the finite μ_c dipole component. Such Stark effects were observed for the $M = 1$ transitions of $1_{01} \rightarrow 2_{02}$ and $1_{11} \rightarrow 2_{12}$ and the $M = 1$ and $M = 2$ transitions of $2_{02} \rightarrow 3_{03}$ and $2_{12} \rightarrow 3_{13}$. These could be fitted semiquantitatively using the treatment of Golden and Wilson[11] for the case of two interacting levels close and the rest far removed. Also, the $M = 1$ transition of $1_{01} \rightarrow 2_{02}$ was measured quantitatively and checked against calculations. The circles in Figure 1 are the experimental values and the solid curve was calculated using the dipole components reported above. The agreement is within the uncertainties of the experiment.

Discussion

It is interesting to compare the structure of HF_2PO to that determined[5] for HF_2P where $d(PF) = 1.582 \pm 0.002$ Å, $d(PH) = 1.412 \pm 0.006$ Å, $\angle FPF = 99.0 \pm 0.2°$, and $\angle HPF = 96.3 \pm 0.5°$. Several qualitative structure models can be examined for consistency in rationalizing the differences in the two structures. The most popular theories to consider are those respectively emphasizing (1) electron-pair repulsions,[12] (2) changes in hybridization,[13] (3) d-orbital participation,[14] (4) formal charges, and (5) valence-bond resonance structures. Considering the bond lengths, each of the above models can account for the shorter d(PH) and d(PF) observed in HF_2PO. The first two models also directly include angle variations and can be used to rationalize the increase in the angles observed in HF_2PO. Upon examination of the basis of the various models, the concept of the electronegativity of the atoms attached to phosphorus is fundamental to each. It is this common idea which prevents the HF_2P–HF_2PO system from providing a meaningful distinction between the various models on the basis of the direction of change of their structural parameters.

The large value of the dipole moment for HF_2PO supports a model with a polar PF and even more polar PO bond. This agrees with inferences on the nature of the PO bond from other evidence including reactivity.[15] A prediction of the dipole moment of HF_2PO from bond moments supports the orientation of the dipole moment in Figure 3. Employing bond moments based on PF_3,[16] PH_3,[17] and PF_3O[18] and assuming that F and O are negative and H is positive with respect to phosphorus, the calculated dipole moment is only 0.08 D too small and the orientation is almost exactly that shown in Figure 3. Owing to the obvious differences in electronic structure between the phosphorus compounds with three or four attached atoms, the close agreement is probably fortuitous and does not necessarily imply that the bond dipoles in all four compounds are quite identical. While the value for the PO bond dipole (~2.8 D) seems large on an absolute basis, Phillips, *et al.*,[19] have pointed out that on a comparative basis it is smaller than the NO bond dipole in R_3NO compounds and so does not negate models employing a PO multiple bond.

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Mössbauer Spectra and Electric Dipole Moments of Tin(IV) Compounds Containing the Thiocyanate Group

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Mössbauer and infrared spectra indicate that both $(n\text{-}C_4H_9)_2Sn(NCS)_2$ and $(C_6H_5)_2Sn(NCS)_2$ are bridged polymeric solids with the hydrocarbon groups *trans* to each other. Quadrupole splittings and electric dipole moments reveal a *trans* arrangement of butyl groups in the dipyridyl and *o*-phenanthroline complexes of $(C_4H_9)_2Sn(NCS)_2$ and a *cis* arrangement of phenyl groups in the corresponding complexes of $(C_6H_5)_2Sn(NCS)_2$. This *cis* arrangement is accompanied by large negative isomer shifts relative to a Pd–Sn source at 80°K. Physical measurements suggest a bridged dimer for solid $(C_4H_9)_2Sn(NCS)(C_9H_6NO)$ and 5-coordinated tin in $(C_6H_5)_2Sn(NCS)(C_9H_6NO)$. Dipole moments indicate a *cis* arrangement of hydrocarbon groups for both compounds in benzene solution. Isomer shifts reveal an order of bond polarity Sn–O > Sn–NCS > Sn–Cl.

As a follow-up on Mössbauer and electric moment studies of the effect of complex formation with donor ligands on electron distribution in di-*n*-butyltin dihalides,[3] dibutyl- and diphenyltin diisothiocyanates have been investigated. This study affords a comparison of the relative geometries of the complexes, the relative polarities of the Sn–Cl and Sn–N bonds,

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and the polarizabilities of the halogens and the NCS group. Mössbauer spectra of diphenyltin dichloride and its complexes with *o*-phenanthroline and α,α-dipyridyl have been obtained for comparison.

