

emission of the Reineckate ion is not so clear. The lower charge should lead to less hydration than for $[\text{Cr}(\text{NCS})_6]^{3-}$, but to counteract this effect is the fact that there are fewer conducting ligands. The quenching constants for these two complexes at room temperature differ by a factor of 3 (Table I).

In Figure 4 the amount of quenching in air-saturated solutions is plotted as a function of temperature and extrapolations are made to room temperature. Owing to its long lifetime, quenching is stronger for $\text{K}_3[\text{Cr}(\text{CN})_6]$. When the temperature is raised other modes of deactiva-

tion compete with quenching. At -10° quenching is negligible for most complexes except for $\text{K}_3[\text{Cr}(\text{CN})_6]$, which is still sufficiently long lived to be quenched by oxygen. The amount is approximately 10–15% at room temperature and hence experiments in photochemistry dealing with this complex at room temperature should be carried out in degassed solutions.

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^{119}Sn Chemical Shifts by the Double Resonance of Organotin Compounds

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Abstract: Tin-119 chemical shifts in 40 organotin compounds have been obtained by $^1\text{H}-\{^{119}\text{Sn}\}$ double-resonance experiments. The tin-119 shifts for organotin compounds where tin is bonded to hydrogen, lithium, and phosphorus atoms are reported along with those for the organotin acetylene, perfluoroalkyl, and perchlorophenyl derivatives for the first time. The most downfield tin shift thus far reported has been measured for the dimethyl-dithiolatotin(IV) heterocycle. Previously drawn correlations with electronegativity are tested with respect to the new substituents. Dispersion forces and effects due to neighboring polarizable groups are seen to be important in raising the shift as with the iodides and unsaturated systems. Higher coordination at tin produces large, upfield shifts, but the cationic organotin complexes appear less shielded than the neutral or anionic complexes. ^{119}mSn Mössbauer quadrupole splitting and $J(^{119}\text{Sn}-^{19}\text{F})$ data are used to establish *intramolecular* coordination in the perfluoroethyl derivatives which are characterized by large, upfield tin shift values.

The first tin chemical shifts were measured by direct observation on 18 compounds by Burke and Lauterbur in 1960.² Precise values were difficult to obtain because of the small natural abundance of the magnetic tin-119 isotope (8.7%) and the low sensitivity and long relaxation times with the resulting saturation problems associated with this nucleus. Hexamethylditin³ and hexamethyldistannoxane⁴ were examined by the same method. In 1968 Hunter and Reeves obtained the tin-119 shifts of 39 additional organotin compounds by direct observation, with enhancement of the signals by heteronuclear decoupling in the proton region.⁵ In 1969 McFarlane, *et al.*, used $^1\text{H}-^{119}\text{Sn}$ double resonance to obtain the tin shifts of 49 additional compounds.⁶ Several advantages follow from the use of this indirect method, among which are that (a) the precision of the measurements is greatly improved, (b) saturation is no longer a problem, and (c) spin-spin coupling relationships between the proton and tin nuclei can be determined.

(1) To whom inquiries should be addressed.

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(4) W. J. Considine, G. A. Baum, and R. C. Jones, *J. Organometal. Chem.*, **3**, 308 (1965).

(5) B. K. Hunter and L. W. Reeves, *Can. J. Chem.*, **46**, 1399 (1968).

(6) A. G. Davies, P. G. Harrison, J. D. Kennedy, T. N. Mitchell, R. J. Puddephatt, and W. McFarlane, *J. Chem. Soc. C*, 1136 (1969).

We report in this paper the tin-119 shifts of 37 organotin compounds measured by heteronuclear decoupling experiments of the $^1\text{H}-\{^{119}\text{Sn}\}$ type. From the data on the 108 compounds in the literature it is known that in general electron withdrawal tends to lower the tin shift while increasing the coordination number at tin tends to raise it. These general trends are also features of the spectra of other magnetic nuclei of the fourth group such as ^{13}C ,⁷ ^{29}Si ,^{5,7,8} and ^{207}Pb .^{7,8}

Results

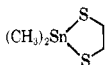
Table I lists the tin-119 chemical shift values of 40 organotin compounds, 37 reported here for the first time, in decreasing order of shift, with tetramethyltin taken as zero. The values of Ξ , defined as the resonant frequency in a polarizing magnetic field of strength such that $(\text{CH}_3)_4\text{Si}$ gives a proton resonance of exactly 100 MHz,⁹ are also listed. Most of the compounds could be recorded as solutions in the noninteracting solvents benzene and methylene dichloride because of the high sensitivity of the double-resonance method. The diamagnetic anisotropy of benzene which can give rise to shifts of up to 1 ppm in proton spectra can be

(7) P. C. Lauterbur, *Determination Org. Struct. Phys. Methods*, **2**, 465 (1962).

