A REVIEW OF (p→d) π-BONDING IN SILICON COMPOUNDS

by

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CONTENTS

I. Introduction

The elements of the second short row of the periodic table have five empty d-orbitals of sufficiently low energy to permit their use in bond formation. The five orbitals are spatially arranged as the schematic diagram below shows:

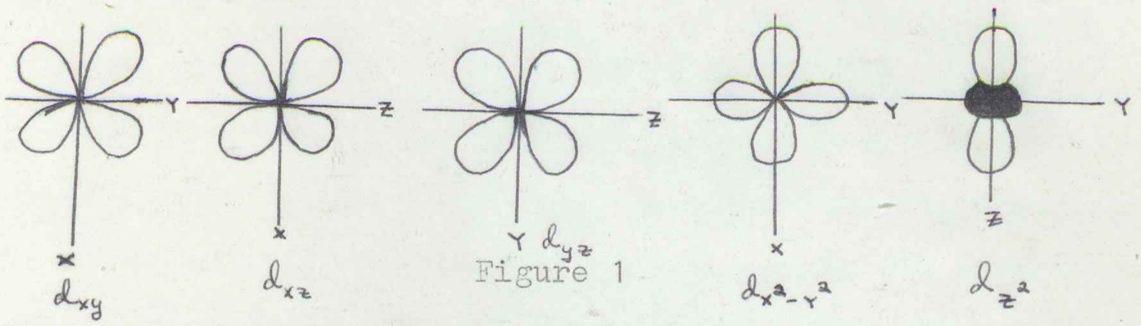


Figure 1

If the sigma bond lies along the x-axis, for instance, then the d_{xy}- and d_{xz}- orbitals have two lobes lying on either side of the sigma bond. If the sigma-bonded neighboring atom has a lone pair of π electrons in the p_y- or p_z- orbitals, the empty d-orbitals could accept the lone pair as shown below:

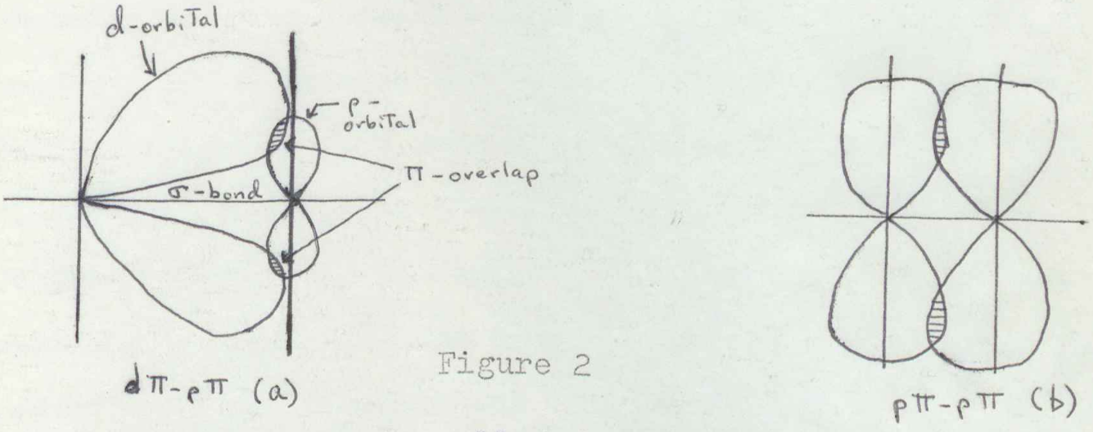


Figure 2

dπ-pπ (a)

pπ-pπ (b)

This sort of overlap is called (p→d) π-bonding or dative π-bonding. The overlap is not, in general, as great as that in a (p—p)π-bond [See Figure 2(b)], but it does lend some double bond character (eg., shortened bond length and increased bond order) where it does exist.

Another effect could exist which looks, inductively, just like dπ-pπ bonding. It might, indeed, be the predominant effect and might be misconstrued as being dative π-bonding. If the atom adjacent to, for example, silicon, is more electronegative than silicon and has a lone pair (eg, $-\ddot{\underset{..}{O}}$, $-\ddot{N}$ or $-\ddot{\underset{..}{X}}\colon$), there could be this sort of picture:

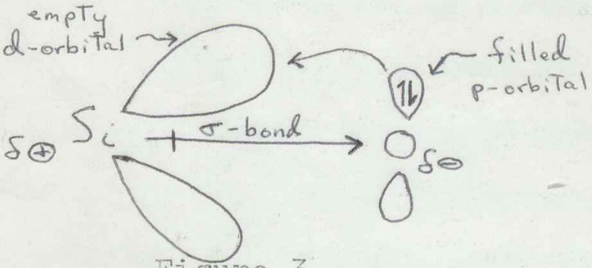


Figure 3

where the sigma bond is polarized by a field effect as shown in Fig.3. As indicated, this effect could act like dative π-bonding. In examining, care should be taken to consider both possibilities.

Considerable work has been done with sulfur, phosphorus, silicon, germanium and arsenic to investigate the possibility, existence and extent of (p→d) π-bonding in their compounds. Work done with sulfur compounds has established the use of its 3d-orbitals in dative π-bonding. Johnson, Blyholder and Cordes (1) investigated the seven-membered ring, $S_4N_3^{\oplus}$, and found it to be planar. Their interpretation of the visible and ultraviolet spectral data was that there is considerable (p→d) π-bonding between the sulfur d_{xy} orbitals and the nitrogen lone pairs. Caserio, Pratt and Holland (2) , in nuclear magnetic resonance comparisons with analogous nitrogen compounds, found that (2p→3d) π-bonding contributes significantly to the bonding of