Wada and Okawara[4] have obtained the spectra of a number of $R_2Sn(NCS)_2$ compounds and their complexes with dipyridyl and concluded that they are isothiocyanates, with Sn–N bonding. The spectra, high melting points, and very low solubilites in nonpolar solvents of the dialkyltin diisothiocyanates suggested bridging through sulfur in the solid compounds, resulting in 6-coordinate tin atoms.

Experimental Section

Preparation and Purification of Compounds.—Diphenyltin dichloride and di-*n*-butyltin dichloride were obtained from Alfa Inorganics, Inc. 8-Hydroxyquinoline, *o*-phenanthroline, and α,α-dipyridyl were supplied by Aldrich Chemical Co. Potassium thiocyanate and sodium thiocyanate were Baker Analyzed reagents. Thiophene-free benzene, supplied by Fisher Scientific Co., was refluxed over phosphorus pentoxide for several hours before being distilled. All other solvents were CP grade or better.

Di-*n*-butyltin diisothiocyanate and **diphenyltin diisothiocyanate** were prepared by the method of Seyferth and Rochow,[5] by mixing hot absolute ethanol solutions of diorganotin dihalide and sodium or potassium thiocyanate in a 1:2 ratio. The filtrates obtained were evaporated under vacuum and recrystallized from benzene. The melting point of $(C_4H_9)_2Sn(NCS)_2$ was 141–142° (lit. mp 144–145°,[5] 142–142.5°[6]). $(C_6H_5)_2Sn(NCS)_2$ decomposes above 155°.

Anal. Calcd for $C_{10}H_{18}N_2S_2Sn$: C, 34.40; H, 5.20. Found: C, 34.86; H, 5.31. Calcd for $C_{14}H_{10}N_2S_2Sn$: C, 43.21; H, 2.59; S, 16.48. Found: C, 43.51; H, 2.67; S, 15.69.

The preparation of the chelate complex of α,α-dipyridyl with **di-*n*-butyltin diisothiocyanate** is described in the literature;[6,7] the ***o*-phenanthroline** complex of **di-*n*-butyltin diisothiocyanate** and the **α,α-dipyridyl** and ***o*-phenanthroline** complexes of **diphenyltin diisothiocyanate** were prepared in a similar manner by mixing absolute ethanol solutions of the diorganotin diisothiocyanate and the ligand in a 1:1 ratio. The complexes formed quickly as white precipitates, were filtered under vacuum, washed with absolute ethanol and light petroleum ether (bp 30–60°), and dried under vacuum at 56° for several hours. Melting points: $(C_4H_9)_2Sn(NCS)_2(C_{10}H_8N_2)$, 150–151° (lit. 150–150.5°,[6] 152.5–153°[7]); $(C_4H_9)_2Sn(NCS)_2(C_{12}H_8N_2)$, 208–210°; $(C_6H_5)_2Sn(NCS)_2(C_{10}H_8N_2)$, 195–197°; $(C_6H_5)_2Sn(NCS)_2(C_{12}N_8N_2)$, above 210°.

Anal. Calcd for $C_{20}H_{26}N_4S_2Sn$: C, 47.54; H, 5.19. Found: C, 47.51; H, 5.26. Calcd for $C_{22}H_{26}N_4S_2Sn$: C, 49.91; H, 4.95. Found: C, 50.03; H, 5.08. Calcd for $C_{24}H_{18}N_4S_2Sn$: C, 52.87; H, 3.34. Found: C, 53.20; H, 3.75. Calcd for $C_{26}H_{18}N_4S_2Sn$: C, 54.89; H, 3.19; S, 11.25. Found: C, 54.91; H, 3.49; S, 10.49.

