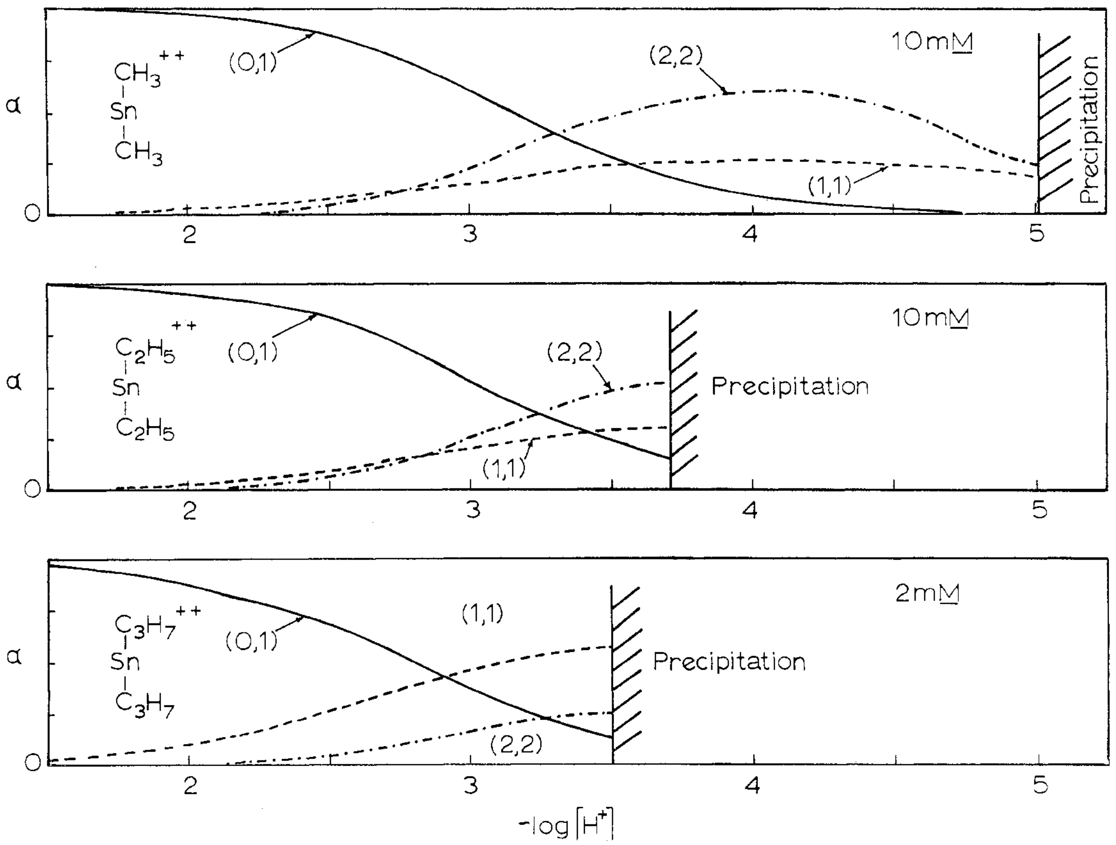

Figure 1.—Distribution of the organotin(IV) moieties among the different species as a function of pH; α is the fraction of the total organotin moiety in the indicated species. The numbers in parentheses indicate the number of hydroxo groups and organometallic moieties, respectively.

The increase in the acidity in the series $(CH_3)_2Sn^{2+}$, $(C_2H_5)_2Sn^{2+}$, and $(C_3H_7)_2Sn^{2+}$ is the opposite of the trend observed with the trimethyl- and triethyltin ions and opposite to what would be expected on the basis of simple inductive effects. A similar increase in acidity with increasing alkyl chain length was observed to occur with the trialkyltin chlorides in going from ethyl to *n*-propyl to *n*-butyl in the mixed ethanol–water solvent.[27] Similar trends with alkylammonium ions have been studied carefully and attributed to decreased solvation of the acid with increasing size of the alkyl group.[32] This effect would be expected to be even more pronounced with the strongly solvated, dipositive dialkyltin ions. As would be anticipated the di-*n*-butyltin ion appears to be at least as strong an acid as the di-*n*-propyltin ion, although its dissociation constants could not be measured accurately.