α,β-unsaturated sulfonium salts. Two views concerning (p→d) π-bonding in divalent sulfur compounds were considered by Goodman and Taft (3). The views are: a) in sulfur-carbon π-bonding, both the 3p- and 3d- S orbitals are used; and b) the use of S 3d-orbitals is unimportant and the bond involves only thi inclusion of the 3p-electrons into an olefinic or aryl π-shell. They decided between these two by a substituent interference experiment. In thiophenol, the band at 2800 Å was assigned to a $^1A \rightarrow {}^1L_b$ transition. If the S 3d-orbitals are used in π-bonding to the ring, the p-CH_3-thiophenol L_b band will have a destructive interference term resulting in the intensity being decreased from that of thiophenol itself. This decrease is seen in that p-$CH_3C_6H_4SH$ has a molar extinction coefficient of approximately 300 where thiophenol's is around 700. Thus, they conclude the first view, that the 3d-orbitals are significant contributors in sulfur π-bonding. Williams (4) discovered that the bond between nitrogen and sulfur is stronger than the theoretical single bond energy by some 9 kcal/mole and he attributed this added stability to resonance by (p→d) π-bonding. Doering and Hoffman (5) demonstrated sulfur and phosphorus $d\pi$-$p\pi$ bonding with carbon by the reaction of trimethylsulfonium iodide and tetramethylphosphonium iodide with sodium deuteroxide in deuterium oxide. Ninety-eight percent of the methyl protons in the sulfonium salt and 73.9 percent of the methyl protons in the phosphonium salt exchanged with deuterons from the solvent after 3 hrs. of heating at 62°C. When tetramethylammonium iodide was reacted with sodium deuteroxide in D_2O, only 1.13 % of the protons exchanged after 358 hours at 100° C. In this ammonium salt, there is no possibility for (p→d) π-bonding. There has been more work done on the possibility of $d\pi$-$p\pi$ bonding in sulfur compounds. (6-9)

Chemical evidence has also supported the contention that phosphorus uses its 3d orbitals in dative π-bonding. Peterson (7) found that, in the preparation of organolithium compounds, $>PCH_3$ reacted faster than expected, although slower than $-SCH_3$ by some 5000 times (10), and attributed this increased rate of metalation to (p→d) π-bonding, making the methyl hydrogens more acidic and therefore more easily removed. Haake, Miller and Tyssee (11) stated that: "The dependence of C^{13}-H coupling constants on the electronegativity of attached groups offers an ideal way to detect the amount of positive charge on phosphorus or sulfur and therefore the amount of (p→d) π-bonding in compounds with PO or SO bonds." Nuclear magnetic resonance studies of PO compounds relative to analogous compounds of nitrogen led them to believe that the PO bonds are best described as double bonds. They concluded the same about SO bonds and therefore dative π-bonding was shown to exist in these compounds. N.m.r. studies by Letcher and VanWager (12) on ^{31}P chemical shifts showed that they are primarily sensitive to asymmetric electron loading. This affords a method for estimating the amount of (p→d) π-bonding to phosphorus.

Thus it has been established and accepted by most chemists that sulfur and phosphorus do use their low-lying d-orbitals in dative π-bonding. When considering silicon, there is varying opinion on the use or non-use of d-orbitals. In general, two effects determine the availability of d-orbitals. First is the size of the d-orbitals; the second, the sigma bond length. These two effects oppose each other. As the atom possessing the empty d-orbitals increases in size, the d-orbitals become larger, thus becoming somewhat more capable of π-overlap. However, the atom's orbital used in the σ-bond also increases in size, increasing the σ-bond length. For sulfur and phosphorus, the orbital size is considered large enough to form this π-overlap, whereas work done with germanium and arsenic, while showing in some cases the existence of this bonding, has shown that it is much less significant here (the σ-bond length has become the predominant effect). It is thought that silicon lies on the border, thus making a definite decision more difficult. Thus, experimental evidence has been interpreted both for and against $(p \rightarrow d)$ π-bonding in silicon compounds. This paper is a literature search of Chemical Abstracts from 1954 through May, 1968 (and references from pertinent articles) which explores the literature and work done concerning silicon bonding.

In 1940, Kimball (13) gave the first theoretical consideration to $(p \rightarrow d)$ π-bonding and concluded that this type of back-bonding was possible in silicon compounds due to its low-lying 3d-orbitals. Craig et al. (14) further substantiated this by saying that it was not only possible, but very likely, that dative π-bonding played a role in silicon chemistry. Although there was some evidence for back-bonding prior to this article (15-18), most of the work done on this problem has arisen since then. This paper considers the literature in four sections: silicon - oxygen bonding, silicon - nitrogen bonding, silicon - halogen bonding, and silicon - carbon bonding.

II. Silicon - Oxygen Bonding

Stone and Seyferth (19) found that trialkylsilanols form sodium salts with aqueous sodium hydroxide at 0°C and corresponding carbon compounds do not under the same conditions. They attribute this to (p→d) π-bonding between silicon and oxygen wherein a lone pair from oxygen is donated to the silicon, making the O-H bond weaker and more easily broken; however, they say that this information may also be explained by inductive effects. Silicon being more electropositive than carbon (1.9 vs. 2.6) (20), the electron flow from the +I alkyl groups is less than in the carbon analogs. Therefore, in the trialkylsilanol, the oxygen acquires more negative charge than in the trialkylcarbinol, making the silanol hydrogen more acidic and more easily removed than the carbinol hydrogen. (It was pointed out by J.R. Sowa (21) that this conclusion is probably incorrect. If oxygen acquires a stronger negative charge, electrostatic attraction between it and the hydrogen nucleus should <u>increase</u>, therefore strengthening the bond between them. Thus, the results obtained should be considered as evidence for (p→d) π-bonding or for the field effect mentioned earlier (see page 2). They did not consider this effect at all).