Di-*n*-butyltin isothiocyanate oxinate was prepared by the reaction of di-*n*-butyltin diisothiocyanate and di-*n*-butyltin dioxinate. The latter compound was prepared by adding an absolute ethanol solution of di-*n*-butyltin dichloride to an ethanol solution of 8-hydroxyquinoline (1:2) to which an ethanol solution of sodium hydroxide had been previously added—bright yellow crystals were obtained from the filtrate. Di-*n*-butyltin diisothiocyanate was added slowly and with constant stirring to di-*n*-butyltin dioxinate in a 1:1 ratio, using benzene–ethanol as the solvent. The oily product obtained after evaporation of the solvent under vacuum was crystallized (yellow-brown) by immersion in Dry Ice–acetone. $(C_4H_9)_2SnNCS(C_9H_6NO)$ decomposed above 74°.

Anal. Calcd for $C_{18}H_{24}N_2OSSn$: C, 49.70; H, 5.56; S, 7.37. Found: C, 49.14; H, 5.54; S, 6.57.

Diphenyltin isothiocyanate oxinate was prepared by the reaction of diphenyltin chloride oxinate and potassium thiocyanate. Diphenyltin chloride oxinate was prepared by adding diphenyltin dichloride to 8-hydroxyqunoline slowly and with stirring using absolute ethanol as the solvent. An orange precipitate formed quickly, was filtered, washed with ethanol and petroleum ether, and dried under vacuum at 56° for several hours. The diphenyltin chloride oxinate was then dissolved in benzene–ether and added very slowly and with constant stirring to a methanol solution of potassium thiocyanate. The solvent was evaporated, benzene was added to precipitate the remaining potassium salt, and the filtrate was evaporated under vacuum. Yellow-orange crystals were obtained by immersion of the oily product in Dry Ice–acetone. $(C_6H_5)_2SnNCS(C_9H_6NO)$ decomposed above 76°.

Anal. Calcd for $C_{22}H_{16}N_2OSSn$: C, 55.60; H, 3.39; S, 6.75. Found: C, 56.14; H, 4.08; S, 6.30.

Dielectric Constants.—These were obtained as in previous investigations,[8] using an oscillator similar to that described by Estok.[9] The relative precision for the values listed in Table I is considered to be ±0.0005. The $\Delta\epsilon/wf_2$ ratios listed in Table II are average values for the concentrations studied. Electric moments were calculated by the method of Higashi,[10] using a value of 0.8481 for β.[11] Density measurements were carried

TABLE I

DIELECTRIC CONSTANTS OF BENZENE SOLUTIONS AT 25°

$1000wf_2$		$1000wf_2$	
$(C_4H_9)_2Sn(NCS)_2$		$(C_6H_5)_2(NCS)_2$	
0.00	(2.2760)	0.000	(2.2760)
2.03	2.2960	0.634	2.2781
2.43	2.3025	0.840	2.2805
3.12	2.3135	1.012	2.2819
$(C_4H_9)_2Sn(NCS)_2$(dipy)		$(C_6H_5)_2Sn(NCS)_2$(dipy)	
0.787	2.3029	3.76	2.3101
1.59	2.3373	5.14	2.3280
2.35	2.3624	7.65	2.3510
3.12	2.3911		
$(C_4H_9)_2Sn(NCS)_2$(o-phen)		$(C_6H_5)_2Sn(NCS)_2$(*o*-phen)	
0.669	2.3046	0.735	2.2781
0.771	2.3097	0.825	2.2795
0.905	2.3141	1.193	2.2808
1.149	2.3253	1.497	2.2836
$(C_4H_9)_2SnNCS$(Ox)		$(C_6H_5)_2SnNCS$(Ox)	
3.86	2.3339	6.06	2.3257
5.19	2.3503	7.23	2.3366
6.88	2.3783	8.90	2.3521
$(C_4H_9)_2Sn(Ox)_2$		$(C_6H_5)_2Sn(Ox)_2$	
18.94	2.3584	9.13	2.3253
21.50	2.3704	14.43	2.3581
33.16	2.4236	18.52	2.3822
		23.76	2.4151
$(C_6H_5)_2SnCl$(Ox)			
10.46	2.3300		
13.93	2.3493		
15.05	2.3561		
22.69	2.4000		

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Table II

Isomer Shifts (δ) Relative to a Palladium–Tin Alloy Source, Quadrupole Splittings (ΔE_Q), and Electric Moments (μ) at 25°

