

CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT,
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Studies on Diamagnetic Susceptibility of Silicon Compounds Containing Sulfur-Silicon and Sulfur-Silicon-Nitrogen Bonds

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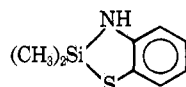
Received December 20, 1971

Diamagnetic susceptibilities of four 5-substituted 2-aminobenzenethiols, five alkylthiotrimethylsilanes, and five heterocyclic derivatives containing S-Si-N linkages are reported. χ_{Si} in alkylthiotrimethylsilanes has been obtained graphically and this value of χ_{Si} agrees with that reported for silicon compounds containing all the four Si-C bonds. χ_{Si} in compounds containing one S-Si-N linkage is almost the same as that of silicon compounds containing one Si-N bond. χ_{Si} in compounds containing two -S-Si-N- bonds agrees with the value of χ_{Si} for compounds containing two Si-N bonds and differs from the χ_{Si} value for compounds containing one -S-Si-N- bond. It is reported that the replacement of a C-Si bond by a S-Si bond does not have any effect on χ_S .

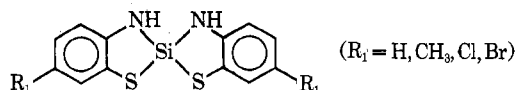
In recent years diamagnetic studies have been proven to be useful in the interpretation of structural silicon chemistry.¹⁻⁵ No studies appear to have been made on silicon compounds containing Si-S bonds and, therefore, it was considered worthwhile to investigate the diamagnetic properties of a number of thiosilane compounds.

Experimental Section

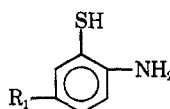
Five alkylthiotrimethylsilane compounds, $(CH_3)_3SiSR$ ($R = CH_3, n-C_2H_7, i-C_3H_7, n-C_4H_9, tert-C_4H_9$), were prepared by the method given by Abel.⁶ The complex



was prepared by the method given by Wieber.^{7,8} Four compounds



were prepared by Goyal.⁵ Diamagnetic susceptibilities of four 5-substituted *o*-aminobenzenethiols



and ten silicon compounds containing Si-S bonds have been measured with a sensitive Gouy balance.⁴ The order of the Gouy force is ± 0.05 mg. Measured χ_M values are summarized in the Table I.

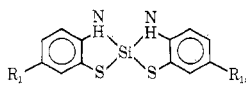
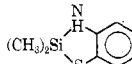
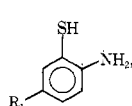
Discussion

A plot of χ_M against n for the series $(CH_3)_3SiS-[(CH_2)_nH]$ has been made. The plot is linear with an ordinate intercept of 80.0 which shows that $\chi_{(CH_3)_3SiS[(CH_2)_nH]} = 3\chi_{CH_3} + \chi_{Si} + \chi_S + \chi_H = 80.0$. Using $\chi_H = 2.0$,⁵ $\chi_{CH_3} = 13.45$,⁵ and $\chi_S = 16.90$,⁵ χ_{Si} has been calculated to be 20.75. This value of χ_{Si} is comparable that reported ($\chi_{Si} = 20.6-21.0$)⁶ for silicon compounds in which the silicon atom is coordinated to four carbon atoms.

- (1) R. L. Mital and R. R. Gupta, *J. Amer. Chem. Soc.*, **91**, 4664 (1969).
- (2) R. D. Goyal, R. R. Gupta, and R. L. Mital, *J. Phys. Chem.*, in press.
- (3) E. W. Abel, R. P. Bush, C. R. Jenkins, and T. Zobel, *Trans. Faraday Soc.*, **60**, 1214 (1964).
- (4) R. R. Gupta, Ph.D. Thesis, Rajasthan University, Jaipur, 1968.
- (5) R. D. Goyal, Ph.D. Thesis, Rajasthan University, Jaipur, 1972.
- (6) E. W. Abel, *J. Chem. Soc.*, 4406 (1960).
- (7) W. Wieber and M. Schmidt, *Z. Naturforsch. B*, **18**, 849 (1963).
- (8) W. Wieber and M. Schmidt, *Angew. Chem., Int. Ed. Engl.*, **3**, 657 (1964).