In a study of triphenylalcohols of Group IV B elements (C,Si,Ge, and Sn), West, Baney and Powell (22) found unusual acidity trends. On the basis of Allred and Rochow electronegativities (20), the acidity should decrease in this fashion: Ø$_3$SiOH > Ø$_3$SnOH > Ø$_3$GeOH > Ø$_3$COH. The electronegativities of the central atoms are 1.9, 1.93, 2.0 and 2.6 respectively. The actual trend is Ø$_3$SiOH > Ø$_3$GeOH > Ø$_3$COH > Ø$_3$SnOH. They conclude that, since Ø$_3$SiOH is a stronger acid and a weaker base than Ø$_3$GeOH, $(p \rightarrow d)$ π-bonding is much stronger in the silanol than in the germanol. (The trend seen is, except for the Sn compound, exactly what might be expected from inductance considerations alone, but their conclusion may be true if π-bonding exists in these compounds at all.)

Ostdick and McCusker (23) did n.m.r. studies on a series of alkylalkoxysilanes, $R_{4-n}Si(OR)_n$. Their results were:

TABLE I. - N.M.R. Chemical Shifts for Alkylalkoxysilanes

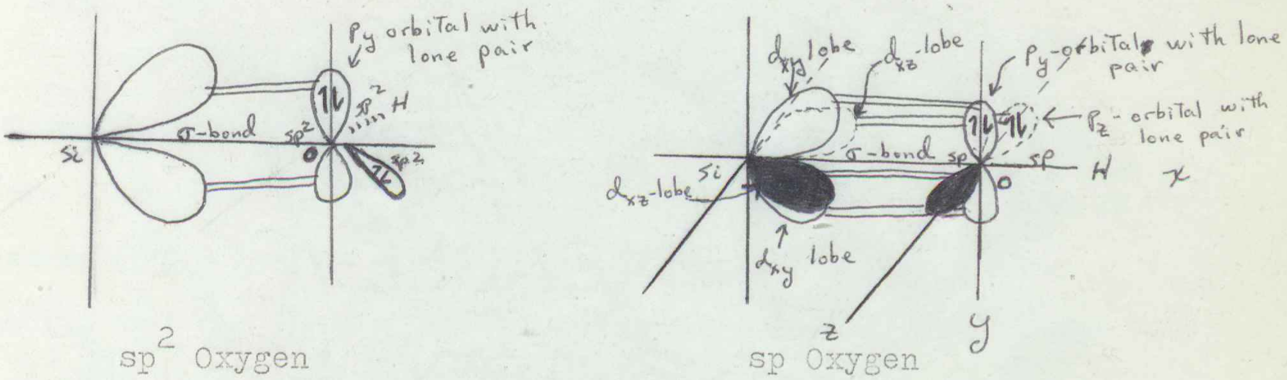
Compound	^{29}Si(ppm)^a	α-alkyl proton(ppm)
$(CH_3)_4Si$ or TMS	-21	0.000
$(CH_3)_3SiOC_2H_5$	-27	-0.055
$(CH_3)_2Si(OC_2H_5)_2$	-16	-0.025
$CH_3Si(OC_2H_5)_3$	+19	0.000

^{a}Reference is the ^{29}Si in a silicone of 100 cp viscosity

Replacing one methyl group of TMS with an ethoxide group, they found a downfield shift of the α-alkyl proton, indicating decreased electron density on silicon. Replacing a second methyl by another ethoxide resulted in an upfield shift relative to the monoalkoxylated compound. Two effects are possible: a) inductive electron withdrawal, and b) (p→d) π-bonding from O to Si. They interpreted their data in the following way: with the first replacement, inductive electron withdrawal was the predominant factor, thus decreasing the electron density on silicon; the relative upfield shift with the second replacement indicated an increase in the effect of the π-bonding. The general trends for this series was that the inductive effect per alkoxy group decreases as the number of alkoxy groups increases whereas the π-bonding per alkoxy group remains about the same or decreases only slightly as the number of alkoxy groups increases.

A detailed examination by West and Baney (24) of the infrared absorption of silanols in the hydroxyl stretching region shed some light on the problem. The acidity of silanols and carbinols as hydrogen donors in hydrogen-bond formation was measured by the shift in the O-H stretch band due to hydrogen bonding of these compounds in diethyl ether and mesitylene. The resulting trends were: <u>acidity</u> - arylsilanols > alkylsilanols > arylcarbinols > alkylcarbinols; and, <u>basicity</u> - alkylcarbinols > alkylsilanols > arylcarbinols ≈ arylsilanols. The overall effect was that silanols exhibit much greater acidity but not substantially less basicity than carbinols, as might have been expected. They propose that these results can be explained by assuming a π-bond between <u>one</u> electron pair of the oxygen and the empty d-orbitals of silicon. Although there are two lone pairs on oxygen, they discount the possibility of an sp-hybridized oxygen with a double (p→d)

π-overlap with two empty silicon d-orbitals (eg., d_{xy} and d_{xz}), since, in hydrogen-bond formation, π-electrons are much less basic than unshared pairs (one of which is in the sp^2 oxygen case) and therefore the basicity should be markedly decreased. Diagrams for the two hybridization cases are below:



sp^2 Oxygen

sp Oxygen

Figure 4

There were similar studies conducted by Allred, Rochow and Stone (25). They studied trimethylsilanol and trimethylcarbinol. On the basis of electronegativity, the hydroxyl proton in the silanol should be relatively more shielded from the silicon atom by the oxygen electron density than the corresponding proton in the carbinol. If the electron density on oxygen is decreased by dative π-bonding or by the field effect, the results will be opposite from the results anticipated by electronegativity considerations. The results were that the silanol proton is <u>less</u> shielded than the carbinol proton. Therefore, they accepted the fact of $(p \rightarrow d)$ π-bonding assuming that effects due to molecular association are similar or negligible in both compounds.

Cruickshank (6) did a detailed study on XO_4^{n-} tetrahedral ions where X = P,S,Si,Cl. He showed here that the Si

$d_{x^2-y^2}$ orbital overlaps with the oxygen combination $\frac{1}{2}(p_1+p_2+p_3+p_4)$ and also the d_{z^2} overlaps with $\frac{1}{2}(p_1'+p_2'+p_3'+p_4')$. He also investigated other Si-O bond-containing ions and, because of their short bond length and increased bond orders, concluded that ($p \rightarrow d$) π-bonding was a contributor to the stabilities of these ions.

