groups, that is: $CH_2F < CHF_2 < CF_3 \approx CH(CF_3)_2 < C_2F_5 < CF(CF_3)_2$. The order $CF_3 < C_2F_5 < CF(CF_3)_2$ is in agreement with an order of effective electronegativities based on the chemical shifts of the H atoms in the nmr spectra of the compounds $HC{\equiv}CR_f$ and $H\overline{C{=}CR_fCF_2}$, assuming that the shifts are due to an increased deshielding of the hydrogen atom caused by an increase in electronegativity of the R_f substituent. In all cases a shift to lower field occurs as the size of the R_f group increases.[6] The apparent equivalence of the electronegativities of CF_3 and $CH(CF_3)_2$ is surprising and it appears that there may be another affect causing an electric field gradient in $(CH_3)_3SnCH(CF_3)_2$. Powell and Lagowski[34] have attempted to estimate the electronegativities of various saturated R_f groups but their results are not definitive.

The constant isomer shift ($\Delta = 1.25 \pm 0.06$ mm/sec) of the vinyltin derivatives implies a constant electron density at the tin nuclei. The quadrupole splitting observed in the spectrum of $(CH_3)_3SnCF{=}CF_2$ ($\Delta = 1.41$ mm/sec) is probably due to the electronegativity effect of the fluorocarbon group rather than π-bonding interactions since no quadrupole splitting is observed in the Mössbauer spectra of the vinyl compounds $R_3Sn{-}CH{=}CH_2$.[11] The quadrupole splitting observed in the spectrum of $(CH_3)_3SnC{\equiv}CCF_3$ is larger than that observed in $(CH_3)_3SnC{\equiv}CC_6H_5$. This increase might be explained by the larger inductive effect of CF_3 relative to the C_6H_5 ring. The still larger splitting observed for $(CH_3)_2Sn(C{\equiv}CCF_3)_2$ ($\Delta = 1.95$ mm/sec) may be due to both the increased total electronegativity effect on the electric field gradient caused by the addition of a second propynyl group and the fact that the asymmetry parameter is now nonvanishing. It cannot be stated, at this time, which mechanism has the greater influence.

If it is assumed that the unsaturated fluorocarbon groups do not π bond to the tin and that the quadrupole splittings are due only to σ-bonding effects, then the results indicate that the electronegativity of the groups increases in the order $CH_2F < CHF_2 < CF{=}CF_2 < CF_3 \approx CH(CF_3)_2 < CF_2CF_3 < C{\equiv}CCF_3 < CF(CF_3)_2$. However, it does not seem possible to extract group electronegativities from these data since although the electronegativities of CF_3 and Cl are believed to be similar[34] the quadrupole splittings observed for $(CH_3)_3SnCl$ and $(CH_3)_3SnCF_3$ are very different.[33]

Several authors have found correlations between the Mössbauer and nmr data of tin compounds.[12,35,36] In the present work no good correlation between Δ and $J_{^{119}Sn-CH_3}$ or between Δ and the chemical shift of the tin methyl group has been found.

Acknowledgment.—We thank the National Research Council of Canada for financial assistance.

---

[34] H. B. Powell and J. J. Lagowski, *J. Chem. Soc.*, 2047 (1962); 1392 (1965).

[35] V. V. Khrapov, V. I. Gol'danskii, A. K. Prokof'ev, and R. G. Kostyanovskii, *Zh. Obshch. Khim.*, **37**, 3 (1967).

[36] B. Gassenheimer and R. H. Herber, *Inorg. Chem.*, **7**, 1120 (1968).

Contribution from the School of Chemistry, Rutgers, The State University,
New Brunswick, New Jersey 08903

