accurately. Figure 1 shows a comparison of the primary experimental data pH(C_H), for the picolinic acid system, the calculated curve for the original constants, and the curve calculated with the refined constants. Figure 2 shows the distribution of complexes in this system. This information, which is printed out by the computer program for each experimental point, is very valuable, for it enables one to determine at a glance the degree of complexing of the metal ion by both the ligand and by hydroxide ion. Considering the intricacy of the calculations used in obtaining these data, it is not feasible to carry out such calculations without using a high-speed computer.

Since these data indicated that the picolinate group did complex the dimethyltin ion quite effectively and that $\bar{n}$ values approaching 1 had been attained, a refinement assuming the formation of two complexes, $[(CH_3)_2SnPic]^+$ and $[(CH_3)_2Sn(Pic)_2]$, was also tried for the case with $C_L > B$, even though it seemed unlikely that the bis-(picolinato) complex would be appreciably soluble. No precipitation had been observed at any point during the experimental study. A trial value of the cumulative constant for the addition of two ligands was obtained assuming the second stepwise constant, K_2, had the same value as the first, K_1. With both the map and Gauss programs, the log of the cumulative constant for the bis complex ($= \log K_1 + \log K_2$) was reduced to about the value of the first stepwise constant, and the estimated standard error in this constant was very large, indicating that it should be set equal to zero. Its inclusion did not reduce the weighted variance. As has been indicated by the earlier studies, there appears to be little tendency for the tin in these dialkyltin compounds to attain a coordination number greater than four. Similar procedures as outlined here could prove quite useful in testing various hypotheses for other systems and could perhaps be used to obtain values for mixed complexing constants.

Calculations of the distribution of the total dimethyltin among the various species for the phenanthroline and acetylacetone systems immediately verified the conclusion that these ligands did not compete favorably with the hydroxide ion. The maximum fraction in the form of the phenanthroline complex was *ca.* 20% while the corresponding value for acetylacetone was but 15%, both at pH values where almost 50% of the dimethyltin was in the form of the monohydroxo complex.

Acknowledgments.—The authors wish to express their appreciation to Professor Z Z. Hugus, Jr., for many helpful discussions and for a matrix inversion subroutine, to Professor L. G. Sillén and Dr. Å. Olin for information on "pit mapping," to Dr. R. M. Rush for copies of ORNL programs, and to Professor M. L. Stein and the Numerical Analysis Laboratory of the University of Minnesota for free computer time.

CONTRIBUTION FROM THE INSTITUTE FOR
ATOMIC RESEARCH AND DEPARTMENT OF CHEMISTRY,
IOWA STATE UNIVERSITY, AMES, IOWA

The Nature of R_2Sn Compounds[1a]

BY D. H. OLSON AND R. E. RUNDLE[1b]

Received July 15, 1963

From the information available on inorganic compounds of divalent tin, one would expect to find organic divalent tin compounds of the type R_2Sn. Unless hindered by steric factors,[2] monomeric R_2Sn compounds tend to polymerize rapidly. With the exception of dicyclohexyltin,[3] no monomeric R_2Sn alkyl species have been reported. A few aryl R_2Sn compounds have been reported to be monomeric, but only when freshly prepared.[2,4–6] Recent chemical work on dimethyltin, diethyltin, and diphenyltin has indicated that polymerization results in the formation of tin–tin bonds and of tetravalent tin. Our X-ray work, reported here, on a diphenyltin polymer has verified this type of polymerization.

Brown and Morgan have reported that $(CH_3)_2Sn$, prepared by reaction of $(CH_3)_2SnCl_2$ with Na in liquid NH_3, has two molecular forms, linear chains of 10–100 catenated tin atoms and a six-membered ring of tin atoms, *i.e.*, dodecamethylcyclohexastannane.[7] Recently, Neumann and Neumann and Konig reported the preparation of several R_2Sn compounds containing five to eight tin–tin bonds in a ring or chain. By decomposing $(C_2H_5)_2SnH_2$ with amines, Neumann[8] prepared $((C_2H_5)_2Sn)_n$, where n is in the range 6–9 and $n = 7$ is the main product. From degradation results and analysis of the n.m.r. spectrum, he has concluded that the structure of $((C_2H_5)_2Sn)_7$ is a seven-membered ring containing tin–tin bonds. In a similar manner Neumann and Konig[9] have prepared $H-((C_6H_5)_2Sn)_6-H$, $((C_6H_5)_2Sn)_6$, and $((C_6H_5)_2Sn)_5$. Based upon the above diethyltin studies and molecular weight and degradation results, they propose an open chained structure for $H-((C_6H_5)_2Sn)_6-H$ and five- and six-membered ring structures for $((C_6H_5)_2Sn)_5$ and $((C_6H_5)_2Sn)_6$, respectively. The X-ray work to be described verifies this six-membered ring structure.