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Table I. Tin-119 Chemical Shifts

No.	Compound	$\Xi(^{119}\text{Sn})$, Hz	$\delta(^{119}\text{Sn})$, ^a ppm	Conditions
1	$\text{C}_2\text{H}_5\text{SnH}_3$	37,280,213 \pm 50	282	50% in $(\text{C}_6\text{H}_5)_2\text{O}$
2	$(\text{CH}_3)_2\text{SnBr}_2 \cdot \text{bipy}$	37,281,610 \pm 100	245	Satd CH_2Cl_2 solution
3	$(\text{CH}_3)_2\text{SnI}_2 \cdot \text{bipy}$	37,281,905 \pm 100	237	Satd CH_2Cl_2 solution
4	$(\text{C}_2\text{H}_5)_2\text{SnH}_2$	37,282,122 \pm 10	231	80% in C_6H_6
5	$(\text{CH}_3)_3\text{SnLi}$	37,283,891 \pm 5	183	20% in THF
6	$(\text{CH}_3)_2\text{SnI}_2$	37,284,853 \pm 2	157	20% in CH_2Cl_2
7	$(\text{CH}_3)_2\text{SnCl}_2 \cdot \text{DMSO}$	37,287,494 \pm 50	86	Satd CH_2Cl_2 solution
8	$(\text{CH}_3)_2\text{SnCl}_2 \cdot 2\text{DMSO}$	37,287,540 \pm 3	84	Satd CH_2Cl_2 solution
9	$(\text{CH}_3)_2\text{SnCl}_2 \cdot 2(\text{C}_6\text{H}_5)_3\text{PO}$	37,287,610 \pm 10	83	Satd CH_2Cl_2 solution
10	$(\text{CH}_3)_3\text{SnC}\equiv\text{CC}_6\text{H}_5$	37,288,103 \pm 3	69	50% in C_6H_6
11	$(\text{C}_2\text{H}_5)_2\text{Sn}(\text{C}_2\text{F}_5)_2$	37,288,274 \pm 10	65	10% in CH_2Cl_2
12	$[(\text{C}_2\text{H}_5)_4\text{N}]^+[(\text{CH}_3)_3\text{SnCl}_2]^-$	37,288,693 \pm 2	53	Satd $(\text{CH}_3)_2\text{CO}$ solution
13	$(\text{CH}_3)_3\text{SnC}_6\text{H}_5(\text{CH}_3)_3-2,4,6$	37,288,830 \pm 30	50	50% in CH_2Cl_2
14	$(\text{C}_2\text{H}_5)_3\text{SnH}$	37,289,219 \pm 15	40	50% in C_6H_6
15	$(\text{CH}_3)_3\text{SnC}_6\text{H}_5(\text{CH}_3)_2-2,3$	37,289,412 \pm 30	34	50% in CH_2Cl_2
16	$(\text{CH}_3)_3\text{C}_6\text{H}_4\text{CH}_3-2$	37,289,421 \pm 30	33	20% in CH_2Cl_2
17	$(\text{CH}_3)_2\text{Sn}(\text{C}_6\text{H}_5)_2 \cdot \text{Cr}(\text{CO})_3$	37,289,502 \pm 30	31	10% in CH_2Cl_2
18	$1,4-[(\text{CH}_3)_3\text{Sn}]_2\text{C}_6\text{H}_4$	37,289,584 \pm 30	29	20% in CH_2Cl_2
19	$[(\text{CH}_3)_3\text{Sn} \cdot \text{bipy}]^+[\text{B}(\text{C}_6\text{H}_5)_4]^-$	37,289,999 \pm 5	18	Satd CH_2Cl_2 solution