Mössbauer Spectroscopy of Organometallic Compounds. Organotin Azides

By HWA-SHENG CHENG[1] and ROLFE H. HERBER

Received November 21, 1969

Infrared, Mössbauer, and related physicochemical data are presented for a series of trialkyltin azides and dialkyltin diazides and interpreted in terms of the structure and bonding in such molecules. From the isomer shift and quadrupole splitting data for $(CH_3)_3SnN_3$ and the temperature dependence of the Mössbauer–Lamb fraction it is concluded that this molecule contains five-coordinate tin atoms with bridging azide groups linking the $(CH_3)_3Sn$ moieties. The higher alkyl homologs of this molecule are probably nonpolymeric at room temperature, as suggested by their liquid nature, but polymeric solids with (weakly) bridging N_3 groups at liquid nitrogen temperature. No evidence is observed for octahedral coordination for $(CH_3)_2Sn(N_3)_2$ or the related higher alkyl homologs at liquid nitrogen temperature. From Mössbauer isomer shift systematics for octahedral halogen complexes of the type SnX_6^{2-} and for trimethyltin halides, a group electronegativity (Mulliken) of 8.54 ± 0.10 has been derived for the nonbridging covalent N_3 group in $[(CH_3)_4N]_2Sn(N_3)_6$ and of 7.66 ± 0.06 for the bridging covalent N_3 group in $(CH_3)_3SnN_3$.

I. Introduction

Extensive study in recent years by a wide variety of physicochemical techniques has shown that the structure and bonding in organotin compounds is sensitively dependent on the nature of the ligands bonded to the metal atom and that four-, five-, and six-coordinations are all observed in closely related molecules. As part of a continuing series of investigations, Mössbauer spectroscopy has been used—in conjunction with other spectroscopic techniques—to elucidate the nature of organotin halides and pseudohalides, and the present study was undertaken to clarify the ligand character of the azide group (N_3) in such compounds.

---

[1] Department of Chemistry, National Tsing-Hua University, Taiwan, China. Fulbright-Hayes Scholar, 1968–1969.

II. Experimental Section

(a) **Preparation of Organotin Azides.**—These compounds were prepared by literature methods[2] involving the reaction between the corresponding trialkyltin halide and an aqueous solution of NaN_3, using water as a reaction medium.

The products were either recrystallized from benzene [$(CH_3)_3SnN_3$, $(C_4H_9)_2Sn(N_3)_2$] or C_2H_5OH [$(CH_3)_2Sn(N_3)_2$, $(C_2H_5)_2Sn(N_3)_2$, $(C_3H_7)_2Sn(N_3)_2$] or purified by vacuum distillation [$(C_2H_5)_3SnN_3$, $(C_3H_7)_3SnN_3$, $(C_4H_9)_3SnN_3$]. The organotin azides so obtained were characterized by their physical properties and infrared spectra. Elemental analyses[3] for C and H were in general satisfactory, but the results for nitrogen were consistently low except for $(CH_3)_3SnN_3$. *Anal.* Calcd: C, 17.51; H, 4.37; N, 20.43. Found: C, 17.51; H, 4.42; N, 20.42.

(b) **Mössbauer Spectra.**—These were obtained at ~80°K in transmission geometry, using a constant-acceleration type of spectrometer described earlier.[4] Solid samples were mounted as thin layers of microcrystalline material between 0.5-mil aluminum foil in a copper sample holder attached to the nitrogen-cooled cold finger of the dewar assembly. Mössbauer measurements on those samples which are liquids at room temperature (*e.g.*, triethyl-, tripropyl-, and tributyltin azide) were effected by impregnating a glass-fiber filter disk (which had been previously oven dried at 105° for several hours) with the organotin azide and immediately immersing this disk in liquid nitrogen prior to mounting on the precooled dewar cold finger as above.

The measurements on alcohol solutions of $(CH_3)_3SnN_3$ and $(C_4H_9)_2Sn(N_3)_2$ were effected by preparing the solutions in small stoppered vials, injecting a small aliquot by means of a hypodermic syringe into a copper sample holder fitted with 5-mil thermoadhesive Mylar windows,[5] and immediately plunging this assembly into liquid nitrogen. The glassy matrix was maintained at ~80°K until mounted on the precooled cold finger of the dewar system.

At least 5×10^5 counts/channel were accumulated using a $BaSnO_3$ source at room temperature so that the signal-to-noise (statistical counting error) was greater than 20. Calibration of the spectrometer was effected using the four inner lines of a Mössbauer spectrum of a 0.5-mil natural iron foil obtained using a Pd(^{57}Co) source at 294°K. The calibration constant of the spectrometer (mm/sec channel) was calculated using the NBS data for SRM1541 iron foil.[6] All isomer shifts are referred to the centroid of a room-temperature $BaSnO_3$ absorption spectrum (identical with that observed for SnO_2 within the experimental error). Sample temperatures were determined using a calibrated thermocouple affixed to the copper sample holder. All spectra were manually fit through the data points and computed by standard methods.