Experimental

The following procedure, which was developed by Kuivila, *et al.*,[10] was used in preparing single crystals of diphenyltin for

---

(1) (a) Contribution No. 1345. Work was performed in the Ames Laboratory of the U. S. Atomic Energy Commission. (b) Deceased, October 9, 1963.

(2) G. Baker and R. Gelius, *Ber.*, **91**, 829 (1958).

(3) E. Krause and Pohland, *ibid.*, **57**, 532 (1924).

(4) E. Krause and R. Becker, *ibid.*, **53**, 173 (1920).

(5) K. A. Jensen and N. Clauson-Kaas, *Z. anorg. allgem. Chem.*, **250**, 277 (1943).

(6) H. G. Kuivila and O. F. Beumel, Jr., *J. Am. Chem. Soc.*, **80**, 3250 (1958).

(7) T. L. Brown and G. L. Morgan, *Inorg. Chem.*, **2**, 736 (1963).

(8) W. P. Neumann, *Angew. Chem.*, **74**, 122 (1962).

(9) W. P. Neumann and K. Konig, *ibid.*, **74**, 215 (1962).

(10) H. G. Kuivila, A. K. Sawyer, and A. G. Armour, *J. Org. Chem.*, **26**, 1426 (1961).

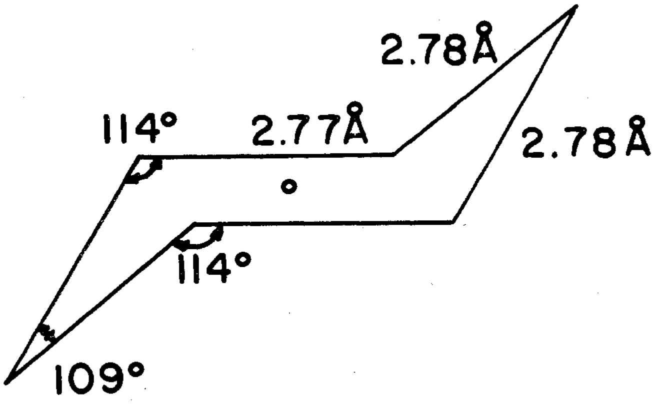

Fig. 1.—Confirmation of tin atoms in $((C_6H_5)_2Sn)_6$.

X-ray study. A light yellow powder, obtained by adding methanol to an ether solution of diphenyltin dihydride, was dissolved in dimethylformamide. The resulting crystals were recrystallized in *m*-xylene. The well-formed, clear, colorless crystals which resulted are monoclinic with a = 12.05, b = 18.17, c = 18.55 Å., and γ = 102.7°. $P2_1/b$ is the probable space group. There are twelve diphenyltin units and four xylene molecules per unit cell; the calculated density is 1.55 g./cc. *vs.* 1.55 g./cc. observed. Complete three-dimensional data were collected on a G.E. XRD-5 crystal orienter using Mo Kα irradiation. These data were corrected for background, streaking, absorption, and Lorentz-polarization factors. The three independent tin positions were obtained from a three-dimensional Patterson map and refined to a reliability index of 27% using 607 reflections with 2θ less than 25°. The positions of all carbon atoms were found from subsequent Fourier maps. The atomic parameters, including anisotropic thermal parameters, were refined using the block diagonal least squares method. The final R values for all data and for observed reflections only are 15.9 and 7.2%, respectively. Final analysis of this structure is still in progress. A full account of this X-ray work is to be published elsewhere.

Discussion

The three asymmetric tin atoms are related to three more by a center of symmetry forming a six-membered ring with the chair configuration. The tin–tin bonds (Fig. 1) have lengths of 2.77, 2.78, and 2.78 Å., compared with the tin–tin distance of 2.80 Å. in gray tin, indicating normal tetrahedral covalent bonds. Two phenyl groups emanate from each tin atom at approximately tetrahedral angles. The xylene molecule is not involved in any type of π-bonding with the tin atoms.

