Proton and Deuteron Magnetic Resonance of Phenylsilane-d_3, Phenylphosphine-d_2, and Benzenethiol-d in Liquid Crystal Solutions

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Abstract: The proton and deuteron magnetic resonance studies of phenylsilane-d_3, phenylphosphine-d_2, and benzenethiol-d in liquid crystal solutions at room temperature are reported. The orientation factors were calculated from the dipole–dipole splittings in the proton nmr spectra. The deuterium quadrupole coupling constants were calculated from the nuclear quadrupole splittings in the deuterium nmr spectra and the orientation factors obtained from proton nmr. Assuming axial symmetry for the field gradient, the deuterium quadrupole coupling constants were calculated to be 91 ± 2, 115 ± 2, and 146 ± 3 kHz, respectively, for the three compounds. They are correlated to bond force constants and atom electronegativities. In addition, the C–P–D bond angle for phenylphosphine-d_2 and the H–P–H bond angle for phosphine in liquid crystal solutions were calculated from their proton nmr spectra. They are 96.4 ± 1.0 and 95.3 ± 1.0°, respectively.

The nuclear quadrupole coupling constant is an important quantity related to chemical bonding and molecular structure.[1] In particular, the quadrupole coupling constant for deuterium has many interesting properties. For example, it bears a linear relation to the force constant in the hydrides of the second row elements.[2] In hydrogen-bonded systems containing the O–D···O bond, the deuterium quadrupole coupling constant is directly related to the O–D distance[3–5] and O–O distance;[5,6] Blinc and Hadzi[3] have suggested that it is a more sensitive quantity than the O–D stretching frequency in evaluating the strength of the hydrogen bond.[3] In deuteriocarbons, the deuterium quadrupole coupling constant increases regularly as the hybridization of carbon changes from sp^3, sp^2, to sp;[7] it decreases with the introduction of electron-withdrawing substituents.[8–10] In ferroelectric materials, the structural changes during the phase transitions are directly related to the deuterium quadrupole coupling constant.[4,11,12]

The quadrupole coupling constants of deuterium are quite small ($e^2qQ/h < 400$ kHz) and difficult to measure directly by the conventional quadrupole resonance technique.[13] They can be obtained from molecular beam and microwave experiments but are usually limited to small molecules in the gaseous state. The majority of data for deuterium quadrupole coupling constants has been obtained from nuclear magnetic resonance. Although deuterium nmr in the liquid state does not always yield reliable values of quadrupole coupling constants because of the difficulty in estimating the correlation time,[14] the deuterium quadrupole coupling constants obtained from resonance experiments in solids and in liquid crystals are quite accurate. Deuterium nmr studies on single crystals of known structure give most detailed information. Polycrystalline samples can also be used in nmr studies, but the analysis of the powder spectra involves larger uncertainties. For compounds which do not readily solidify and whose signals are easily saturated at low temperatures, the deuterium nmr study in the liquid crystalline state[9,15,16] is most convenient. In this paper we report the result of our nmr study on phenylsilane-d_3, phenylphosphine-d_2, and benzenethiol-d in liquid crystal solutions. The quadrupole coupling constants of deuterium in those compounds are calculated and correlated to force constants and electronegativities.

Experimental Section

Phenylsilane-d_3 (*ca.* 98% D) was prepared from the reaction of lithium aluminum deuteride with trichlorophenylsilane in ether.[17]

Phenylphosphine was prepared from the reduction of dichlorophenylphosphine with lithium aluminum hydride in ether and purified by vacuum distillation (bp$_{26}$ 62–63°).[18] **Phenylphosphine-d_2** was prepared by stirring phenylphosphine with the same weight of D_2O for 2 hr at room temperature. After three successive exchanges it was dried over $CaCl_2$ and *ca.* 97% deuteration was obtained.