(c) **Nmr Data.**—These were obtained in $Cl_3CCOCCl_3$ solutions (~10%) using a Varian A-60 spectrometer. All shifts are reported with reference to an internal standard of TMS.

III. Results and Discussion

The Mössbauer, infrared, and physical data obtained in the present investigation are summarized in Table I, and a typical Mössbauer spectrum is shown in Figure 1.

The most prominent features in the infrared spectra of azides are the asymmetric stretching frequency, ν_3, which is generally observed[7] in the range 2200–2000 cm^{-1} and the weaker symmetric mode at about 1170–1350 cm^{-1}. In covalent azides such as CH_3N_3 and HN_3, ν_3 occurs at 2143 and 2140 cm^{-1}, respectively.[8] In HN_3, the HNN bond angle is 110° 52′ and the two NN bond distances are 1.241 and 1.128 Å. In ionic azides such as NH_4N_3, ν_3 has shifted[9] to 2030 cm^{-1}. In such compounds, the azide groups are linear and symmetric (both NN bond distances are 1.15 Å) and oriented at tetrahedral bond angles around the monovalent cation. Moreover, in such ionic azides, the symmetric stretching frequency is insensitive to the size of the cation and is observed[9,10] at ~1338 cm^{-1}. The asymmetric stretching frequency, ν_3, in both ionic and covalent azides, on the other hand, is sensitive to the mass of the cation or group to which the N_3 moiety is bonded. The shift

TABLE I

INFRARED AND MÖSSBAUER DATA FOR THE COMPOUNDS DISCUSSED IN THE TEXT

Compound	ν_{asym}, cm^{-1}	ν_{sym}, cm^{-1}	IS,[a,b] mm/sec	QS,[b] mm/sec
NaN_3	2091[c]	1302[c]		
$[(CH_3)_4N]_2Sn(N_3)_6$	2071[c]	1289[c]	0.48	0
$(CH_3)_3SnN_3$	2054[c]	1292[c]	1.43	3.67
$(CH_3)_3SnN_3$ (0.6 *M* in C_2H_5OH)			1.48	3.29
$(C_2H_5)_3SnN_3$	2066	1277	1.24	3.04
$(C_3H_7)_3SnN_3$			1.21	2.96
$(n\text{-}C_4H_9)_3SnN_3$	2067	1290	1.26	3.17
$(CH_3)_2Sn(N_3)_2$	2045		1.06	2.61
$(C_2H_5)_2Sn(N_3)_2$	2066[c]	1277[c]	1.23	2.94
$(C_3H_7)_2Sn(N_3)_2$			1.15	2.74
$(n\text{-}C_4H_9)_2Sn(N_3)_2$			1.29	2.99
$(n\text{-}C_4H_9)_2Sn(N_3)_2$ (0.5 *M* in C_2H_5OH)			1.30	2.84

[a] With respect to the centroid of a $BaSnO_3$–$BaSnO_3$ spectrum. Such isomer shifts are identical with those calculated with respect to SnO_2 within the quoted experimental error. [b] All values ±0.02 mm/sec at 82 ± 4°K. [c] Infrared spectra on Nujol mulls; all others neat liquids.

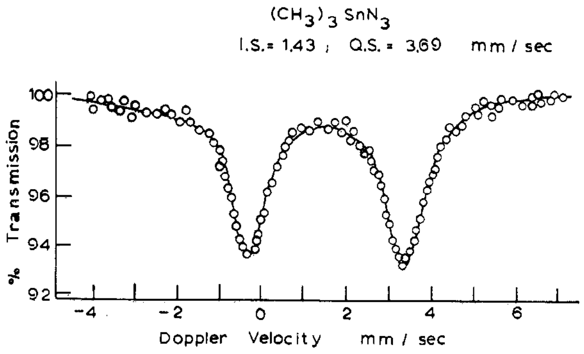

Figure 1.—Mössbauer spectrum of $(CH_3)_3SnN_3$ at 80°K taken with a $Ba^{119}SnO_3$ source at room temperature. The Doppler velocity is quoted relative to the centroid of a $BaSnO_3$–$BaSnO_3$ spectrum at room temperature.