Compound	No.	δ, mm/sec	ΔE_Q, mm/sec	% absn	$\Delta\epsilon/wf_2$	μ_H, D	Inferred coordn no.	Inferred arrangement of hydrocarbon groups
$(C_4H_9)_2Sn(NCS)_2$	**1**	+0.02	3.90	8.4	12.1	6.2 ± 0.2	6^b	*trans*
$(C_6H_5)_2Sn(NCS)_2$	**2**	−0.07	3.96	9.9	8.5	5 ± 0.5	6^b	*trans*
$(C_4H_9)_2Sn(NCS)_2(dipy)^a$	**3**	−0.09	4.04	7.4	38.5	13.3 ± 0.1	6	*trans*
$(C_6H_5)_2Sn(NCS)_2(dipy)$	**4**	−0.70	2.13	4.7	10.3	7.2 ± 0.2	6	*cis*
$(C_4H_9)_2Sn(NCS)_2(o\text{-phen})^a$	**5**	−0.10	4.18	6.3	46	15.0 ± 0.2	6	*trans*
$(C_6H_5)_2Sn(NCS)_2(o\text{-phen})$	**6**	−0.71	2.34	9.5	7	6 ± 0.5	6	*cis*
$(C_4H_9)_2Sn(NCS)(Ox)$	**7**	−0.19	3.25	8.6	15.3	7.8 ± 0.1	6^c	*trans*^{c}
$(C_6H_5)_2Sn(NCS)(Ox)$	**8**	−0.54	2.48	2.4	8.79	6.20 ± 0.03	5	*cis*
$(C_6H_5)_2SnCl(Ox)$	**9**	−0.44	2.39	5.5	5.51	4.76 ± 0.04	5	*cis*
$(C_6H_5)_2Sn(Ox)_2$	**10**	−0.80	1.63	8.9	5.87	5.48 ± 0.07	6	*cis*
$(C_4H_9)_2Sn(Ox)_2$	**11**	−0.59	2.05	6.3	4.52	4.63 ± 0.03	6	*cis*
$(C_6H_5)_2SnCl_2$	**12**	−0.15	2.76	9.5			4	
$(C_6H_5)_2SnCl_2(o\text{-phen})$	**13**	−0.31	3.37	5.2			6	*trans*
$(C_6H_5)_2SnCl_2(dipy)$	**14**	−0.30	3.39	9.5			6	*trans*

[a] These measurements were made with the source at room temperature; all other measurements were made with both source and absorber at 80°K, using a Pd filter. [b] Tetrahedral in benzene solution. [c] Five-coordinate in benzene solution with *cis* arrangement of butyl groups.

out on benzene solutions of $(C_4H_9)_2Sn(Ox)_2$ and $(C_6H_5)_2Sn(Ox)_2$ (Ox = oxine = C_9H_6NO); these yielded $\Delta d/wf_2$ ratios of 0.344 and 0.404 g/ml, respectively. Molecular weights were obtained for four compounds in benzene solution using a Mechrolab 302 vapor pressure osmometer. Infrared spectra were obtained with a Perkin-Elmer 421 spectrometer.

Mössbauer Spectra.—Instrumentation, including the calibration, and the computer program were described previously.[3] In the present investigation measurements were made with both source and absorber at 80°K, using a Texas Instruments cryoflask, Model CLF-3, modified and adapted by Nuclear Science and Engineering Corp. for use with the Model AM-1 Mössbauer effect spectrometer. The per cent absorption was greatly improved by using a palladium filter, 57 mg/cm², in front of the counter tube; this reduced the tranmission of X-rays by 50%. Only 0.03–0.07 g of finely divided absorber, placed between two sheets of collodion-coated aluminum foil, was required for the sample holder provided with the cryoflask. All values are reported to an accuracy of ±0.07 mm/sec, with relative precision of ±0.05 mm/sec.

Discussion of Results

The dipole moments, isomer shifts relative to the palladium–tin source, and quadrupole splittings obtained for the compounds studied are listed in Table II. The Mössbauer spectrum of $(C_4H_9)_2Sn(NCS)_2(o\text{-phen})$ is illustrated in Figure 1. As reported previously,[3] a comparison of dipole moments obtained by the calculations of Higasi with those from the Lefevre and Vine modifications of the Hedestrand equation indicate that density and index of refraction measurements are unnecessary. A further check for the values obtained by both methods for $(C_4H_9)_2Sn(Ox)_2$ and $(C_6H_5)_2Sn(Ox)_2$ showed that they agreed within the listed experimental errors. The moment of 5.48 D obtained for $(C_6H_5)_2Sn(Ox)_2$ compares with a reported value of 5.3 D.[12]