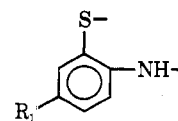
TABLE I

DIAMAGNETIC SUSCEPTIBILITY DATA

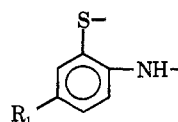
Compd	χ_M^a	χ_{Si}
$(CH_3)_3SiR$, $R = C_2H_5$	102.61	20.75 ^b
$n-C_2H_7$	114.09	20.75 ^b
$i-C_3H_7$	115.11	
$n-C_4H_9$	125.73	20.75 ^b
$tert-C_4H_9$	126.65	
	$R_1 = H$ 153.71 CH_3 170.26 Cl 183.29 Br 199.37	17.39 17.52 17.47 17.45
	114.44	19.38
	$R_1 = H$ 75.94 CH_3 85.15 Cl 91.69 Br 99.74	68.16 76.37 82.91 90.96

^a All the χ_M values are $\times 10^{-6}$ cgsu throughout the paper.
^b Determined from the plot of χ_M against n in the series $(CH_3)_3SiS-[(CH_2)_nH]$.

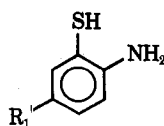
χ_{Si} in heterocyclic compounds of silicon has been calculated by subtracting the diamagnetic contributions of the CH_3 group and of



from χ_M of the corresponding compounds. The diamagnetic contribution of

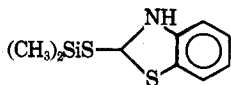


has been calculated by subtracting χ_H for an N-H bond and for an S-H bond from χ_M of



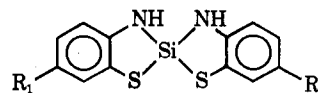
as suggested by Haberditzl.⁹

χ_{Si} in



(9) W. Haberditzl, *Sitzungsber. Deut. Akad. Wiss. Berlin, Kl. Chem., Geol. Biol.*, No. 2 (1964).

is 19.38 and in



is 17.39–17.52. $\chi_{Si} = 19.38$ is comparable with $\chi_{Si} = 19.40$ for the series $R_3-Si-N-$ and $\chi_{Si} = 17.39-17.52$ is comparable with $\chi_{Si} = 17.40$ for the compounds containing the linkage $R_2-Si \leftarrow N$. These studies show that the replacement of a C-Si bond by a S-Si bond does not have any effect on χ_{Si} .

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Synthesis and Chemistry of μ -Silyl and μ -Germlyl Carboranes^{1a}

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Received December 1, 1971

The bridged carborane derivatives $\mu-MR_3C_2B_4H_7$ ($M = Si, Ge$; $R = H, CH_3$) have been prepared in high yield (except for the germlyl compound) from reactions of the 2,3- $C_2B_4H_7^-$ ion with silyl or germlyl halides and structurally characterized from their ¹¹B and ¹H nmr, infrared, and mass spectra. In each compound the MR_3 bridging group replaces one of the bridge protons in 2,3-dicarba-*nido*-hexaborane(8), $C_2B_4H_8$, and is presumably bound to the adjacent boron atoms by a two-electron, three-center bond. The silyl, trimethylsilyl, and trimethylgermyl species are stable at 25° but at higher temperatures isomerize quantitatively and irreversibly to the respective 4-substituted species; the μ -germyl compound probably undergoes a similar rearrangement. Pyrolysis of μ - or 4- $(CH_3)_3SiC_2B_4H_7$ at 220–230° for 1 hr yields the 1- and 2-substituted isomers, but prolonged heating produces *closo*-carborane derivatives. Pyrolysis of μ - or 4- $SiH_3C_2B_4H_7$ at 230° yields 1- and 2- $SiH_3C_2B_4H_7$, 2,3- $C_2B_4H_8$, silyl *closo*-carboranes, and *closo*- $C_2B_5H_7$. Reaction of 2- $(CH_3)_3SiC_2B_4H_7$ with NaH in THF followed by addition of trimethylsilyl chloride yields $\mu,2-[(CH_3)_3Si]_2-2,3-C_2B_4H_6$.