One other spectral datum was attributed to dative π-bonding by Schmidbaur and Schmidt (26). They found that there were small low-field shifts of the proton resonances in hexamethyldisiloxane against TMS and concluded that back-bonding was the reason for this. However, Ebsworth and Frankiss (27) have found this "anomaly" (and others to be mentioned later) to be present in carbon analogs and have therefore rejected these data as conclusive proof of ($p \rightarrow d$) π-bonding.

III. Silicon - Nitrogen Bonding

Silicon-nitrogen bond-containing compounds have been shown to generally be weaker bases than corresponding C-N compounds. On the basis of electronegativity, the opposite might be expected. Silicon is less electronegative than carbon and therefore the electrons in the Si-N bond lie closer to the nitrogen atom than in the C-N bond. Thus, the nitrogen lone pair is more available for bonding and should show enhanced basicity relative to C-N compounds. The field effect would provide the same sort of redistribution of the electron density of the nitrogen atom. If ($p \rightarrow d$) π-bonding exists, the lone pair, tied up in the silicon d-orbital, is not as readily available for donation and these compounds should then be weaker Lewis bases. This is the case.(19,28,29) The existence of dative π-bonding has been invoked by some chemists to explain this observation. Here again there is controversy.

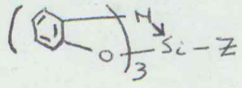
Aylett and Peterson (28) prepared the series $H_{4-n}Si[N(CH_3)_2]_n$ from n=1 to n=4. They studied the addition of these compounds to Lewis acids. There was no addition. They expected the addition of $Si[N(CH_3)_2]_4$ to BH_3 to form the adduct $Si[N(CH_3)_2]_4 \cdot 2BH_3$ on two grounds: a) ~~from~~ from electronegativity considerations, Si-N compounds should be more basic than C-N compounds; and, b) silicon is a larger atom than carbon; therefore adducts of substituted silanes should be, in general, less crowded than similar adducts of substituted methanes. Since they did not form this adduct, the authors concluded that Si-N dative π-bonding is sufficiently strong in these compounds to overcome both of these factors. Once assuming the existence of this bonding, they went on to say: "It seems likely that the lone-pair electrons of all the nitrogen atoms will combine with one silicon 3d-orbital, so that delocalization is as extensive as possible. In that case, the π-bond order in these compounds [$SiH_2(NMe_2)_2$ and $SiH(NMe_2)_3$] will be 1/2 and 1/3, respectively." These expected π-bond orders were later observed.

Randall, Ellner and Zuckerman (30), performing n.m.r. studies, disagree with the above contentions. They studied coupling constants for various ^{15}N systems and found that J (^{15}N-H) in Ø -^{15}NH-$SiMe_3$ is 73.7 cps and, for sp^3-hybrid ^{15}N-ammonium chloride, J (^{15}N-H) is 73.2 cps (31). It has been contended that the amount of s character in the nitrogen hybrid should increase with $(p \rightarrow d)$ π-bonding between N and Si, since this interaction requires the use of a N orbital with large, perhaps pure, p character. The negligible difference in coupling constants shows that the silicon-bound nitrogen does not take on appreciably more s character. Therefore, they claim that $(p \rightarrow d)$ π-bonding is not appreciable in this compound. An interesting sidelight here is that Ebsworth (32), who has been an agnostic at times concerning $(p \rightarrow d)$ π-bonding, argued that the above studies are not necessarily an indication of the lack of dative π-bonding. He demonstrated the possibility of a $(sp^3 \rightarrow d)$ π-bond from nitrogen to silicon, thus accounting for the chemical reactivity and the planarity of such compounds as trisilylamine. It has also been suggested that the lone pair is donated to a 4s orbital.

Ebsworth and Emeléus (29) studied methylated silylamines and silylated silylamines and found them to be very weak bases. They found that N,N-dimethylsilylamine forms an adduct with trimethylboron, but no acceptor differentiated between N-methyldisilylamine and trisilylamine, both of which form only unstable adducts. All of these facts agree with the theory of back-bonding between silicon and nitrogen - or with the field effect theory.

Schmidbaur and Schmidt (33) found small low-field shifts in the proton resonances in tris(trimethylsilyl)-amine relative to TMS and attributed these to $(p \rightarrow d)$ π-bonding between the nitrogen and silicon atoms. Once again, Ebsworth and Frankiss (27) found similar results in corresponding carbon compounds and rejected this evidence as conclusive proof of back-bonding.

Randall and Zuckerman (34) were led to take an agnostic view of supposed large (p→d) π-contributions to the Si-, Ge- and Sn-N bonds on the basis of n.m.r. experiments on the M-N-H skeleton. An increased J (^{15}N-H) from ^{15}N-aniline to trimethylsilyl-^{15}N-aniline is expected, because of the (p→d) π-bond formation. However, they found no such increase. Also, Si-N bonds have been shown to exhibit single bond character, via infrared and Raman spectra of gaseous, liquid and solid $N(SiH_3)_3$, $N(SiD_3)_3$, $P(SiH_3)_3$ and $P(SiD_3)_3$. (35,36) Because of this fact and their own experimental results, Randall and Zuckerman rejected dative π-bonding as a possibility.

Friedman (37), in reviewing pentaco-ordinate or pentacovalent silicon, discusses the properties of $CHF_2CF_2SiH_3N(CH_3)_3$. This is the first complex of silicon to have no oxygen or halogen directly bonded to the silicon atom. Studying the IR spectrum, the band at 2780 cm^{-1} is absent. This band would show C-H stretching in the amine. Thus, the extra pair of electrons on the nitrogen atom are shown to be dative-π bonded to the silicon. He also shows that (p→d) π-bonding exists in trisilylamine and 

, where Z = Cl, CH_3, OCH_3, Ø, or CH_3-CO_2.