Benzenethiol-d (*ca.* 95% D) was obtained by direct deuterium exchange of benzenethiol with D_2O, repeated three times.[19]

Phosphine was prepared from the decomposition of H_3PO_3 *in vacuo* at 230°; the phosphorous acid used was prepared from the hydrolysis of distilled trichlorophosphine in ether. **Phosphine-d_3** was prepared similarly, using D_2O for the hydrolysis.[20]

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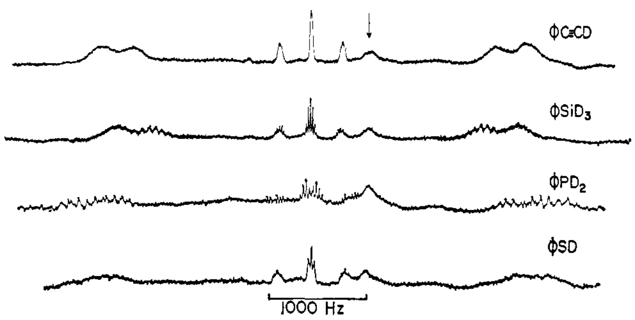

Figure 1. Proton nmr spectra of phenylacetylene-*d*, phenylsilane-d_3, phenylphosphine-d_2, and benzenethiol-*d* in liquid crystal solutions at 100 MHz and 25°. The compositions of the solutions in mole fraction are: solute, 0.20; *p*-(*p*-ethoxyphenylazo)phenyl heptanoate, 0.20; butyl *p*-(*p*-ethoxyphenoxycarbonyl)phenyl carbonate, 0.60. The arrow indicates a hump due to the solvent.

The liquid crystal solutions were prepared by mixing 60 mol % of butyl *p*-(*p*-ethoxyphenoxycarbonyl)phenyl carbonate, 20 mol % of *p*-(*p*-ethoxyphenylazo)phenyl heptanoate, and 20 mol % of solid or liquid solute.[21] Best results were obtained by melting the solvent and cooling it down to room temperature before introducing the solute. The solutions were liquid crystalline at room temperature. For making the solution of phosphine, the liquid crystalline solvent was degassed; then the phosphine was trapped in the sample tube with liquid nitrogen and the tube was sealed off.

The proton nmr spectra were taken with a Varian HA-100 spectrometer at room temperature and 100 MHz in the field-sweep mode. The field-sweep scale was calibrated either by the side band technique or by measuring the separation between the two peaks in the spectrum of 10% tetramethylsilane in chloroform.

The deuterium nmr spectra were taken at 8.0 MHz and 12.3 kG using a Varian VF-16 spectrometer, with the samples used in taking the pmr spectra. The field-sweep scale was calibrated by measuring the D_2O resonance at slightly different frequencies, using a Hewlett-Packard 5245M counter to measure the frequency. The spectra were recorded in the dispersion mode.

Since the pmr and the dmr spectra were measured at different magnetic fields, it was necessary to make sure that the orientation factor did not change. To check this, the proton nmr of a liquid crystal solution was measured at magnetic fields of 14,092 and 23,487 G. At the same temperature, the dipolar splittings were unchanged within experimental error.

Polycrystalline samples of phenylsilane-d_3, phenylthiol-*d*, and phosphine-d_3 were measured at low temperature down to 103°K, but only partially resolved spectra were obtained because the reorientational motion of the molecules did not stop at that temperature.

Results and Discussion

The quadrupole splitting in the nmr spectrum of a liquid crystal has been formulated.[9,15,22] In the case where an X–D bond is rapidly reorienting about a molecular axis, the previous treatments have assumed a zero asymmetry factor η. If the quadrupole Hamiltonian[23]

$$\mathcal{H}_Q = \frac{e^2qQ}{4I(2I-1)}[3I_z^2 - I^2 + \eta(I_x^2 - I_y^2)] \quad (1)$$

is treated as a perturbation to the Zeeman term for an $I = 1$ nucleus rapidly reorienting about a molecular axis, the quadrupole splitting (in Hz) for nonzero asymmetry factor is readily found to be