---

(2) J. S. Thayer and R. West, *Inorg. Chem.*, **3**, 889 (1964); J. S. Thayer and D. P. Strommen, *J. Organometal. Chem.*, **5**, 383 (1966). Although no explosive decompositions were experienced in the course of this work (including the running of infrared spectra of Nujol mulls of AgN_3), it should be remembered that metal azide compounds are sensitive to shock, and adequate care in the handling of these materials should be exercised.

(3) G. I. Robertson Microanalytical Laboratories, Florham Park, N. J.

(4) N. B. Koller and R. H. Herber in "Chemical Application of Mössbauer Spectroscopy," V. I. Gol'danskii and R. H. Herber, Ed., Academic Press, New York, N. Y., 1968, Chapter 2.

(5) G. T. Schjeldahl Co., Northfield, Minn., Type GT-300.

(6) J. J. Spijkerman, J. R. DeVoe, and J. C. Travis, NBS Special Publication 260-20, "Standard Reference Materials: Standards for Mössbauer Spectroscopy," National Bureau of Standards, Washington D. C., 1970.

(7) L. J. Bellamy, "The Infra-red Spectra of Complex Molecules," Methuen and Co. Ltd., London, 1958.

(8) E. H. Eyster, *J. Chem. Phys.*, **8**, 135 (1940); E. H. Eyster and R. H. Gillette, *ibid.*, **8**, 369 (1940).

(9) D. A. Dows, E. Whittle, and G. C. Pimentel, *ibid.*, **23**, 1475 (1955). This frequency pertains to the ordered phase (I) observed above 150°K. A disordered crystal phase (A) observed at ~68°K has ν_3 at 2050 cm^{-1}.

(10) L. Kahovec and L. W. F. Kohlrausch, *Monatsh. Chem.*, **77**, 180 (1947).

from NaN_3 (2091 cm^{-1}) to AgN_3 (2000 cm^{-1}) is 91 cm^{-1}, while that from HN_3 (2169 cm^{-1}) to CH_3N_3 (2143 cm^{-1}) is 26 cm^{-1}. Finally, in relating ν_3 to the bonding character of the azide group, it has been pointed out by Fujita, *et al.*,[11] that ν_3 increases with increasing covalency, as exemplified in their data for a series of cobalt and chromium amine azide complexes.

Representative Nujol mull infrared spectra for $(CH_3)_3SnN_3$, $[(C_2H_5)_4N]_2Sn(N_3)_6$, and NaN_3 are shown in Figure 2. As indicated in Table I, ν_3 for the organotin azides here reported lies at about 2066 cm^{-1} (except for $(CH_3)_3SnN_3$ at 2054 cm^{-1}), which at first glance suggests that the nature of the azide group in these molecules is not very different from what it is in the ionic azides NaN_3 and NH_4N_3. When correction is made for the observed mass effect on ν_3, however, it is seen that the azide group in organotin azides appears to absorb at frequencies which are very similar to those found in the covalent compounds HN_3, CH_3N_3, and $C_6H_5N_3$. In this context then it is difficult to draw definite conclusions concerning the structures of these molecules on the basis of the infrared data alone.

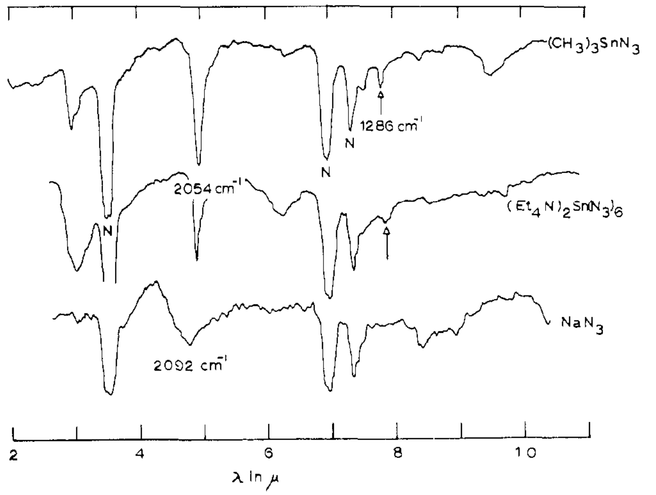

Figure 2.—Representative infrared spectra of Nujol mulls of $(CH_3)_3SnN_3$, $[(C_2H_5)_4N]_2Sn(N_3)_6$, and NaN_3, showing the symmetric and asymmetric azide stretching frequencies of particular interest. The bands marked N are Nujol absorptions and should be disregarded in terms of the azide structure problem.