20	$(\text{C}_2\text{H}_5)_2\text{Sn}(\text{I})\text{C}_2\text{F}_5$	37,290,035 \pm 10	17	10% in CH_2Cl_2
21	$(\text{CH}_3)_2\text{Sn}[\text{C}_6\text{H}_5 \cdot \text{Cr}(\text{CO})_3]_2$	37,290,515 \pm 30	4	5% in CH_2Cl_2
22	$(\text{CH}_3)_3\text{SnP}(\text{C}_6\text{H}_5)_2$	37,290,559 \pm 5	3	50% in C_6H_6
23	$(\text{CH}_3)_4\text{Sn}$	37,290,662 \pm 2	0	50% in CH_2Cl_2
24	$(\text{C}_2\text{H}_5)_4\text{Sn}$	37,290,705 \pm 10	-1	50% in C_6H_6
25	$(\text{CH}_3)_3\text{SnC}_6\text{H}_5 \cdot \text{Cr}(\text{CO})_3$	37,290,787 \pm 40	-3	5% in CH_2Cl_2
26	$(\text{CH}_3)_3\text{SnCH}_2\text{C}_6\text{H}_5$	37,290,823 \pm 30	-4	50% in CH_2Cl_2
27	$1,4-[(\text{CH}_3)_3\text{Sn}]_2\text{C}_6\text{H}_4 \cdot \text{Cr}(\text{CO})_3$	37,290,794 \pm 50	-4	5% in CH_2Cl_2
28	$(\text{CH}_3)_3\text{SnCH}_2\text{C}_6\text{H}_5 \cdot \text{Cr}(\text{CO})_3$	37,290,960 \pm 5	-8	10% in CH_2Cl_2
29	$(\text{CH}_3)_3\text{SnOP}(\text{H})\text{C}_6\text{H}_5$	37,291,163 \pm 10	-13	10% in C_6H_6
30	$(\text{CH}_3)_3\text{SnP}(\text{H})\text{C}_6\text{H}_5$	37,291,310 \pm 18	-18	10% in C_6H_6
31	$(\text{CH}_3)_3\text{SnON}=\text{C}(\text{C}_6\text{H}_{11})_2$	37,291,391 \pm 5	-20	50% in C_6H_6
32	1,1-Dimethyltetraphenylstannole	37,292,584 \pm 10	-52	Satd CH_2Cl_2
33	$(\text{CH}_3)_3\text{SnN}(\text{C}_6\text{H}_5)\text{Si}(\text{CH}_3)_3$	37,293,030 \pm 2	-64	50% in C_6H_6
34	$(\text{C}_2\text{H}_5)_3\text{SnOSn}(\text{C}_2\text{H}_5)_3$	37,293,896 \pm 50	-87	90% in CH_2Cl_2
35	$(\text{CH}_3)_3\text{SnC}_6\text{Cl}_5$	37,295,202 \pm 10	-123	Satd CH_2Cl_2 solution
36	$(\text{CH}_3)_4\text{Sn}_2\text{Br}_2\text{S}$	37,295,211 \pm 20	-123	20% in CH_2Cl_2
37	$(\text{CH}_3)_2\text{SnS}$	37,295,498 \pm 2	-131	20% in CH_2Cl_2
38	$(\text{CH}_3)_3\text{SnON}=\text{C}_6\text{H}_{10}$	37,295,537 \pm 30	-132	20% in CH_2Cl_2
39	$(\text{CH}_3)_4\text{Sn}_2\text{Cl}_2\text{S}$	37,295,996 \pm 3	-144	20% in CH_2Cl_2
40		37,297,827 \pm 2	-194	20% in CH_2Cl_2