Figure 1 illustrates the distribution of tin among the various hydrolysis products for the R_2Sn^{2+} ions listed in Table I. All diagrams are appropriate for 10 m*M* organotin ion except for the di-*n*-propyltin system, which is for 2 m*M*. At the higher concentrations, precipitation of hydrolysis products occurs at rather low pH with this ion.

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(32) E. J. King, "Acid-Base Equilibria," The Macmillan Co., New York N. Y., 1965, p 149.

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Infrared Spectra of Group IV *gem*-Diamines and Their Cyclic Derivatives

By C. H. YODER AND J. J. ZUCKERMAN

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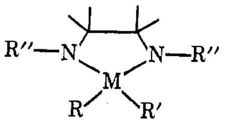
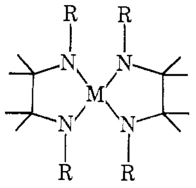
One of the advantages of studying homologous series of compounds is that variations in a property can be assigned to a structural or electronic change in the series. The infrared spectrum is such a property to the extent that absorptions are characteristic of independently vibrating groups. We report in this communication the results of our examination of three series of fourth group amines: *gem*-diamines, $RR'M[NR'']_2$, where M = carbon, silicon, germanium, and tin and the various R's can be H, CH_3, C_2H_5; monocyclic imidazolidines



where M = carbon, silicon, and germanium and the various R's can be H, CH_3, and C_6H_5; and spiro-[imidazolidines]



where M = silicon and germanium and R = CH_3 and C_2H_5.

Results and Discussion

Absorptions characteristic of silylamines occur in the 1000–900-cm^{-1} region.[1] A recent study in this laboratory of N^{14}- and N^{15}-trimethylsilylaniline isotopomeric pairs allowed unequivocal assignment of an absorption at 899 ± 1 cm^{-1} as the Si–N^{14} stretching frequency in this compound.[2] All silicon–nitrogen compounds examined by us exhibit a single absorption in the 1000–900-cm^{-1} region which is absent in carbon, germanium, and tin amines. This absorption can be assigned, in conformity with the literature,[1] to the silicon–nitrogen asymmetric stretching mode.

Henglein and Lienhard assigned an absorption at 950–930 cm^{-1} to the silicon–nitrogen bond in silaimidazolidine derivatives and also noted that a rather sharp absorption at 1350 cm^{-1} appears to be characteristic of these five-membered ring systems, as it was not observed in bis(diethylamino)dimethylsilane.[3] Following this suggestion, other investigators have ascribed absorptions in this region to ring vibrations in several similar silaimidazolidine derivatives.[4] We have observed a sharp, rather intense absorption in the 1350–1330-cm^{-1} region in the spectra of the silaimidazolidines of our series which is absent from the spectra of noncyclic derivatives. For example, the spectrum of bis(diethylamino)dimethylsilane exhibits several absorptions in the 1450–1250-cm^{-1} region, the most intense of which occurs at 1380–1370 cm^{-1}. The spectra of N,N′-diethylsilaimidazolidines, both spiro and monocyclic, contain three absorptions in the 1380–1330-cm^{-1} region. Two of these, between 1380 and 1345 cm^{-1}, also appear in the spectra of the acyclic bis(diethylamino)silane derivatives and would seem to be associated with the N-alkyl group.[5] The third of these absorptions, at 1330 ± 6 cm^{-1} (sharp) in the cyclic compounds, is apparently then associated with the five-membered imidazolidine ring structure itself.[6]