The proton nmr spectrum of $(CH_3)_3SnN_3$ in hexachloroacetone solution (~10%) is shown in Figure 3. The sharp proton resonance occurs at δ −0.622 ± 0.010 ppm with respect to TMS and the coupling constants are $J_{^{117}Sn-C-H}$ = 55 ± 1 Hz and $J_{^{119}Sn-C-H}$ = 58 ± 1 Hz. The peak observed at δ −2.70 ppm is due to the solvent (possibly a small contamination from a hydrolysis product of $Cl_3CCOCCl_3$). These results are in good agreement with those reported earlier[12] for 10% solutions of $(CH_3)_3SnN_3$ in benzene. The proton shift in trimethyltin azide is close to that reported[13] for $(CH_3)_3SnCl$ in CCl_4 (δ −0.627 ppm) and consistent with the reported proton shift data for related trimethyltin halides and pseudohalides.[14] The proton nmr shift for $(CH_3)_3SnCN$ in $CDCl_3$ is observed at δ −0.45 ppm and that for $(CH_3)_3SnSCN$ at δ −0.625 ppm,[15] the resonance in each case corresponding to an unsplit singlet absorption peak. These shifts, while related to the s character of the metal–ligand bonds, are not particularly useful in the understanding of the molecular structure of the trialkyltin pseudohalides and do not appear particularly sensitive to the coordination number of the metal atom.

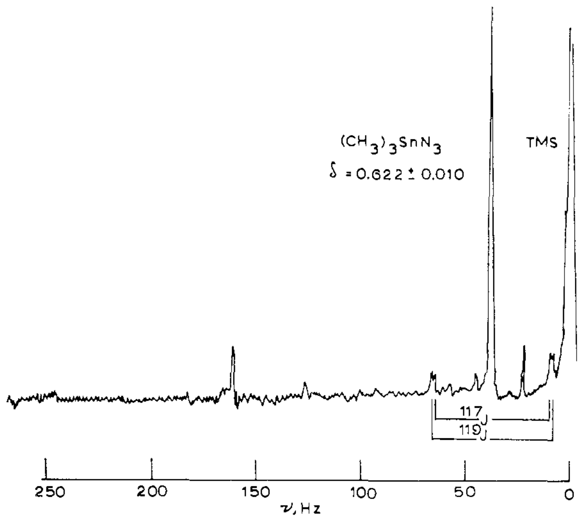

Figure 3.—Proton nmr spectrum of $(CH_3)_3SnN_3$ in $Cl_3CCOCCl_3$. The chemical shifts (δ) and proton–tin coupling constants (J) are discussed in the text. The resonance at ~163 Hz is due to a small solvent impurity.

The structural characteristics of these molecules are, however, elucidated by the Mössbauer data summarized in Table I. The ratio ρ = QS/IS (where the isomer shift is referred to the SnO_2 standard) has a value of 2.57 for $(CH_3)_3SnN_3$. On the basis of available structural information it has been suggested earlier[16] that ρ values larger than ~2.1 would be associated with five- or six-coordinate covalent organotin compounds and the present evidence implies that such five-coordinate structure is present in $(CH_3)_3SnN_3$. This conclusion is consistent with the physical properties of this compound (*i.e.*, that, despite its relatively low molecular weight compared to its homologs, it is a solid at room temperature) and the fact that the temperature dependence of the recoil-free fraction (the Mössbauer–Lamb fraction, which can be estimated from the temperature dependence of the area under the resonance doublet) is very similar to that observed for $(CH_3)_3SnF$ which is known[17] to form polymeric chains with bridging (albeit probably asymmetric) fluoride atoms. This temperature dependence (normalized to the 120°K

---

[11] J. Fujita, K. Nakamoto, and M. Kobayashi, *J. Amer. Chem. Soc.*, **78**, 3295 (1956).

[12] J. Lorberth, H. Krapf, and H. Nöth, *Chem. Ber.*, **100**, 3511 (1967).

[13] H. Schmidbauer and I. Ruidisch, *Inorg. Chem.*, **3**, 599 (1964); J. R. Holmes and H. D. Kaesz, *J. Amer. Chem. Soc.*, **83**, 3903 (1961).

[14] G. P. van der Kelen, *Nature*, **193**, 1069 (1962); H. C. Clark, J. T. Kwon, L. W. Reeves, and E. J. Wells, *Inorg. Chem.*, **3**, 907 (1964).