^a A positive sign indicates a shift upfield of tetramethyltin.

ignored here where the shifts occupy a range of almost 500 ppm.

Discussion

It is now generally accepted that the paramagnetic term dominates the chemical shifts of heavier nuclei. The theoretical treatment of this contribution to the shielding includes parameters sensitive to change in coordination number, hybridization, and ionicity. It can be shown that in series of compounds where coordination number and hybridization do not change, the chemical shifts should decrease with increasing electron-withdrawing power of attached groups.¹⁰ The data for the heavier nuclei ^{13}C , ^{19}F , and ^{29}Si generally follow this pattern.^{7,8,11} However, other factors besides the electronegativity of the substituents can affect the screening. These factors are thought to operate by influencing the magnitude of the paramagnetic contribution to the screening. For example, it has been suggested that intramolecular dispersion forces from adjacent groups or atoms can increase the paramagnetic contribu-

tion to the shielding of ^{13}C ¹² and ^{19}F ¹³ nuclei. Dispersion forces will be most important for highly polarizable atoms or groups, or when the groups concerned are in close proximity to the magnetic nucleus. Consequently, the effect will be largest for the heavier atoms such as iodine, for unsaturated groups which are polarizable, and for bulky groups which crowd the atom containing the magnetic nucleus. It has been observed that these effects influence the chemical shifts of ^{13}C ¹⁴ and ^{19}F ¹⁵ in a manner opposite to that expected on electronegativity grounds. A further contribution may be expected from π interactions involving low-lying electronic energy levels, which, if they have the correct symmetry for mixing with the ground state, can induce a large paramagnetic shielding effect. Deviations from the linear electronegativity correlation of ^{29}Si shifts when silicon is bonded to nitrogen, oxygen, and fluorine have been discussed in ($p \rightarrow d$) π bonding terms,⁵ but since a similar displacement is also seen in the ^{13}C spectra of the analogous methyl compounds,¹⁴ such interpretations would seem to be unjustified.

(12) W. G. Schneider, private communication quoted in ref 11, p 997.

(13) D. F. Evans, *J. Chem. Soc.*, 877 (1960).

(14) H. Spiessbeck and W. G. Schneider, *J. Chem. Phys.*, **35**, 722 (1961).

(15) G. V. D. Tiers, *J. Amer. Chem. Soc.*, **78**, 2914 (1956).

(10) H. S. Gutowsky and C. Juan, *J. Chem. Phys.*, **37**, 2198 (1962).
 (11) J. W. Emsley, J. Feeney, and L. H. Sutcliffe, "High Resolution Nuclear Magnetic Resonance Spectroscopy," Vol. 2, Pergamon Press, Oxford, 1966.

Previous workers have plotted heavy nuclei shifts against the electronegativities of the bonded atoms¹⁴ or electronegativity differences.⁵ For the trialkyltin compounds the difference plot against C, Cl, Br, Sn, and Mn in ref 5 can be extended to include H, Li, O, P, S, and N atoms, and we have examined the dependence of the tin-119 shift in the dialkyl derivatives where tin is bonded to H, C, Cl, Br, I, and N atoms. Within very broad limits, the tin shift does not appear to be very sensitive to changes among methyl, ethyl, or butyl groups of from three to two such alkyl groups. While in each case changes outside experimental error are recorded, no reversals of the general trends with electronegativity are observed.

In the ethyltin hydride series (**1**, **4**, **14**, and **24**), there is an increase in chemical shift with increasing numbers of hydrogen atoms from $n = 0$ to 3 in $(C_2H_5)_{4-n}SnH_n$. Such increases are also seen in ^{13}C ,¹⁶ ^{15}N ,¹⁷ ^{29}Si ,⁵ and ^{31}P ¹⁸ chemical shifts in replacing methyl groups by hydrogen. While complete series of the closely related methylsilanes have not been studied, data available for the methyl, phenyl, and mixed methylphenyl derivatives suggest that an increment of 20–25 ppm is added per hydrogen. Likewise, in the tin hydride series the change from zero to one, and two to three is accompanied by an increase of *ca.* 40–50 ppm. From one hydrogen to two, however, the increase is 190 ppm. Ethyltin trihydride has the largest shift of any four-coordinated organotin compound thus far studied. Extrapolation of an electronegativity plot containing the tetrahalides alone to hydrogen would predict a shift for stannane itself of *ca.* 3500 ppm, but this merely reflects the effect of polarization and dispersion forces which act to raise the chemical shifts of the heavier tetrahalides such as SnI_4 (1700 ppm), but which are absent in SnH_4 . The value for carbon [$(CH_3)_4Sn=O$] lies considerably below this as is the case for ^{13}C ¹⁴ and ^{29}Si ⁵ shifts. It is likely that the SnH_4 and $(CH_3)_4Sn$ shift values will lie upon a second, parallel line at lower shift values as is found for the ^{13}C data.⁷ A shift for SnH_4 *ca.* 200 ppm to high field of ethyltin hydride (*ca.* 500 ppm) would also establish the "sagging dependence" of shift on substitution in $X_{4-n}MY_n$ seen for ^{13}C , ^{29}Si , ^{31}P , etc., for all but the halo compounds, where the shifts of the mixed compounds are always to lower fields than would be predicted by linear interpolation between the end members of the series.

