted that a similar conclusion was reached in section I from a study of certain β proton shieldings. No major interaction of this type across C–C or Si–C bonds has been observed. The observation is consistent with the report that there is a strong interaction between phenyl groups across the Si–Si bond in $(C_6H_5)_3Si$-$Si(C_6H_5)_3$.[23]

TABLE IV

CONTRIBUTIONS BY CH_3 AND SiH_3 GROUPS TO $J_{^{29}Si-H}$ (SiH_2) VALUES IN METHYLSILYL AND DISILANYL COMPOUNDS

Compound (M = C or Si)	ΔJ^{CH_3},[a] c.p.s.	ΔJ^{SiH_3}, c.p.s.
MH_3SiH_2F	−6.7	−12.0
MH_3SiH_2Cl	−9.1	−16.9
MH_3SiH_2Br	−9.4	−14.7
MH_3SiH_2I	−9.1	−15.7
$(MH_3SiH_2)_2S$	−9.0	−10.4
$(MH_3SiH_2)_3N$	−7.8	− 6.8
$(MH_3SiH_2)_2O$	−9.2	− 6.7

[a] Calculated from data given in ref. 5.

Although chemical shift and coupling constant data for silyl and disilanyl compounds are in many respects analogous to those obtained for methyl and ethyl compounds, respectively, there are several important differences. These may be due, at least in part, to the presence of low-energy 3d orbitals of silicon which permit interactions of a type not possible in carbon compounds.

Experimental

All compounds were synthesized according to the method given in the reference quoted for each compound listed in Table I. Several criteria of purity, such as molecular weight, vapor pressure at a given temperature, elemental analysis, etc., were obtained for each substance.

The proton nuclear magnetic resonance spectra were measured with a Varian Associates HR 60 spectrometer, Model 4300D with flux stabilizer, operated at 60 Mc./sec. at room temperature. The data obtained for disilanyl compounds may be compared directly with the corresponding data reported by Ebsworth and co-workers[2,3,5] for silyl and methylsilyl compounds in cyclohexane solution. In all cases except the iodide no correction for concentration was necessary since the proton chemical shifts of silyl and methylsilyl compounds have only a very small dependence on concentration. When calculating $\Delta^{I}{}_{Si-Si}$ the observed δ SiH_3 (infinite dilution) for SiH_3I was changed from −2.00 to −2.05 p.p.m. to convert δ SiH_3I at infinite dilution to what it would be at 25% concentration.[24]

In certain cases where one of the satellite peaks was masked by a parent or solvent peak the $J_{^{29}Si-H}$ values reported were obtained by doubling the value between the observed satellite and parent peaks. Since in those cases where both satellites of a given peak were observed, the isotope shift, δ SiH ($^{29}Si - {}^{28}Si$),

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was less than the experimental error in measuring the resonance frequency, it appears likely that the error introduced by the above procedure will not affect the significance of the results.

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CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
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Boron–Nitrogen Compounds. XVI.[1,2] Some New Boron–Nitrogen Heterocycles

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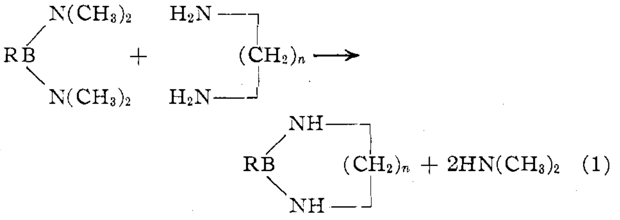
Several new 1,3,2-diazaboracycloalkanes have been prepared by a transamination reaction. In an analogous procedure, the first representative of the 1,8,10,9-triazaboradecalin system was obtained. Spectroscopic data of the newly synthesized materials were evaluated.

The utilization of heterocyclic boron–nitrogen–carbon compounds for cancer treatment is presently being studied.[3] However, one class of such compounds, the 1,3,2-diazaboracycloalkanes, has not yet been investigated for its physiological effects; indeed, the preparation of these compounds has received only causal attention. Of ring systems of this type only those that possess five or six annular atoms have been described. Among the five-membered rings, five derivatives have been reported[4–8] and only one six-membered ring is known.[4] In view of the recent preparation of a 1,2-azaboracycloalkane and its successful dehydrogenation,[9] an application of similar techniques on the 1,3,2-diazaboracycloalkane system should afford interesting results.

The present study reports on the synthesis of several new 1,3,2-diazaboracyclohexanes and the heretofore unknown 1,3,2-diazaboracycloheptanes. These compounds (I) are readily produced through a transamination reaction between bis(dimethylamino)boranes and aliphatic α,ω-diamines in inert solvents such as hexane or benzene (eq. 1). In addition, the transamination of tris(dimethylamino)borane with 3,3′-diaminodipropylamine was also studied. In dilute solutions, 1,8,10,9-triazaboradecalin (II) was obtained in good yield. It is the first example of this hitherto unknown boron–nitrogen–carbon ring system.



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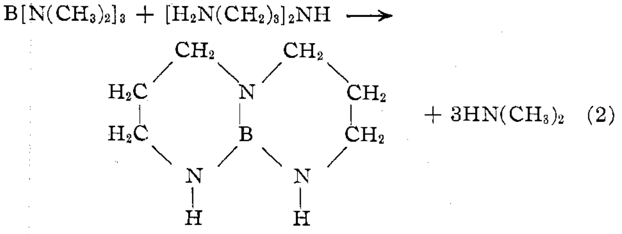

II

Experimental[10]

2-Ethyl-1,3,2-diazaboracyclohexane (Typical Experiment).—A quantity, 14.8 g. (0.2 mole), of 1,3-diaminopropane was added to a solution of 25.6 g. (0.2 mole) of bis(dimethylamino)ethylborane in 150 ml. of dry hexane in an inert atmosphere. Dimethylamine evolved slowly at room temperature. On refluxing the reaction mixture, additional dimethylamine was evolved; the reaction was complete within approximately 2 hr. The solvent was stripped off and the residue distilled under reduced pressure to yield 16.1 g. (72%) of 2-ethyl-1,3,2-diazaboracyclohexane, b.p. 44–45° (13 mm.). The analytical data are compiled in Table I.

In an analogous procedure, the compounds listed in Table I were prepared by the reaction of 0.2 mole of various B-substituted bis(dimethylamino)boranes with 1,3-diaminopropane and 1,4-diaminobutane.

1,8,10,9-Triazaboradecalin (II).—A solution of 26.2 g. (0.2 mole) of 3,3′-diaminodipropylamine in 50 ml. of dry benzene was

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[2] Supported by the U. S. Army Research Office—Durham.

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[10] Infrared spectra of the materials were recorded on a Perkin-Elmer Model 21 double-beam spectrophotometer using sodium chloride optics; ^{1}H nuclear magnetic resonance data were obtained with a Varian A-60 high resolution n.m.r. spectrometer, using tetramethylsilane as an external standard while ^{11}B data were obtained with a Varian V-4300-B n.m.r. spectrometer, operated at 19.3 Mc., using the diethyl etherate of BF_3 as external standard. Melting points were taken on a Mel-Temp block. Analyses were furnished by the Schwarzkopf Microanalytical Laboratory, Woodside 77, N. Y.