X-Ray studies have revealed M–NCS–M bridging in copper, cobalt,[13] and cadmium[14] complexes of the type $M(NCS)_2L_2$. Infrared evidence for M–NCS–M bridging includes the values 2096, 2088, and 2096 cm^{-1}, respectively, for the CN stretching frequencies in the above three compounds.[15] The strong absorption at 2100 cm^{-1} in the spectrum of solid diphenyltin diisothiocyanate (compared to 2020–2040 cm^{-1} for the solid monomeric 6-coordinate complexes with dipyridyl and *o*-phenanthroline) indicates –NCS– bridging as in the dibutyl compound.[4] The increase in quadrupole splitting from the chlorides to the isothiocyanates also suggests bridging in the latter solids, with the hydrocarbon groups *trans* to each other.

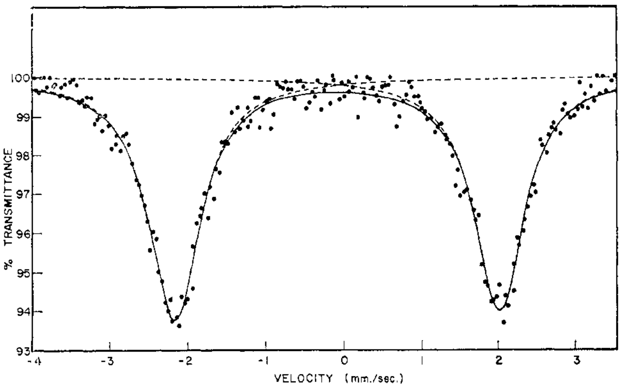

Figure 1.—Mössbauer spectrum of $(C_4H_9)_2Sn(NCS)_2(o\text{-phen})$.

The more positive isomer shifts for the bridged $R_2Sn(NCS)_2$ polymers relative to the values for the corresponding dipyridyl and *o*-phenanthroline complexes suggest that the bridging sulfur atom affords a greater electron release than do the nitrogen donors. This increase in s-electron density could result in part from S=Sn bonding involving tin 4d electrons, which would decrease the shielding of the s electrons. The algebraic decrease in isomer shift on replacing butyl by phenyl groups is only 0.09 mm/sec for the isothiocyanates as compared to 0.23 mm/sec for the chlorides,

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suggesting that the increased s-electron density at the tin atom in the sulfur-bridged compounds results in some $^{+}Sn{=}C_6H_5^{-}$ bond character.

The CN absorption band for each of the isothiocyanates in Table II in benzene solution is in the 2005–2035-cm^{-1} region, indicating the lack of –NCS– bridging in solution. The absence of any significant regular variation in $\Delta\epsilon/wf_2$ ratios with concentration indicates that the compounds listed in Table I are neither associated nor dissociated in these solutions and that the electric moments listed in Table II are for the undissociated monomers. Values of molecular weights obtained in benzene solution for $(C_4H_9)_2SnNCS(Ox)$, $(C_4H_9)_2Sn(NCS)_2(dipy)$, $(C_6H_5)_2Sn(NCS)_2(dipy)$, and $(C_6H_5)_2Sn(NCS)_2(o\text{-phen})$ are 454, 490, 504, and 531, respectively, compared to formula weights of 435, 505, 545, and 569.

The increase in dipole moment from $(C_4H_9)_2SnCl_2$ to $(C_4H_9)_2Sn(NCS)_2$ is 1.8 D, compared to a difference of 1.4 D for the tetrahedral bis-pyridine complexes of $Zn(NCS)_2$ and $ZnCl_2$,[16] indicating similar polarizabilities for tin(IV) and zinc(II). The moment of $(C_4H_9)_2Sn(NCS)_2(o\text{-phen})$, 15.0 D—the largest value of which we are aware for a coordination compound—indicates that the butyl groups are *trans* to each other. From the observed moments of $(C_4H_9)_2SnCl_2(o\text{-phen})$, $(C_4H_9)_2SnCl_2$, and $(C_4H_9)_2Sn(NCS)_2$—11.3,[3] 4.37,[3] and 6.2 D—a moment of 13.5 D is calculated for the above complex. The difference between this value and 15 D indicates an increased $^{+}N{\equiv}CS^{-}$ character for the isothiocyanate group in the octahedral relative to the tetrahedral compound. This is expected, as the formation of the two N—Sn dative bonds results in an increased polarity for the Sn—NCS bond. The large moment of the dipyridyl complex, 13.3 D, indicates a *trans* arrangement of the butyl groups in this compound in solution also. The moment of this complex is expected to be smaller than the value for the phenanthroline complex because of the greater flexibility of dipyridyl—possible rotation and bending about the bond joining the two rings—and increased resonance (involving electron release to the nitrogen atoms) in *o*-phenanthroline because of the extra double bond, but the difference in moment, 1.7 D, is larger than anticipated. The large quadrupole splittings observed for these two complexes, 4.18 and 4.04 mm/sec, indicate a *trans* configuration for both compounds in the solid state. The average algebraic decrease in isomer shifts on replacing chlorine atoms by isothiocyanate groups in the dipyridyl and phenanthroline complexes, 0.15 mm/sec, reveals that the Sn–N bond is more polar than the Sn–Cl bond.