More straightforward electronegativity effects seem to be operating in the decrease in shift on chlorosubstitution of **36** and **39**, or from trimethylphenyltin (+30 ppm⁵) to its perchlorophenyl analog (**35**). However, other effects dominate the shift relationships in the trimethyltin series: CH_3 (**23**) < C_6H_5 (+30 ppm⁵) < $CH=CH$ (+35 ppm⁵) < $C\equiv CC_6H_5$ (**10**). Smaller changes are seen on methyl substitution on the phenyl group in $(CH_3)_3SnC_6H_5$ (**13**, **15**, and **16**), where a large increase is seen when two ortho methyls are present (**13**). Intramolecular dispersion forces are undoubtedly important for the polarizable unsaturated substituents and in the steric crowding of the 2,6-disubstituted derivative. The low-field shift of *ca.* 130 ppm from the

acyclic dimethyltin divinyl (+79.4 ppm⁵) to the dimethylstannole **32** is more interesting. Dispersion forces arising from the tetraphenyl substitution of the latter heterocycle would raise the shift and are probably unimportant, and the same can be said for $(\pi \rightarrow d)\pi$ effects with the adjacent double bonds. The effect of a sustained ring current would be to induce low-field shifts only if the tin nucleus lay outside the radius of the current. Comparisons with ^{13}C , ^{14}N , or ^{15}N chemical shifts in aromatic compounds are not useful, since these atoms undergo primary hybridization changes on aromatization of the rings. The stannoles lack aromatic properties.¹⁹ There seems to be some general movement to low field on incorporation of the magnetic nucleus into a small ring, as seen in **40**, which has the lowest tin shift thus far measured.^{19a} Dimethyltin sulfide (–125 ppm in CS_2 solution⁵) probably also takes a cyclic structure, and the six-membered cyclic trimer has been measured at –128 ppm.⁶ Such effects are not seen in the ^{11}B shifts of $RB(SR)_2$ *vs.*



which are nearly identical.²⁰

Unusual changes are seen in the perfluoroalkyl compounds **11** and **20**. Substitution of perfluoroethyl groups would be expected to drive the shift value downfield, contrary to observation. Dispersion forces should be at a minimum in such nonpolarizable groups, while, as discussed above, they bring about highfield shifts for iodo compounds. The decrease in shift from **11** to **20** is thus contrary to that expected on both polarization and electronegativity grounds, since the electronegativity of the perfluoroalkyl group is usually thought to fall between that of bromide and chlorine.²¹ Dimethyltin diiodide (**6**) has a large, positive shift, while that of its dibromo analog is large and negative (–74.3 ppm⁵). Organohalotins other than the iodides which have large, positive shifts are likely higher than four-coordinated in the solutions employed. In fact, almost all the organotin compounds with high shifts, except those in which tin is bound to a metal or hydrogen, contain higher coordinated tin or tin atoms affected strongly by dispersion forces. Ruling out the latter leads to the suggestion that the high shifts of **11** and **20** arise from interaction between tin and the α -fluorine atoms of the perfluoroethyl group. A similar suggestion has been put forward to rationalize electron return to the phenyl ring in benzotrifluoride.²² In our perfluoroethyltins the Sn – α -fluorine internuclear distance should be *ca.* 2.9 Å, assuming tetrahedral carbon and reasonable values for $d(Sn-C)$ and $d(C-F)$. While reliable estimates for van der Waals radii are difficult to obtain, their sum for fluorine and carbon is *ca.* 3 Å. Thus it is likely that tin and fluorine are well within the distances for significant interaction. Evi-

(19) F. C. Leavitt, T. A. Manuel, F. Johnson, L. U. Matternas, and D. S. Lehman, *ibid.*, **82**, 5099 (1960).

(19a) NOTE ADDED IN PROOF. The tin-119 chemical shifts of $(CH_3)_nSn(SCH_3)_{4-n}$, where $n = 4$ (0), 3 (–90), 2 (–144), 3 (–167), and 4 (–165 ppm) [E. V. Van Den Berghe and G. P. Van Der Kelen, *J. Organometal. Chem.*, **26**, 207 (1971)], can be taken as corroboratory.