IV. Silicon - Halogen Bonding

The earliest evidence of some sort of back-bonding in silicon compounds was found by Brockway and Coop (15). They investigated bond lengths and bond angles in chlorosilanes and chloromethanes. Their results are tabulated below:

TABLE II

Compound	Si-Cl Bond Length	Cl-Cl Interatomic Dist.	Cl-Si-Cl Angle
SiH_3Cl	2.06±0.05 Å	———	———
SiH_2Cl_2	2.02±0.03 "	3.31±0.04 Å	110±1°
$SiHCl_3$	2.01±0.03 "	3.29±0.03 "	110±1°
$SiCl_4$	2.00±0.02 "	3.27±0.03 "	109° 28′

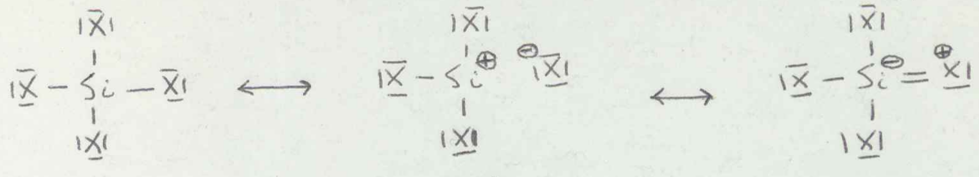
Covalent Radius Sum = 2.16 Å

Compound	C-Cl Bond Length	Cl-Cl Interatomic Dist.	Cl-C-Cl Angle
CH_3Cl	1.77±0.02 Å	———	———
CH_2Cl_2	1.77±0.02 "	2.93±0.02 Å	112±2°
$CHCl_3$	1.77±0.02 "	2.93±0.02 "	112±2°
CCl_4	1.755±0.005"	2.87±0.01 "	109° 28′

Covalent Radius Sum = 1.76 Å

These data show that the Si-Cl bond length is substantially (2.3 to 8.3%) less than the covalent radius sum of 2.16 Å. This demonstrated partial double bond character with resulting bond shortening. They interpreted these data to mean some sort of back-bonding in the chlorosilanes. It should be noted, however, that an increase in the π-bonding would also increase the Cl-M-Cl bond angle toward 120°. As shown in Table II, the methanes have greater bond angles than the silanes. The situation offers no clear conclusions.

Pauling (16) attributed these unusually short bonds, and similarly short silicon-halogen bonds in general, to resonance. He gave the following structures for SiX_4:



(I) (II) (III)

In structure III, the halogen donates a pair of π-electrons to one of silicon's empty d-orbitals.

Pitzer (17) took exception to Pauling's reasoning about the short bond lengths. He stated that the two atoms can approach each other closer than the covalent radius sum before the repulsions between the completed inner shells become large enough to establish the desired bond distance.

The most significant exception to Pauling's formulations came from Schomaker and Stevenson (18). They formulated an equation by which interatomic bond lengths may be calculated:

$$r_{AB} = r_A + r_B - \beta \left| x_A - x_B \right| \qquad \text{(Eq. 1)}$$

where $r_{AB} \equiv$ interatomic bond length

$r_i \equiv$ covalent radius of atom i

$x_i \equiv$ electronegativity of atom i

$\beta \equiv 0.09$

The term to be subtracted out takes into consideration the fact that the two atoms are of different electronegativities and that therefore the bond is slightly ionic in character. Tables III and IV contain data which show how well this equation agrees with experimental data (see page 16).

TABLE III

Element	Covalent Radius	Element	Covalent Radius
S	1.04 Å	P	1.10 Å
C	0.77 "	Br	1.14 "
O	0.66 "	Cl	0.99 "
N	0.70 "	F	0.64 "
Si	1.17 "	H	0.37 "

TABLE IV

Compound	Bond	$r_{obs.}$ (Å)	$r_A + r_B$ (Å)	$r_{calc.}$ (Å)
SiH_4	Si-H	1.42	1.54	1.51
SiC	Si-C	1.89	1.94	1.88
$Si(CH_3)_4$	Si-C	1.93	—	1.94
SiF_4	Si-F	1.54	1.89	1.69
$SiCl_4$	Si-Cl	2.02	2.16	2.05
$SiBr_4$	Si-Br	2.14	2.31	2.22

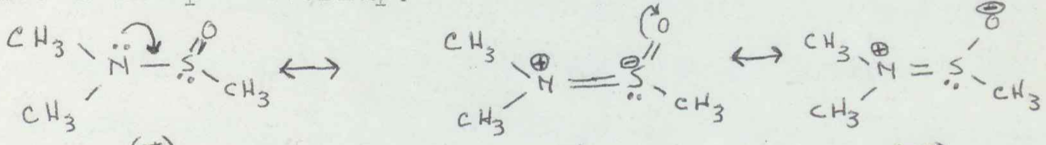
It can be seen that the Schomaker-Stevenson equation affords more consistent results in all cases cited in Table IV. This was their basis for disagreeing with Pauling and Brockway and Coop, there being no need to invoke partial double bonding to explain shorter bonds. The value of β has been improved on recently (38), giving better correlation between theory and experiment.

Ebsworth and Turner (39) measured the coupling constants of H-H, H-Si, H-F, and Si-F in halosubstituted monosilanes, disiloxane, disilylsulfide and trisilylamine. They found that simple valence bond calculations failed to interpret the

J(H-H) as a function of the H-Si-H bond angle. They interpreted this failure to the use of the silicon's d-orbitals.

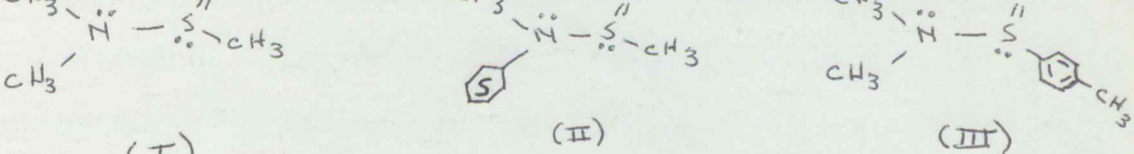
More recently, Wilson (40) studied internal rotation in compounds containing an Si-F bond . If ($p \rightarrow d$) π-bonding existed in these compounds, the double bond should inhibit free rotation about the Si-F bond. Taking non-bonded interactions into account, Wilson found no additional barrier to rotation about the Si-F bond. From these results, he concluded that $d\pi$-$p\pi$ bonding does not exist in these compounds.