It is not to be expected that R_2Sn compounds will remain monomeric, since this would leave a valence orbital of tin vacant and is contrary to valence principles which have now been established.[11] It is interesting to note that for R_2Sn compounds, where R is an organic group, the tendency to use all valence orbitals leads to tin–tin bonds and to tetravalent tin. In inorganic compounds,[12] it is most usual to find that tin(II) uses its three 5p-orbitals to form three electron-pair bonds either by forming halogen bridges or by accepting electron pairs from such donors as water.[12] Without tin–tin bonds in R_2Sn compounds, the extra valence orbital could only be filled by some sort of bond delocalization as, for example, in trimethylaluminum,[13] and in organometallic tin compounds it is apparently energetically more favorable to form electron-pair tin–tin bonds. In inorganic compounds, where unshared pairs abound, tin(II) is stabilized by acting as an electron acceptor for some of these unshared pairs to form nondelocalized electron pair bonds.

Acknowledgment.—We wish to thank Professor H. G. Kuivila for supplying us with crystalline samples of several modifications of diphenyltin.

[11] (a) R. E. Rundle, *J. Am. Chem. Soc.*, **69**, 1327, 2075 (1947); (b) *J. Chem. Phys.*, **17**, 671 (1949).

[12] SnS: W. Hofmann, *Z. Krist.*, **92**, 161 (1935); SnSe: A. Okazaki and I. Ueda, *J. Phys. Soc. Japan*, **11**, 470 (1956); $SnCl_2$: J. M. Van den Berg, *Acta Cryst.*, **14**, 1002 (1961); $SnCl_2 \cdot 2H_2O$: B. Kamenar and D. Grdenic, *J. Chem. Soc.*, 3954 (1961); $K_2SnCl_4 \cdot H_2O$: B. Kamenar and D. Grdenic, *J. Inorg. Nucl. Chem.*, **24**, 1039 (1962); $SnSO_4$: P. J. Rentzeperis, *Z. Krist.*, **117**, 431 (1962). See also R. E. Rundle and D. H. Olson, *Inorg. Chem.*, submitted for publication.

[13] P. H. Lewis and R. E. Rundle, *J. Chem. Phys.*, **21**, 986 (1953).

CONTRIBUTION FROM THE ROHM AND HAAS COMPANY,
REDSTONE ARSENAL RESEARCH DIVISION,
HUNTSVILLE, ALABAMA

Further Nuclear Magnetic Resonance and Electron Paramagnetic Resonance Studies on the System $N_2F_4 \rightleftharpoons 2NF_2$

BY RAYMOND ETTINGER AND CHARLES B. COLBURN

Received July 19, 1963

Since the first synthesis of tetrafluorohydrazine in 1958[1] and the observation of the dissociative equilibrium between tetrafluorohydrazine and the difluoramino free radical,[2,3] considerable interest has been shown in many of the physical properties of this system. We wish to report here some further observations on the n.m.r. and e.p.r. spectra of this system.

E.p.r. Spectrum

The first e.p.r. spectrum of NF_2 was observed in the gas phase at approximately 40 mm. pressure and over the temperature range 340–435°K.[4] The spectrum observed was a single broad line with a g-value of 2.010 and a peak to peak line width of 104 gauss. Recently, the spectrum of NF_2 in solid argon has been observed.[5] In the solid matrix, Adrian and co-workers were able to observe some hyperfine structure; in particular, a center triplet arising from interaction with the N^{14} nucleus (16 gauss) and corresponding to the NF_2 spin state in which the two fluorine nuclei are antiparallel. Two side lines were also found about 47 gauss from the center line, but, like the outer lines of the triplet, they

[1] C. B. Colburn and A. Kennedy, *J. Am. Chem. Soc.*, **80**, 5004 (1958).

[2] C. B. Colburn and F. A. Johnson, *J. Chem. Phys.*, **33**, 1869 (1960).

[3] F. A. Johnson and C. B. Colburn, *J. Am. Chem. Soc.*, **83**, 3043 (1961).

[4] L. H. Piette, F. A. Johnson, K. A. Booman, and C. B. Colburn, *J. Chem. Phys.*, **35**, 1481 (1961).

[5] F. J. Adrian, E. L. Cochran, and V. A. Bowers, "Free Radicals in Inorganic Chemistry," Advances in Chemistry Series, No. 36, American Chemical Society, Washington, D. C., 1962, p. 50.