(20) Reference 11, p 975.

(21) J. Hinze, M. A. Whitehead, and H. H. Jaffe, *J. Amer. Chem. Soc.*, **85**, 148 (1963).

(22) W. A. Sheppard, *ibid.*, **87**, 2410 (1965).

(16) P. Pregosin and E. W. Randall, *Determination Org. Struct. Phys. Methods*, **4**, 263 (1971).

(17) R. Lichter, *ibid.*, **4**, 195 (1971).

(18) S. L. Manatt, G. L. Juvinal, R. I. Wagner, and D. D. Elleman, *J. Amer. Chem. Soc.*, **88**, 2689 (1966).

dence already exists from ^{119m}Sn Mössbauer quadrupole splitting (QS) data for such interactions,²³ although the splittings observed for polyhaloaryltins have been rationalized on the basis of the high electronegativity of these groups,²⁴ and the low shift of **35** supports this view. The distance between tin and an ortho-fluorine atom is *ca.* 3.2 Å, likely outside the distance for significant interaction. Additional support for intramolecular coordination by the α fluorines in the SnCF_2CF_3 system is found in the large $J(^{119}\text{Sn}-^{19}\text{F})$ value of *ca.* 300 Hz (the β coupling is too small to resolve, or <0.5 Hz). Coupling to the ortho-fluorine atoms in perfluorophenyltin compounds has not been resolved.²⁵ The same view can be used to rationalize the previously reported shifts of the compounds $(\text{CH}_3)_3\text{SnCH}_3\text{-}_n\text{X}_n$, where the $\text{X} = \text{Cl}$ derivatives are to higher field for all values of n than are the $\text{X} = \text{Br}$ derivatives.⁶ Mössbauer QS values have been resolved for the chloro derivatives,²⁶ and intramolecular association would explain both this and the higher shift value despite the more polarizable and less electronegative nature of bromine.

The shift of hexamethylditin (110 ppm)^{3,5} is that expected from the electropositive trimethyltin substituent, and the even higher shift of the lithio derivative **5** (the highest of any trimethyltin compound yet measured) is also understandable in these terms. The only other compound with a tin-metal bond yet examined, $(\text{CH}_3)_3\text{SnMn}(\text{CO})_5$, has a shift (-66.3 ppm⁵) which is clearly anomalous on any reasonable estimate of the electronegativity of the $\text{Mn}(\text{CO})_5$ group. Both dispersion effects and $(d \rightarrow d)\pi$ interactions between filled Mn 3d orbitals and empty Sn 5d orbitals would be expected to raise the shift value. ^{119m}Sn Mössbauer, nmr, and structural data have been used to show that π interactions do not predominate in such systems.²⁷

In this connection, other interesting tin-transition metal compounds are those in which a tin-phenyl group is complexed by $-\text{Cr}(\text{CO})_3$.²⁸ Such complexation decreases the tin shift by *ca.* -30 ppm per $-\text{Cr}(\text{CO})_3$ group (see **17**, **18**, **21**, **25**, and **27**). When the phenyl is insulated from tin by a methylene group, as in $(\text{CH}_3)_3\text{SnCH}_2\text{C}_6\text{H}_5$ (**26**), the effect of complexation is to lower the shift by only -4 ppm (**28**). The possibility of across-space $(d \rightarrow d)\pi$ interactions utilizing the filled chromium d orbitals has been discussed in such systems,²⁹ but such effects would be expected to raise, not lower, the shift.

The five- and six-coordinated tin complexes in Table I (**2**, **3**, **7-9**, **12**, and **19**) all show high-field shifts, in conformity with earlier findings.^{2,5,6} We note, however, that the five-coordinated complex $(\text{CH}_3)_3\text{SnCl}$

DMSO^{30} (**7**) has virtually the same shift as the six-coordinated complex $(\text{CH}_3)_3\text{SnCl}_2 \cdot 2\text{DMSO}^{31}$ (**8**).