Moriarty (41) found that, in -$\ddot{\text{N}}$-CO compounds, there is a barrier to internal rotation because of $p\pi$-$p\pi$ delocalization resulting in interconverting, planar rotamers. Applied to -$\ddot{\text{N}}$-SO systems, analogous delocalization would involve a $d\pi$-$p\pi$ overlap:



(I) (II) (III)

He also states that the electron accepting ability of the diffused 3d-orbitals of sulfur in -$\ddot{\text{N}}$-SO compounds would be enhanced relative to -$\ddot{\text{N}}$-S- due to the electronegative oxygen on the sulfur atom. He studied, by n.m.r., these three compounds:



(I) (II) (III)

Figure 5

The results are tabulated in Table V on p. 18:

TABLE V - Temperature Range: -60°C to +25°C

Compound	Solvent	S-CH_3 (δ)	$N(CH_3)_2$ (δ)
I	neat	2.50	2.68
	$CDCl_3$	2.50	2.68
	pyridine	2.08	2.28
	benzene	1.75	2.02
II	$CDCl_3$	2.59	2.70
III	CCl_4		2.60
	$CDCl_3$		2.69

It is contended that, due to the multiple degeneracy of sulfur's 3d-orbitals, a $(p\rightarrow d)$ π-overlap does not have any strict conformational requirements. The fact that $N(CH_3)_2$ groups are equivalent at 25° and -60° is in agreement with this contention. Moriarty argues that one orientation for N-S $d\pi$-$p\pi$ overlap may be converted to a second by the rotation the nitrogen p-orbital through 90° with respect to the XZ-plane of the sulfur d-orbitals. But in contrast to the planar structure required for $2p\pi$-$2p\pi$ or $2p\pi$-$3p\pi$ overlap, only little overlap is lost by rotation about the N-S bond. With appropriate p-d hybridization of the sulfur orbitals, positions of maximum overlap are separated by only small angular increments with considerable overlap at all intermediary conformations. He states: " An apparently significant conclusion which may be drawn is that essentially free rotation may exist in this system with continuous and effective overlap." If this system is applicable to silicon compounds, as Sowa (21) suggests, Wilson's results are inconclusive.

V. Silicon - Carbon Bonding

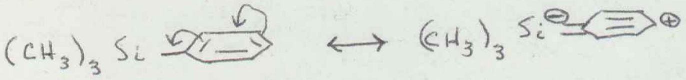
Considerable attention has been paid to the bonding of silicon to adjacent aromatic rings. This is the area in which most of the research has been done and also in which there is the most controversy.

Bedford, Bolton, Carrington and Prince (42) studied the electron spin resonance of anions of phenyltrimethylsilane and -germane and found that, relative to $-CH_3$, both $-SiMe_3$ and $-GeMe_3$ are electron attracting. Considering electronegativity, these groups should be electron releasing relative to $-CMe_3$. The effect of electronegativity is found in the dissociation constants of anilines, dimethylanilines, phenols and benzoic acids with trimethylsilyl groups in the meta position and also in the para position in the benzoic acids. In general, the trimethylsilyl group can be either an electron pair donor or acceptor, depending on the para substituent. In their studies of $p\text{-}R_3M\text{-}C_6H_4COOH$ (where M = Si, Ge or Sn and R is methyl or ethyl), they found that the dissociation constants are greater than expected relative to the unsubstituted benzoic acid. These are the effects to be expected if $(p \rightarrow d)$ π-bonding between the d-orbitals of Si, Ge and Sn and the ring's π-cloud electrons exists.

They also studied the series, $p\text{-}Me_3M\text{-}CH_2\text{-}C_6H_4COOH$, where M = C, Si, Ge and found that germanium is more electron attracting than silicon. Here there is no possible dative π-bonding to the ring by M. However, in the previous series, silicon was more electron attracting than germanium. They concluded that: a) $(p \rightarrow d)$ π-bonding does exist in the Si and Ge compounds; and b) it is a much greater factor in silicon bonding than in germanium bonding. This second conclusion is rationalized by the knowledge that the σ-bond distance in the Ge compounds is enough larger than in the Si compounds to more than balance off the greater size (availability for bonding) of the germanium d-orbitals.

Studies on this same series, $R_3M-C_6H_4COOH$, were done by Chatt and Williams (43). If (p→d) π-bonding were to exist, the electron withdrawal from the ring's π-cloud (a negative mesomeric effect) would enhance the strengths of the acids. The acids were found to have increased strength. Relating the amount of increased strength to the amount of (p→d) π-bonding, they found that the amount of bonding was roughly independent of the principal quantum number or the size of the atom M. This information related well to Craig's (14) statement in his theoretical consideration of this type of bonding that (p→d) π-bonding should be more or less independent of the relative sizes of the bonded orbitals. However, Craig also stated that the amount of this bonding was dependent on the electron attracting or releasing effects of substituents attached to the benzene ring or to the atom in question (Si, Ge or Sn).

Preliminary results by Zuckerman and Fenton (44) showed that silicon substituents on benzoic acids behave as if they possess a negative Hammett σ-constant (+I), exactly as would be expected from electronegativity considerations alone. MacDiarmid and Rabel (45) did computer analyses of the n.m.r. spectrum of the phenyl group in trimethylsilyl-benzene. The spectra showed that the resonance of the para proton had no downfield shifts, as might be expected (if (p→d) π-bonding between silicon and the ring were present) by virtue of the following resonance:

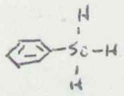


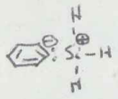
Hetflejs, Mares and Chvalovsky (**46**) studied quantitatively the alkali-catalyzed hydrolysis of silanes carrying substituents which may form (p→d) π-bonds. In the phenylsilanes of the type R-C_6H_4Si Me_2H, where R = m-CF_3, p-Cl, p-CH_3, H, p-CH_3O and p-$N(CH_3)_2$, the rate of hydrolysis appeared to be directly correlated to the σ° constants of the phenyl substituents, while the dπ -pπ changes appeared to be insignificant. In the hydrolyses of vinylsilanes, $(CH_2{=}CH)_nEt_{3-n}SiH$, the rate increases from n=0 to n-3, also showing that dπ-pπ conjugation is negligible.