The relatively small moments obtained for the phenanthroline and dipyridyl complexes of $(C_6H_5)_2Sn(NCS)_2$, 6 and 7.2 D, indicate that the phenyl groups are *cis* in these complexes. Values of 12.5 ± 1 and 6.5 ± 1 D are calculated for the moments of the *o*-phenanthroline complex with the phenyl groups *cis* and the NCS groups *cis* and *trans*, respectively. The observed moments indicate that the NCS groups are *trans* in solution.

Recent evidence suggests that for R_2SnX_4 complexes $\Delta E_Q(\text{R } trans) = 2\Delta E_Q(\text{R } cis)$.[17] The observed quadrupole splittings of the *o*-phenanthroline and dipyridyl complexes of $(C_6H_5)_2Sn(NCS)_2$, 2.34 and 2.13 mm/sec, indicate a *cis* arrangement of the phenyl groups in these two solid complexes. The splittings do not reveal whether the isothiocyanate groups are *cis* or *trans*, but the *trans* arrangement in solution is very likely preserved in the solids. The reason for the difference in configuration of the phenyl and butyl compounds is not evident. In contrast, the splittings for $(C_6H_5)_2SnCl_2(o\text{-phen})$ and $(C_6H_5)_2SnCl_2(dipy)$ are 3.37 and 3.39 mm/sec, suggesting a *trans* arrangement of phenyl groups in these complexes. The sharp Mössbauer spectra rule out solid mixtures of geometric isomers.

The large algebraic decrease in isomer shift for the phenanthroline and dipyridyl complexes with $R_2Sn(NCS)_2$ on replacing butyl by phenyl groups, 0.6 mm/sec compared to 0.35 mm/sec for the corresponding chlorides, suggests appreciable $^{+}C_6H_5{=}Sn^{-}$ character in the isothiocyanate complexes. This appears to be related to the *cis* arrangement of the phenyl groups, as the decrease is only 0.09 mm/sec from $(C_4H_9)_2Sn(NCS)_2$ to $(C_6H_5)_2Sn(NCS)_2$, both of which appear to have bridged *trans*-octahedral configurations.

$(C_6H_5)_2Sn(NCS)(Ox)$ is an example of a 5-coordinate tin complex containing a thiocyanate group. Absorption by this compound at 2025 cm^{-1} in KBr compared to 2035 cm^{-1} in benzene solution indicates that –NCS– bridging does not occur in the solid. The isomer shift for this compound, −0.54, compared to −0.44 mm/sec for the corresponding chloride, is further evidence of a greater polarity for the Sn–NCS than for the Sn–Cl bond. The quadrupole splittings for these two compounds are similar, suggesting similar configurations. The dipole moments of these compounds in solution, 6.20 and 4.79 D for the isothiocyanate and chloride, respectively, suggest similar configurations in benzene solution. Nmr, ir, and uv studies of compounds of the type $R_2SnX(Ox)$[18–20] have been interpreted as indicating monomers in solution containing pentacoordinated tin atoms having a probable trigonal-bipyramidal configuration with the R groups *trans*. However, an X-ray study of $(CH_3)_2Sn(Ox)_2$[21] indicates an N–Sn–O angle of about 74° in the chelate ring. Such a bond angle in the 5-coordinate tin compounds would result in appreciable distortion of the bipyramidal configuration. Calculated moments for $R_2SnX(Ox)$, taking 2.8 D as the Sn–O bond moment and neglecting the contribution of the small Sn–C bond moment, for the configurations listed in Figure

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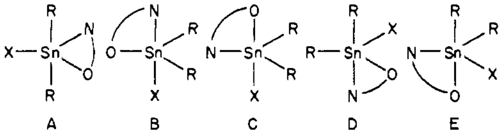

Figure 2.—Possible configurations for $R_2SnX(Ox)$.