Spectra of the silicon and germanium homologs of the bis(diethylamino)dimethyl derivatives, the 1,2,2,3-tetramethylimidazolidines, and the N-methyl- and N-ethylspiro[imidazolidines] in the 4000–650-cm^{-1} region differ mainly in two respects: (i) the absorption at 970–930 cm^{-1} in the silicon–nitrogen compounds shifts to 930–870 cm^{-1} in their germanium–nitrogen analogs; and (ii) the pattern of absorptions in the 870–650-cm^{-1} region changes, but in no apparently systematic manner. As all the germanium–nitrogen compounds examined exhibit a single absorption in the 930–870-cm^{-1} region absent in the organic amine and chlorogermane starting materials, it seems likely that this region can be assigned to the germanium–nitrogen asymmetric stretching vibration.[6a]

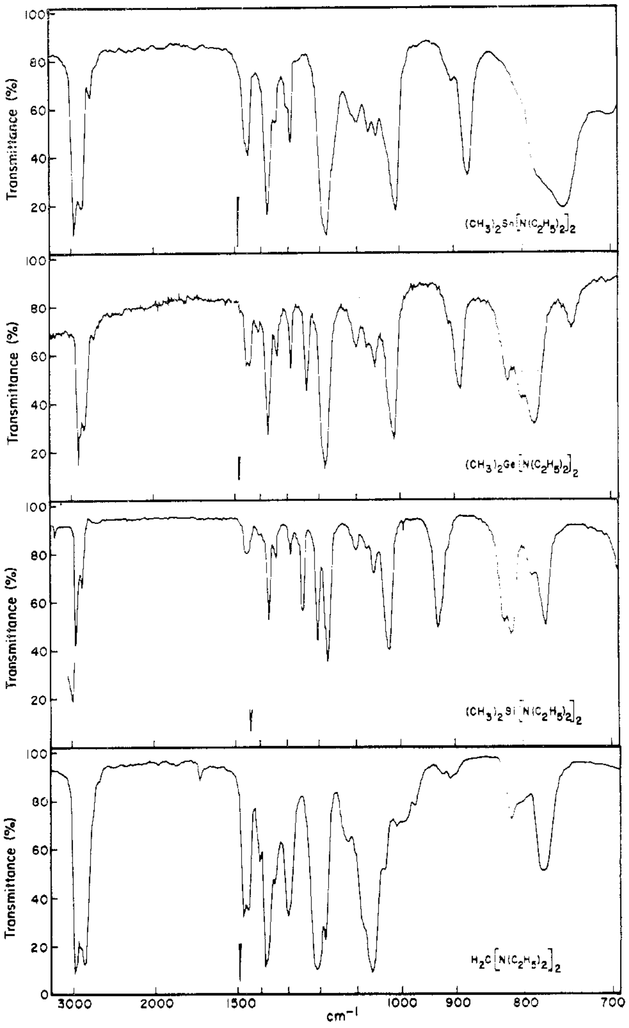


Figure 1.—Infrared spectra of group IV *gem*-diamines.

The spectra of the five-membered germanium ring compounds also contain a sharp absorption in the region 1330 ± 10 cm^{-1} which does not appear either in the spectrum of the organic amine starting material or in the spectra of noncyclic derivatives. This would then appear to be associated with the imidazolidine ring structure. Table I lists the frequencies of those absorptions which we have assigned to the M–N stretch and those associated with the ring structure in our compounds.

By arguments similar to those outlined above we

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[1] R. Fessenden and J. S. Fessenden, *Chem. Rev.*, **61**, 360 (1961); U. Wannagat, *Advan. Inorg. Chem. Radiochem.*, **6**, 225 (1964).

[2] E. W. Randall, J. J. Ellner, and J. J. Zuckerman, *Inorg. Nucl. Chem. Letters*, **1**, 109 (1966); Abstracts, 151st National Meeting of the American Chemical Society, Pittsburgh, Pa., March 1966.

[3] F. A. Henglein and K. Lienhard, *Makromol. Chem.*, **32**, 218 (1959).

[4] D. Kummer and E. G. Rochow, *Z. Anorg. Allgem. Chem.*, **321**, 21 (1963); *Inorg. Chem.*, **4**, 1450 (1965); E. W. Abel and R. P. Bush, *J. Organometal. Chem.* (Amsterdam), **3**, 245 (1965).