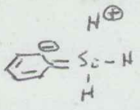
Other work by Chvalovsky (**47**) considered silicon hydrides with Ø, Cl, and $OSi(CH_3)_3$ substituents. Here he found that the sigma constants were more negative than expected from the Taft polar substituent constants: for Ø, 0.0 obs. vs. +0.6 Taft; for Cl, -0.24 obs. vs. +2.9 Taft; and for $OSiMe_3$, -0.14 obs. vs. expected + Taft value. These data seem to establish a case in favor of dative π-bonding.

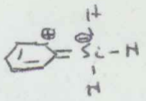
Perhaps the most significant work was done by Goodman, Konstam and Sommer (**48**). They performed a substituent interference experiment on the intensity of ^1L_b bands in phenylsilanes and demonstrated that the SiH_3 actually does withdraw electrons from the benzene ring into the silicon 3d-orbitals.

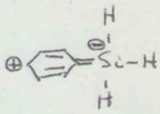
There are two effects apparent when the silicon atom is bonded to a benzene ring: a) Si acts as a +I group and releases electrons into the ring ; and, b) resonance interaction can either release or withdraw π-electrons. There are five possible resonance structures for phenylsilane:


(I)


(II)


(III)


(IV)


(V)

Structure II shows the (+I) electron releasing effect and is reinforced by the hyperconjugation of III. Structures IV and V oppose the inductive effects by d-orbital electron withdrawal from the ring. For substituted benzenes of C_{2v} or higher symmetry, the probability of the 2600 Å transition ($^1A \rightarrow {}^1L_b$) depends on the electronic distributions of the ring alone. This transition is forbidden for benzene itself, but is formally allowed for mono- or paradisubstituted benzenes, with the transition moment, M_{Lb}, perpendicularly polarized to the symmetry axis:

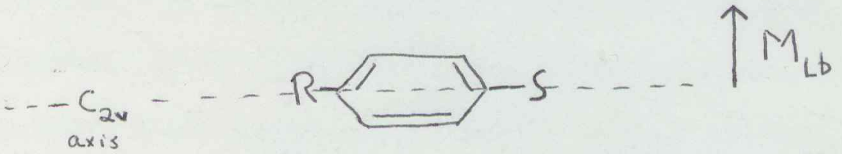
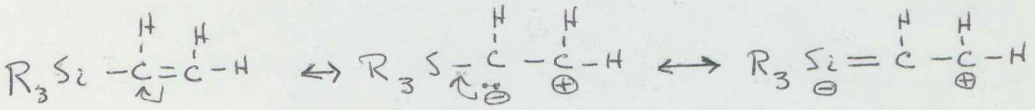


Figure 6

Because of this, the only effects observed are by those structures which are not symmetric along the C_{2v} axis. Thus- II and V are discounted, and only the effects from structures III and IV will be observed. The intensity of the band should decrease from anisole to p-methoxyphenylsilane if d-orbital resonance is important. The hyperconjugation effect of structure III should lead to an increase in band intensity from anisole to p-methoxyphenylsilane. They found that the intensity of the 2600 Å band decreased quite markedly. This marks the first reasonably clear-cut evidence in favor of $(p\rightarrow d)$ π-bonding between the ring and silicon.

Work has been done concerning $(p\rightarrow d)$ π-bonding between silicon and a non-aromatic carbon. Brown and Webster (49,50) found that, in the series $(CH_3)_{4-n}MCl_n$ and $(CH_3)_{3-n}MHCl_n$, as n increases, there are smaller low-field n.m.r. shifts when M is silicon than when M is carbon. Schmidbaur (51) found a decrease in shielding along the series $(CH_3)_3SiX$ from X = F,Cl,Br,I, an increase in $J(^{13}C\text{-}H)$ in $(^{13}CH_3)SiX(^{12}CH_3)_2$ and an increase in $J(^{29}Si\text{-}H)$ in $(CH_3)_3{}^{29}SiX$ from X = CH_3,F, Cl,Br,I. They interpreted these effects to be due to backbonding between silicon and either carbon or X. Ebsworth and Frankiss (27) found similar trends in corresponding carbon compounds and rejected these as evidence for $(p\rightarrow d)$ π-bonding. Their own work showed a decrease in shielding of the β-proton in the series CH_3SiH_2X from X = H,N,O,F. This trend is consistent with increasing inductive deshielding in the series. They also found an increase from I,Br,Cl,F and similar effects in dimethylsilyl and trimethylsilyl halides. This trend has been explained by assuming dative π-bonding in the order $I < Br < Cl < F$. However, they observed the same effects in ethyl, isopropyl, t-butyl and cyclohexyl halides. They offered no explanation but also saw no good reason to invoke $(p\rightarrow d)$ π-bonding in an α-silicon since these same trends occur when there is an α-carbon.

Eisch and Beuhler (52) investigated vinylsilanes to see if they would form alkali metal adducts as arylethylenes do. They found facile reductive coupling of the vinylsilanes by Li metal and gave this as strong chemical evidence in favor of the capacity of vinyl groups adjacent to silicon to yield reactive metal adducts due to (p→d) π-bonding. Possible resonance structures are:



$$R_3Si-\overset{H}{C}=\overset{H}{C}-H \leftrightarrow R_3Si-\underset{\ominus}{\overset{H}{C}}-\underset{\oplus}{\overset{H}{C}}-H \longleftrightarrow R_3\underset{\ominus}{Si}=\overset{H}{C}-\underset{\oplus}{\overset{H}{C}}-H$$

(I) (II) (III)

where structure III represents the (p→d) π-bond.