2 are 8.2, 9.5, 4.8, 6, and 8.5 D for X = NCS and 7.2, 7.9, 4.2, 5.1, and 7 D for X = Cl. The experimental values of 6.20 and 4.79 D are indicative of a configuration similar to D in benzene solution.

Absorption at 2065 cm^{-1} by $(C_4H_9)_2Sn(NCS)(Ox)$ in a KBr disk compared to 2035 cm^{-1} in benzene solution strongly suggests –NCS– bridging in the solid (probable dimer formation) resulting in 6-coordination for tin. The quadrupole splitting, 3.25 mm/sec, suggests a *trans* arrangement for the butyl groups. The molecular weight obtained for this compound in benzene solution is 454, compared to 435 for the monomer, indicating that these bridges are broken in solution; the lack of a shoulder on the high-frequency side of the 2035 cm^{-1} absorption indicates a negligible percentage of dimers in solution. Dimerization rather than polymerization in the solid is indicated by the greater solubility and lower melting point than observed for $(C_4H_9)_2Sn(NCS)_2$. The dipole moment of $(C_4H_9)_2Sn(NCS)(Ox)$, 7.8 D, suggests a configuration similar to E (A is ruled out because of the required 120° NSnO angle) in benzene solution.

The $N \rightarrow Sn$ dative bonding in $R_2Sn(Ox)_2$ is expected to be similar to that in $R_2Sn(NCS)_2$(*o*-phen) and $R_2Sn(NCS)_2$(dipy). The more negative isomer shifts obtained for compound **10** than for **4** and **6** and for compound **11** than for **3** and **5** (Table II) indicate that the Sn–O bond is more polar than the Sn–NCS bond. The small quadrupole splittings obtained for the $R_2Sn(Ox)_2$ compounds indicate that the phenyl and butyl groups are not in *trans* positions, in line with the 111° CSnC bond angle found by Schlemper[21] in $(CH_3)_2Sn(Ox)_2$. The electric moments obtained for $(C_4H_9)_2Sn(Ox)_2$ and $(C_6H_5)_2Sn(Ox)_2$ indicate a *cis* arrangement of phenyl and butyl groups in these compounds in solution.

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A Study of Some Germanium Porphins and Some Silicon and Germanium Phthalocyanines[1]

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The nuclear magnetic resonance spectra of two unsymmetrically substituted silicon phthalocyanines have been studied. The results indicate that the shielding furnished by the ring drops off without major reversals in the region above its surface and near its fourfold axis. In addition, the spectra of two germanium porphins and two analogous germanium phthalocyanines have been compared. The results from this work show that the porphin ring offers more shielding than the phthalocyanine ring. An attempt to interpret this in terms of aromaticity is made.

In a number of recent papers describing nmr work on porphyrins and porphyrin-like compounds, the shielding region above the ring surface has figured prominently. This is true, for example, of the work done by Abraham and coworkers[2] on the π–π association of coproporphyrin I, II, III, and IV tetramethyl esters and the work done by Katz and colleagues[3] on the coordination association of chlorophylls and chlorophyll-like substances. It is also true of the work of Storm and Corwin[4] on the pyridine and methanol complexes of magnesium etioporphyrin II and magnesium *meso*-tetraphenylporphin and the work of Caughey and Iber[5] on N-methyletioporphyrin II and N-ethyletioporphyrin II. The shielded region has also figured prominently in the alkyl-, aryl-, and acylcobalt(III) etioporphyrin I work of Johnson and coworkers,[6] the methylcobalt(III) phthalocyanine work of Day, Hill, and Price,[7] and the siloxysilicon, -germanium, and -tin phthalocyanine work of this laboratory.[8]

Because of the importance of this shielded region in porphyrin-like compounds there is a need for a more detailed understanding of the region for various typical ring systems. The present paper deals with two aspects of this need, one part of it being concerned with the way in which the shielding falls off with distance from

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