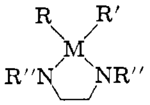
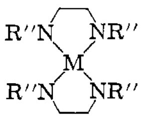
[5] Bands in the 1380–1345-cm^{-1} region are also found in the N-methyl derivatives.

[6] Further work is needed to elucidate the exact nature of this absorption. The band may arise, for example, through a CH_2 wagging motion in the 4 and 5 carbons of the methylene bridge.

[6a] NOTE ADDED IN PROOF.—The N^{14}- and N^{15}-trimethylgermylaniline isotopomeric pairs yielded an assignment of the Ge–N^{14} stretch at 855 ± 1 cm^{-1} in this compound [E. W. Randall and J. J. Zuckerman, unpublished results].

TABLE I

INFRARED SPECTRAL PARAMETERS OF GROUP IV *gem*-DIAMINES

M	R	R′	R″	$\nu_{M-N} \pm 5$ cm^{-1}	$\nu_{ring} \pm 5$ cm^{-1}
			$RR'M(NR''_2)_2$		
Si	CH_3	CH_3	C_2H_5	931	
Si	CH_3	C_6H_5	C_2H_5	934	
Si	C_6H_5	C_6H_5	CH_3	995	
Ge	CH_3	CH_3	C_2H_5	896	
Sn	CH_3	CH_3	C_2H_5	880	
					
Si	CH_3	CH_3	CH_3	933	1342
Si	CH_3	CH_3	C_2H_5	951	1330
Si	CH_3	CH_3	C_3H_7	963	*a*
Si	CH_3	CH_3	$C_6H_4CH_3$	962	*a*
Si	CH_3	CH_3	$C_6H_4OCH_3$	959	*a*
Si	CH_3	C_6H_5	CH_3	931	1340
Si	CH_3	C_6H_5	C_2H_5	952	1331
Si	C_6H_5	C_6H_5	CH_3	932	1344
Ge	CH_3	CH_3	CH_3	907	1333
Ge	C_6H_5	C_6H_5	CH_3	907	*b*
					
Si			CH_3	943	1349
Si			C_2H_5	967	1333
Si			$C_6H_4CH_3$	965	*a*
Ge			CH_3	910	1342
Ge			C_2H_5	926	1331

[a] Region obscured. [b] Weak.

have assigned the absorption at 880 cm^{-1} in the spectrum of bis(diethylamino)tin dimethyl to the tin–nitrogen asymmetric stretch. This is in agreement with the assignment based on a study of isotopomeric N^{14}- and N^{15}-trimethylstannylaniline of 843 ± 1 cm^{-1} for the $Sn-N^{14}$ stretch in this compound.[2,7]

The data of Table I show the silicon and germanium nitrogen stretching frequencies to be virtually independent of the group attached to these elements. The insulating effect of silicon toward changes in infrared absorption has been noted in numerous systems.[8] On the other hand, stretching frequencies and ring vibrations are rather dependent upon the group attached to nitrogen. The silicon–nitrogen stretch shifts to higher frequency in changing N-methyl for N-phenyl or larger N-alkyl groups while ring frequency decreases from N-methyl to N-ethyl.

Experimental Section

The preparation of the carbon,[9] silicon,[10] and germanium[11] imidazolidines, the spiro silicon and germanium imidazolidines,[12] and bis(diethylamino)dialkylgermanes[9,11] has been reported previously. Preparation of the bis(diethylamino)dialkylsilanes and stannanes followed procedures reported by Henglein and Lienhard[3] and Jones and Lappert,[13] respectively.

The infrared spectra of the compounds as liquid smears were recorded on a Perkin-Elmer infracord in the 4000–650-cm^{-1} range. All spectra were calibrated with polystyrene.

Acknowledgment.—This investigation was supported by Public Health Service Research Grant CA-07064-03 from the National Cancer Institute and by the Advanced Research Projects Agency. We are indebted to the National Science Foundation for a Predoctoral fellowship to C. H. Y. and to Texas Instruments, Inc., for a generous gift of germanium.