Based on Doering and Hoffman's work (see pp.3,4), Price and Sowa (8,53) first studied deuterium exchange of $(CH_3)_4Si$, $(CH_3)_2S$, $(C_2H_5)_2S$, $(C_2H_5)_3N$ and $C_6H_5CH_2Si(CH_3)_3$. The best correlation would have been to study exchange of the pentamethylsiliconium ion, but, since this has not been prepared, neutral compounds were used. The reaction of the silane can be pictured as follows:

$$\begin{array}{ccc} (CH_3)_4Si + B^{\ominus} & \rightleftharpoons & {}^{\ominus}CH_2Si(CH_3)_3 + HB \\ & & \updownarrow \\ & & CH_2=\overset{\ominus}{Si}(CH_3)_3 \end{array}$$

$${}^{\ominus}CH_2Si(CH)_3 \overset{BD}{\rightleftharpoons} DCH_2Si(CH)_3 + B^{\ominus}$$

These compounds were reacted with sodium dimsyl(${}^{\ominus}D_2C-\overset{O}{\overset{\uparrow}{S}}-CD_3$) in DMSO-$d_6$, pK_a of approximately 40. The reaction mixtures contained 15% dimsyl ion and 10% reactant in DMSO-d_6. They obtained the following results:

1 - $(CH_3)_2S$ - 29% and 66% exchange at 15 and 60 min. of heating at 95°C

2 - $(C_2H_5)_2S$ - 14, 21 and 30% exchange of α-hydrogens at 15, 45 and 105 min. of heating at 95°C

3 - $(C_2H_5)_3N$ - no exchange after three hours at 95°C

4 - $(CH_3)_4Si$ - immiscible in the reaction medium; no exchange after three hours at 95°C

Sowa, Young, Roosevelt and Scheib (21) continued the project. They prepared $\text{Ø-S-CH}_2\text{-Si(CH}_3)_3$ and $\text{Ø}_2\text{P-CH}_2\text{-Si(CH}_3)_3$. Since S and P are known to use their d-orbitals, the ØS- and Ø_2P- should stabilize the carbanion formed in the exchange. The series of compounds, $\text{Ø-S-CH}_2\text{-M(CH}_3)_n$, where M = Si, C, O, N, P, S and n = the number of methyl groups necessary to fulfill the normal valence shell of M, was prepared. It was hoped that these would provide conclusive evidence (p→d) π-bonding because: a) steric factors should be unimportant; and, b) the sulfur, as mentioned above, should assure formation of the carbanion, and therefore assure the H-D exchange. The exchange reaction is related to the stability of the anion.(In studies independent of this project, Yukuta (54) has shown that the stability trend in general is $S > P > Si$.) With steric factors insignificant, the two effects which should govern the anion stability are inductance and resonance. If silicon uses its d orbitals in π-bonding, the silane should react faster than expected from inductance and field effects alone. A plot of electronegativity vs. rate of exchange should factor out the elecrtonegativity or inductive effects. Any points above the linear portion should indicate some sort of extra stabilization, which could be either resonance from dative π -bonding or stabilization from the field effect mentioned earlier(p. 2). Figure 7 qualitatively indicates what might be expected:

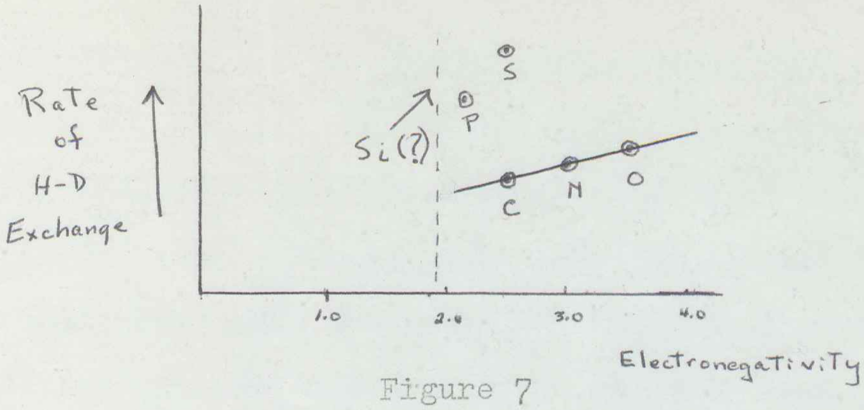


Figure 7

Their results thus far are incomplete: the $\emptyset SCH_2SiMe_3$ showed exchange in a reaction mixture of 0.5 % dimsyl ion and 14.5 % reactant in DMSO-d_6; the $\emptyset_2PCH_2SiMe_3$ reacted immediately under these same conditions, giving either exchange or a new compound. The other compounds have not been studied as yet.

VI. Conclusions

In spite of all the work done since Brockway and Coop's articles appeared in 1938 (15), the problem of the use of silicon's 3d-orbitals in bonding still remains inconclusive. Most considerations have been in the four areas discussed. West (55) discussed the bonding of silicon in polysilanes and the possibility of $d\pi$-$p\pi$ or even $d\pi$-$d\pi$ overlap. Silicon, it is sure, exhibits quite different chemistry than its first short row counterpart, carbon. Stone and Seyferth (19) comment on this: " It is interesting that in silicon chemistry the familiar double and triple bonding of carbon compounds is replaced by polymerization as in $(SiH_2)_n$, $(SiCl_2)_n$, $(R_2SiO)_n$, $(SiO_2)_n$ and $(SiS_2)_n$. These effects may also relate to the possible use of 3d-orbitals of silicon. "

Expect for perhaps the work of Goodman, Konstam and Sommer (pp.21-3), there have been no <u>conclusive</u> chemical evidences concerning silicon ($p \rightarrow d$) π-bonding.

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