Another five-coordinated complex, $[(\text{CH}_3)_3\text{Sn} \cdot \text{bipy}]^+[\text{B}(\text{C}_6\text{H}_5)_4]^-$ (**19**), has a relatively low-field shift in contrast to its anionic counterpart $[(\text{CH}_3)_3\text{SnCl}_2]^-[(\text{C}_2\text{H}_5)_3\text{N}]^+$ (**12**). Apparently, the tin atom in the cation is relatively deshielded by the positive charge. Other neutral organotin complexes listed in the literature as having downfield shifts⁵ are probably dissociated in solution. The high shift of trimethyltinlithium (**5**) may also be attributed to a complexed, anionic species. The sample we examined was prepared from trimethyltin chloride and lithium metal shot²² and exhibits a $J(^{117,119}\text{Sn}-^1\text{H})$ value of 7.2 ± 0.5 Hz as a 1 M solution in THF. Different methods of preparation yield samples of this compound with different spin-spin coupling values (5.2–7.4 Hz) in THF.³³ The combination of the highest upfield tin shift thus far measured for a triorganotin compound with the lowest methyltin spin-spin coupling constant is indicative of bonding to a strongly electron-releasing moiety or of the presence of $[(\text{CH}_3)_3\text{Sn}]^-$ species solvated by THF.

Experimental Section

Compounds. Compounds **13**, **15**, and **16** were supplied by Professor C. Eaborn, University of Sussex, England, **35** by Professor H. Gilman, Iowa State University, and **40** by Dr. E. W. Abel, University of Bristol, England. Compounds **23** and **24** were commercial samples (M & T Chemicals, Inc.). The ethylstannanes, $(\text{C}_2\text{H}_5)_n\text{SnH}_{4-n}$, were prepared by standard routes for $n = 1,^{34,2}$ $2,^{35}$ and 3^{36} (**1**, **4**, and **14**). Preparations of **11**,³⁷ **12**,³⁸ **17**,^{28,29} **18**,²⁹ **19**,³⁸ **20**,³⁷ **21**,^{28,29} **22**,³⁹ **25**,^{28,29} **26**,²⁹ **27**, **28**,^{28,29} **29**, **30**,³⁹ **31**,⁴⁰ **32**,⁴¹ and **38**,⁴⁰ are being reported from this laboratory.

Instrumentation. Data were obtained using a Varian HA-100D spectrometer with the probe modified to transmit two radiofrequencies, ν_1 and ν_2 . A single transmitter coil was used, with a circuit similar to that developed by Charles and McFarlane.⁴³ The decoupling frequency ν_2 (*ca.* 37.3 MHz for tin-119) was derived from a frequency generation unit consisting of a Hewlett Packard Model 5105 frequency synthesizer, a Hewlett Packard Model 5110B synthesizer driver, and a Hewlett Packard Model 230 power amplifier.

Since ν_1 and ν_2 were derived from different oscillators, it was necessary to monitor both frequencies. The Hewlett Packard unit has a specified stability of $6 \times 10^{11} \text{ sec}^{-1}$ with a standard frequency deviation of ± 0.003 Hz at an output of 50 MHz (better than ± 3 parts in $10^9/24$ hr). The Varian V-4311 radiofrequency unit was found to drift by as much as 50 Hz/hr, and its output was monitored during each run with a General Radio Type 1191Z 500-MHz counter.

Measurements. The tin-119 frequencies listed in Table I are derived from the expression

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$$\bar{\nu} = 10^8 \chi_{\text{obsd}} / (10^8 + f) - 100\delta$$

where χ_{obsd} is the tin shift measured, δ is the chemical shift of the compound whose frequency is used to lock the spectrometer relative to tetramethylsilane (TMS), $(10^8 + f)$ is the frequency of the lock signal, and f is the frequency of the manual oscillator. Use of the factor 10^8 assumes an absolute $\nu_1 = 100$ MHz for TMS on the Varian HA-100D spectrometer employed. The HA-100D spectrometer employed in this work was found to have a frequency range of 100,001,600.0–100,001,900.0 Hz, and the appropriate corrections have been made in the tabulated tin frequencies.

The tin chemical shifts are relative to a 50% solution of tetramethyltin in methylene dichloride, with a positive sign used to denote a shift upfield from tetramethyltin. This "standard solution" was found to have a tin-119 resonance frequency of $37,290,662 \pm 2$ Hz. This value compares favorably with that reported by McFarlane, *et al.*, for a 95% solution $37,290,665 \pm 2$ Hz).⁶ Tin frequencies were calibrated with the standard after each run.