[15] B. J. Gassenheimer and R. H. Herber, unpublished results.

[16] R. H. Herber, H. A. Stöckler, and W. T. Reichle, *J. Chem. Phys.*, **42**, 2447 (1965).

[17] H. Kriegsmann and S. Pischtschan, *Z. Anorg. Allg. Chem.*, **306**, 212 (1961); H. C. Clark, R. J. O'Brien, and J. Trotter, *Proc. Chem. Soc.* (London), 85 (1963).

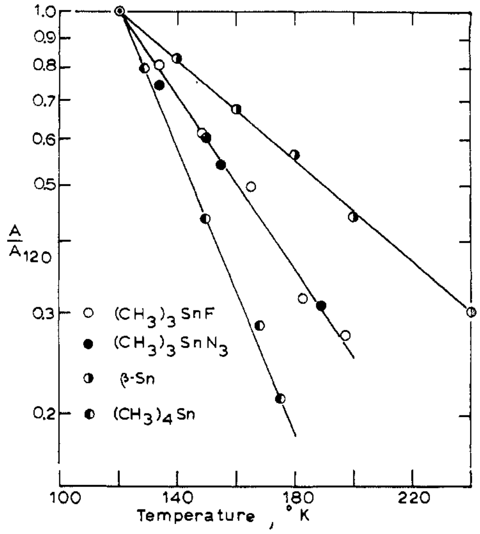

Figure 4.—Temperature dependence of the area under the Mössbauer resonance curve (normalized to the data at 120°K) for $(CH_3)_3SnF$ (five-coordinate, polymeric), $(CH_3)_3SnN_3$, β-Sn (four-coordinate, polymeric), and $(CH_3)_4Sn$ (four-coordinate, monomeric).

data point to facilitate comparison) is summarized in Figure 4.

The presence of an infrared absorption for $(CH_3)_3SnN_3$ at 1292 cm^{-1}, which is tentatively assigned to the symmetric stretching mode of the N_3 group, can arise in one of two ways and still be consistent with the bridging nature of this ligand. It is possible that the azide group is bonded asymmetrically with respect to the two metal atoms [as has been suggested for the halogen atom in $(CH_3)_3SnF$] thus causing a noncoplanarity of the three methyl groups with respect to the tin atom and hence an infrared-active vibration. It is also possible that the Sn–N–N bond angle is not 180°, as for example in HN_3 and CH_3N_3, which would again give rise to an infrared-active symmetric stretching mode if the normal modes of the two methyltin moieties are out of phase. On the basis of the presently available data it is not possible to decide between these two rationalizations.

Chemical evidence suggests that the metal–nitrogen bond is relatively easily broken, since $(CH_3)_3SnN_3$—in contrast to other organotin polymers—is readily soluble in a variety of polar organic solvents. In this context it is interesting to note that the Mössbauer parameters observed for a frozen (glassy) $\sim$0.6 *M* ethanol solution give a ρ value of 2.22. The decrease from the value of 2.59 observed for the neat solid can be understood on the basis of a five-coordinate nonpolymeric structure in the glass in which one of the coordination sites has been occupied by an alcohol molecule. This interpretation is also consistent with that of Thayer and West,[18] who noted that $(CH_3)_3SnN_3$, unlike other azides, shows a marked high-frequency shift for the N_3 asymmetric stretch when the infrared spectrum is run in methylene chloride or chloroform, as compared to Nujol mulls of the neat solid. This shift suggests a structural change on dissolution in which the five-coordinate structure is preserved, but the electron-withdrawing properties of one of the (axial in $\sim C_{3v}$ symmetry) ligands is significantly different from that of the remaining N_3 moiety.

In this context it is interesting to note that the solvation of organotin azides in polar solvents may not be completely reversible in all cases. A sample of $(CH_3)_3SnN_3$, which had been prepared from an alcoholic solution of the chloride and subsequently purified from benzene, gave a Mössbauer spectrum having an isomer shift of +1.29 mm/sec (with reference to SnO_2) and a quadrupole splitting of 3.24 mm/sec. Another sample of $(CH_3)_3SnN_3$, prepared from alcoholic $(CH_3)_3SnBr$, purified from benzene solution, and subsequently sublimed, gave an IS of +1.12 mm/sec and a QS of 3.28 mm/sec. No such changes in the Mössbauer parameters were observed in analogous synthetic procedures for $(C_4H_9)_2Sn(N_3)_2$. Whether the data for the methyltin azide suggest an irreversible solvolysis cannot be unambiguously extracted from the presently available information.