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(7) Assignment of $\nu_{asym}(Sn-N)$ has been the subject of some controversy. A band at 510 cm^{-1} in the spectrum of N′,N′-dimethyl-N-phenylureidotin trimethyl has been assigned to $\nu(Sn-N)$ on the basis of the similarity of mass of the Sn–N and Sn–C groups in four-coordinate tin compounds: T. A. George, K. Jones, and M. F. Lappert, *J. Chem. Soc.*, 2157 (1965). Infrared spectra of tris(tri-*n*-alkyltin)amines containing methyl, ethyl, and propyl groups yielded an assignment of $\nu_{asym}(Sn-N)$ at 728, 712, and 712 cm^{-1}, respectively: K. Sisido and S. Kojima, *J. Org. Chem.*, **29**, 907 (1964). More recently infrared and Raman spectra of tris(trimethyltin)amine and tetrakis-(dimethylamino)tin have yielded assignments of $\nu_{sym}(Sn_3-N)$ at 514, $\nu_{asym}(Sn_3-N)$ at 672, and $\nu_{asym}(Sn-N_4)$ at 538 cm^{-1} in the two compounds [R. E. Hester and K. Jones, *Chem. Commun.*, 317 (1966)]. Bands in these regions, although present in the spectrum of N-trimethylstannylaniline, failed to shift to lower frequencies on N^{15} substitution.[2]

(8) A. L. Smith, *Spectrochim. Acta*, **16**, 87 (1960).

(9) C. H. Yoder and J. J. Zuckerman, *J. Am. Chem. Soc.*, **88**, 4831 (1966).

(10) C. H. Yoder and J. J. Zuckerman, *Inorg. Chem.*, **4**, 116 (1965).

(11) C. H. Yoder and J. J. Zuckerman, *J. Am. Chem. Soc.*, **88**, 2170 (1966).

(12) C. H. Yoder and J. J. Zuckerman, *Inorg. Chem.*, **3**, 1329 (1964).

(13) K. Jones and M. F. Lappert, *J. Chem. Soc.*, 1944 (1965).

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The Reaction of Xenon Hexafluoride with Stannic Fluoride

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Xenon hexafluoride is known to form the following compounds by combination with the appropriate reactants: $XeF_6 \cdot AsF_5$,[1] $XeF_6 \cdot BF_3$,[1] $XeF_6 \cdot 2SbF_5$,[2] $XeF_6 \cdot SbF_5$,[2] $2XeF_6 \cdot SbF_5$,[2] $CsF \cdot XeF_6$,[3] $2CsF \cdot XeF_6$,[3] $RbF \cdot XeF_6$,[3] $2RbF \cdot XeF_6$,[3] $2KF \cdot XeF_6$,[3] and $2NaF \cdot XeF_6$.[3] The reaction of excess XeF_6 with SnF_4 has now been found to proceed readily to yield the compound $4XeF_6 \cdot SnF_4$. When this compound is heated to about 50° while under vacuum, XeF_6 is slowly lost. The rate of loss of XeF_6 decreases somewhat when the molar ratio of XeF_6 to SnF_4 becomes less than 2.0. Below a molar ratio of 1.3 XeF_6 is lost only very slowly even when the solid is held at 110° under vacuum. While XeF_6 is being removed, the X-ray powder pattern of the solid remains substantially unchanged down to a molar ratio approaching 2.0. At molar ratios somewhat below 2.0 the powder pattern contains lines that can be attributed to uncombined SnF_4. Other lines that do not belong to either $4XeF_6 \cdot SnF_4$ or SnF_4 are also present and in some cases diffuse broad diffraction halos possibly due to extremely small crystallites are observed. Stoichiometric proportions of any compound(s) having molar ratio(s) of XeF_6 to SnF_4 less than 4.0 have not been established.

(1) H. Selig, *Science*, **144**, 537 (1964).

(2) G. L. Gard and G. H. Cady, *Inorg. Chem.*, **3**, 1745 (1964).

(3) R. D. Peacock, H. Selig, and I. Sheft, *Proc. Chem. Soc.*, 285 (1964).