Although the family of known heterocarborane cage systems is steadily growing and now includes species containing heteroatoms of groups II, III, IV, and V, and a number of transition metals,² a rather conspicuous exception occurs in the case of silicon. Efforts to extend the known icosahedral $MC_2B_9H_{11}$ series³ ($M = Ge, Sn, or Pb$) to silicon have been unsuccessful, at least at this writing, and extensive studies⁴ of gas-phase silane-borane and silane-carborane reactions have not produced identifiable silacarboranes (terminally substituted silyl carborane derivatives were obtained instead). These results are contrasted with the interesting fact that every element surrounding silicon in the periodic table has been incorporated into characterizable borane or carborane cage species.

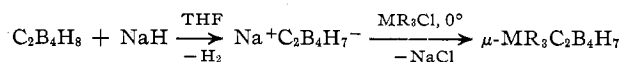
A potential route to silacarboranes and germacarboranes which appeared worthy of exploration is the insertion of silyl or germlyl groups into bridging positions in the 2,3- $C_2B_4H_8$ (dicarba-*nido*-hexaborane) cage, utilizing reactions of the corresponding $C_2B_4H_7^-$

ion.⁵ This approach represents an extension to the carborane field of earlier work by Gaines and Iorns,⁶ who prepared pentaborane(9) derivatives containing silicon or heavier group IV bridging atoms.

Results and Discussion

Synthesis and Structures of Bridged Carboranes.—

The general preparative scheme utilizes the reaction of silyl chloride, trimethylsilyl chloride, or their germanium analogs with the sodium salt⁷ of $C_2B_4H_7^-$, which in turn is prepared from 2,3- $C_2B_4H_8$ and sodium hydride. The pure trimethylsilyl and trimethyl-



$M = Si, Ge$; $R = H, CH_3$

germyl compounds are obtained in yields of >60%, but substantially less of the silyl and germlyl derivatives have been isolated by this method. However, an alternative route which utilizes the lithium salt has given

(1) (a) Presented in part at the 162nd National Meeting of the American Chemical Society, Washington, D. C., Sept 1971; Abstract INOR-6. Portions of the work were also presented at the International Meeting on Boron Compounds, Prague, Czechoslovakia, June 1971; Abstract No. 19. (b) On sabbatical leave from the Department of Chemistry, Lake Forest College, Lake Forest, Ill., 1970–1971 academic year.

(2) For recent reviews see R. N. Grimes, "Carboranes," Academic Press, New York, N. Y., 1970, Chapter 9; L. J. Todd, *Advan. Organometal. Chem.*, **8**, 87 (1970); and M. F. Hawthorne, *Accounts Chem. Res.*, **1**, 281 (1968).

(3) R. W. Rudolph, R. L. Voorhees, and R. E. Cochoy, *J. Amer. Chem. Soc.*, **92**, 3351 (1970).

(4) W. A. Ledoux and R. N. Grimes, *J. Organometal. Chem.*, **28**, 37 (1971).

(5) Related studies involving the $C,C'-(CH_3)_2C_2B_4H_5^-$ ion have been recently reported by C. G. Savory and M. G. H. Wallbridge, International Meeting on Boron Compounds, Prague, Czechoslovakia, June 1971, Abstract No. 17; see also C. G. Savory and M. G. H. Wallbridge, *J. Chem. Soc. A*, 622 (1971). The bridged trimethylsilyl and trimethylgermyl $\mu-(CH_3)_3M-C,C'-(CH_3)_2C_2B_4H_5$ species reported by these workers were not observed to isomerize at 25°; behavior at higher temperatures was evidently not studied.

(6) (a) D. F. Gaines and T. V. Iorns, *J. Amer. Chem. Soc.*, **90**, 6617 (1968); (b) D. F. Gaines and T. V. Iorns, *ibid.*, **89**, 4249 (1967).

(7) T. Onak and G. B. Dunks, *Inorg. Chem.*, **5**, 439 (1966).