The liquid nature (at room temperature) of the triethyl-, tri-*n*-propyl-, and tri-*n*-butyltin azides suggest that these molecules are nonpolymeric at $\sim$300°K. On the other hand, the ρ values determined from the Mössbauer spectra at $\sim$80°K are consistent with a pentacovalent structure from which it may be inferred that the energy which stabilizes the bridging azide configuration is comparable to (or less than) $\sim kT \approx$ 600 cal mol^{-1}.

This relatively small tendency for the N_3 group to act as a bridging ligand (which is observed in the case of the $(CH_3)_3SnN_3$ species because of the favorable steric properties of the methyl groups) is also observed for the dialkyltin diazides. For these molecules, the quadrupole splittings which are observed are $\sim$3 mm/sec or less, in contrast to a value of 4.31 mm/sec observed for $(CH_3)_2SnF_2$ and 3.87 mm/sec observed for $(CH_3)_2Sn(SCN)_2$, both of which are known[19] from other evidence to form distorted octahedral polymeric solids. Moreover, $(CH_3)_2Sn(N_3)_2$ shows no observable resonance effect at room temperature, in contrast to the readily observable effect in the case of $(CH_3)_2SnF_2$ under comparable conditions, although such evidence can give only a qualitative guide to the structural features of such molecules.[20] On this basis it is concluded that the structures of the dialkyltin diazides reported in the present study correspond to distorted tetrahedral entities, in which the quadrupole splitting which is observed arises from the difference in electronegativity of the Sn–C and Sn–N bonds in agreement with the postulates of Bent[21] and the Mössbauer data reported earlier.[22] Such a distorted tetrahedral struc-

---

(18) J. S. Thayer and R. West, *Inorg. Chem.*, **3**, 889 (1964).

(19) (a) E. O. Schlemper and W. C. Hamilton, *Inorg. Chem.*, **5**, 995 (1966); (b) B. Gassenheimer and R. H. Herber, *ibid.*, **8**, 1120 (1969).

(20) In particular, see the discussion by R. H. Herber and H. A. Stöckler in IAEA Technical Reports Series No. 50, International Atomic Energy Agency, Vienna, 1966, p 110.

(21) H. A. Bent, *Chem. Rev.*, **61**, 275 (1961).

(22) J. C. Hill, R. S. Drago, and R. H. Herber, *J. Amer. Chem. Soc.*, **91**, 1644 (1969).

ture is also consistent with the Mössbauer parameters observed for a frozen glassy ~0.5 *M* ethanolic solution of $(n\text{-}C_4H_9)_2Sn(N_3)_2$, in which the quadrupole splitting is only ~0.15 mm/sec smaller than that observed for the neat solid. While it is conceivable that two polar solvent molecules could occupy octahedral bonding sites (as has been inferred in the case of $(n\text{-}C_4H_9)_2Sn(SCN)_2$ in ref 19b), the small quadrupole splitting (2.84 mm/sec) is not consistent with an octahedral formulation in which the two butyl groups are *trans* to each other.

From the data summarized in Table I it is seen that both the IS and QS parameters for $(C_3H_7)_2Sn(N_3)_2$ and for $(C_3H_7)_3SnN_3$ are smaller than those for the corresponding ethyl and *n*-butyl homologs. A similar nonlinear dependence of these parameters (although barely outside the quoted experimental error) is evident in the R_2SnX_2 data of Bryukhanov, *et al.*[23] A detailed study of the dependence of the IS and QS parameters on alkyl chain length in R_nSnX_{4-n} will be reported elsewhere.[24] The present data are completely consistent with presently available data on other halides and pseudohalides.