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The Crystal and Molecular Structure of 2,2'-Bis(6-methyl-3-pyridinol)

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Abstract: 2,2'-Bis(6-methyl-3-pyridinol) is a highly fluorescent homolog of a new family of 3-pyridinol dimers. The structure of the 6-methyl dimer was determined by single-crystal X-ray diffraction methods to better understand its physical properties. The compound crystallized in space group $P2_1/n$ with $a = 7.62$, $b = 4.61$, $c = 20.59$ Å, $\beta = 134.07^\circ$, and $Z = 2$. The positions of all eight nonhydrogen atoms in the asymmetric unit were located by the symbolic addition method. A difference Fourier gave the six hydrogen atom positions. Full-matrix least-squares refinement (eight atoms anisotropic, six hydrogens isotropic) using 592 reflections ($F > 3\sigma$) resulted in a conventional R factor of 0.071. The molecules are discrete and planar and contain strong intramolecular hydrogen bonds (N–O, 2.568 Å); there are no intermolecular hydrogen bonds. The 1.347-Å C–O and 1.459-Å C–C (bridge) bonds are about halfway between the typical double and single bond distances. This is consistent with other evidence which suggests the existence of a tautomeric equilibrium involving a form with quinoid character.

In the course of an investigation of the oxidation of heterocyclic phenols,¹ a pale yellow crystalline compound was isolated from a reaction medium consisting of PbO_2 , 6-methyl-3-pyridinol, and petroleum ether. The yellow compound fluoresced a brilliant yellow-green when excited with uv light. Nmr and ir spectra, molecular weight, and elemental analyses indicated that the compound was a 2,2' dimer of 6-methyl-3-pyridinol with an empirical formula of $\text{C}_{12}\text{H}_{12}\text{N}_2\text{O}_2$ and contained a strong hydrogen bond.¹ In order to verify these findings and firmly establish the details of the molecular structure, we undertook a single-crystal X-ray diffraction analysis. In particular, we wanted to define those features of the structure that could be useful in understanding the mechanism of the exceptionally intense fluorescence, *viz.*, whether the molecule shows any quinoid character (why it is yellow rather than colorless), whether it is planar, if there are any intermolecular interactions, and whether the hydrogen bond is as strong as suggested by the ir spectrum.

Experimental Section

The compound was prepared by the oxidation of 6-methyl-3-pyridinol as described earlier¹ and was recrystallized from petroleum ether (30–60°) to give long, thin, pale yellow plates. Preliminary cell and space group data were collected on precession and Weissenberg cameras using $\text{Cu K}\alpha$ radiation. The long direction of the crystal corresponded to the b axis of the monoclinic unit cell. A

General Electric automated (Datex) XRD-6 diffractometer, with a quarter-circle goniostat, was used to obtain the final cell parameters based on $\text{Cu K}\alpha_1$ 1.54051 Å and to collect the integrated intensity data (using θ - 2θ scans and a 4° takeoff angle). Table I gives the

Table I. Experimental Data

a , Å	7.62 ± 0.02
b , Å	4.61 ± 0.04
c , Å	20.59 ± 0.02
β , deg	134.07 ± 0.02
$\rho(\text{X-ray})$, g/cm^{-3} ; $\rho(\text{measd})$	1.38; 1.36 ± 0.01
Space group ^a	$P2_1/n$
Molecules/unit cell	2
Total obsd reflections ^b	592
$\langle E \rangle$	0.751
$\langle E^2 - 1 \rangle$	0.916
Crystal size, mm	$0.50 \times 0.07 \times 0.02$

^a The equivalent positions are $\pm(x, y, z)$ and $\pm(x + 1/2, y - 1/2, z + 1/2)$ with b as the unique axis. ^b The intensities of 1095 reflections ($2\theta \leq 154^\circ$) were measured, but only those whose F 's were $> 3\sigma$ were considered as observed.

pertinent experimental data. The intensity of the 020 reflection, monitored twice daily during the data collection, remained essentially constant, indicating that the crystal was stable during this period. Corrections were applied to the data for Lorentz and polarization effects but not for absorption or extinction.

The standard deviation of $|F_o|$ ($=\sqrt{I}$), where the integrated intensity I is $I = TC - (B_1 + B_2)(t_c/2t_b)$, was assumed to be²

$$\sigma(F) = [TC + (t_c/2t_b)^2(B_1 + B_2) + 0.05I]^2]^{1/2}/2F$$

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