Finally, it is worth noting that the Mössbauer data presented in the present study for trimethyltin azide and those reported earlier[25] for trimethyltin halides and pseudohalides, as well as those for $[(CH_3)_4N]_2SnX_6$[26] (including $X = N_3$), permit an evaluation of the group electronegativity for the azide moiety in these molecules. In a refinement[27] of the earlier data[26] on octahedral hexahalogen complexes of Sn(IV) a good correlation is observed between the Mulliken electronegativity (χ_M) and the isomer shift. This correlation is summarized in Figure 4. The χ_M values (in electron volts) were taken from the data of Politzer[28] to be: F, 10.433; Cl, 8.287; Br, 7.587; I, 6.756. The value for N can be estimated from the data summarized by Moiseivich[29] to be 7.15. Using the isomer shift–χ_M correlation, a value of 8.54 ± 0.10 is interpolated for the azide group in the hexahalogen complexes and 7.66 ± 0.06 for the N_3 moiety in trimethyltin azide as shown in Figure 5. This difference in the electronegativity for the azide group in the two species is again indicative of the difference between the nonbridging nature of this group in the octahedral complex[30] and its postulated bridging nature in the trimethyltin compound. The smaller value in the latter may well be due to the expected extensive electron delocalization along the π-bonding framework of the (linear) N_3 bridge, but a quantitative estimate of this effect is not yet possible in view of the unsatisfactory status of MO treatments for this system. It is, however, clear from these data that IS–χ_M correlations can have significant utility in estimating the bonding characteristics of polyatomic ligands. A related study on organotin cyanates[31] is currently underway in these laboratories.

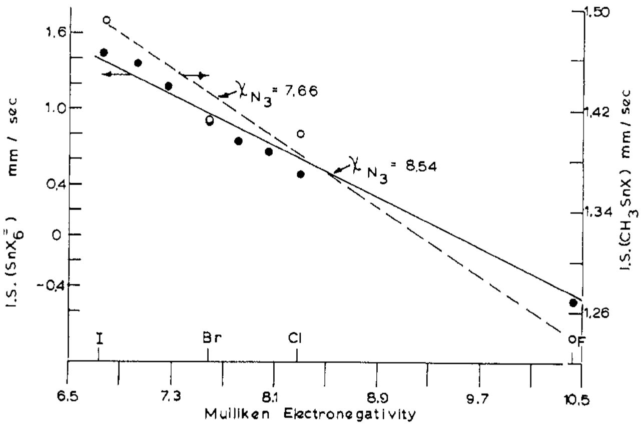

Figure 5.—Isomer shift–Mulliken electronegativity correlation for the SnX_6^{2-} and $(CH_3)_3SnX$ compounds discussed in ref 19b and in the text. The octahedral complexes not specifically labeled are the mixed-halogen complexes described in ref 19b.

Acknowledgments.—The authors are indebted to Dr. S. Chandra for extensive help with instrumentation and for the temperature-dependence data on $(CH_3)_3SnF$ and $(CH_3)_3SnN_3$ and permission to quote these results prior to publication. This work has been supported in part by the U. S. Atomic Energy Commission and constitutes Document NYO-2472-65. The support of the Petroleum Research Fund, administered by the American Chemical Society, and the Research Council of Rutgers University is also gratefully acknowledged.

---

(23) V. A. Bryukhanov, *et al.*, *Sov. Phys. JETP*, **16**, 321 (1963).

(24) R. H. Herber and Y. Goscinny, unpublished results. The authors are grateful to M. Goscinny for access to these data prior to publication.

(25) See for example V. I. Gol'danskii, V. V. Khrapov, O. Yu. Okhlobystin, and V. Ya. Rochev, ref 4, Chapter 6; R. H. Herber and Y. Goscinny, unpublished results.

(26) H.-S. Cheng and R. H. Herber, *Inorg. Chem.*, **8**, 2145 (1969).

(27) Suggested to us by Professor M. L. Good, private communication. See also C. Clausen and M. L. Good, *Inorg. Chem.*, **9**, 817 (1970).

(28) P. Politzer, *J. Amer. Chem. Soc.*, **91**, 6235 (1969).

(29) B. L. Moiseivich, *Advan. At. Mol. Phys.*, **1**, 61 (1965).

(30) D. Forster and W. D. Horrocks, Jr., *Inorg. Chem.*, **5**, 1510 (1966). On the basis of extensive infrared and Raman data, these authors concluded that the symmetry of the $Sn(N_3)_6^{2-}$ ion is lower than O_h, with nonlinear Sn–N–N–N groups. A decision between D_{3d} and S_6 symmetry cannot be made on the basis of the spectral evidence.

(31) A preliminary discussion of these results was presented at the 1969 Venice Conference, and are summarized in *Inorg. Chim. Acta*, 85 (1969).