$$\Delta\nu_Q = (^3/_4)e^2qQ(3\cos^2\theta - 1 - \eta\sin\theta)S/h \quad (2)$$

where θ is the angle between the principle axis (z) of the quadrupole nucleus and the molecular axis of reorientation, and S is the orientation factor of the molecular axis. The x axis appearing in the expression of the asymmetry factor $\eta = (V_{xx} - V_{yy})/V_{zz}$ is taken to be perpendicular to both the z axis and the molecular axis. Equation 2 is applicable to the quadrupole splitting in the solid provided the orientation factor S is replaced by a suitable angular factor $(3\cos^2\alpha - 1)/2$, where α is the angle between the molecular axis and the magnetic field. It is obvious from (2) that if there is rapid reorientation involving the quadrupole nucleus, the quadrupole coupling constant and the asymmetry parameter *cannot* be separately determined from the nmr spectrum, whether for a solid or for a liquid crystal.[24] In order to calculate the quadrupole coupling constant e^2qQ/h from the spectrum, the asymmetry factor η has to be known. Fortunately, η for deuterium in covalent compounds without anomalous crystalline distortion[25] is usually very small. For example, in naphthalene-d_{10} it was found that $\eta = 0.06$.[26] The assumption that the field gradient is axially symmetrical ($\eta = 0$) for deuterium normally would only introduce an error of about 5% or less, depending upon η and θ.

The orientation factor S in (2) can be obtained from the dipole–dipole splitting in the proton nmr spectrum of the unsubstituted or deuterated compounds. For two different magnetic nuclei A, B whose vector r forms an angle β with a certain molecular axis and rapidly reorients about it, the dipole–dipole splitting is

$$\Delta\nu_D = [(\gamma_A\gamma_B\hbar/\pi r^3 + J_{AB})(3\cos^2\beta - 1)/2](S) \quad (3)$$

where the orientation factor S is the same as that in (2) if the same molecular axis is referred to.

The proton nmr spectra of phenylacetylene-*d*, phenylsilane-d_3, phenylphosphine-d_2, and benzenethiol-*d* in liquid crystal solutions are shown in Figure 1. These spectra are relatively simple and may be called "first order" because the peaks can be readily identified without computer analysis. For phenylacetylene-*d* (Figure 1), couplings between the deuterium and the protons were too small to be resolvable; therefore the spectrum appears to be that of a five spin-$^1/_2$ system. There are five peaks in the center of the spectrum with an intensity ratio of roughly 1:4:6:4:1 (the peak at the highest field was obscured by a hump arising from solvent absorption). They were due to the *para* (4) proton split by the *ortho* (2,6) and *meta* (3,5) protons, with all four dipole–dipole interactions being approximately equal. The adjacent *ortho* and *meta* (2,3 and 5,6) protons had a large dipolar splitting and gave rise to two groups of peaks symmetrical about the center, neglecting the very small chemical shifts. Each group was further split into a doublet due to the interaction with the *para* proton. Other dipole–dipole interactions (2,3; 2,6; 3,5; 3,6) were small and unresolvable, thus contributing only to the breadth of the two doublets and the quintet. Computer analysis

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using a modified LAOCOON III program[27] gave the same conclusions. However, the low resolution of the spectra does not warrant exact calculations of the coupling constants and orientation factors. In fact, a number of other monosubstituted benzenes gave similar spectra in liquid crystal solutions.[28]

For phenylsilane-d_3, phenylphosphine-d_2, and benzenethiol-d, the proton absorptions were further split by the proton–deuteron dipole–dipole interactions. The splittings were clearest for the central peaks, which were recorded at enlarged scales to obtain more accurate values for the couplings. As an example, the central part in the pmr spectrum of phenylphosphine-d_2 in a liquid crystal solution is shown in Figure 2A. It is composed of two slightly superimposed quintets. The larger splitting was due to the interaction between phosphorus and the *para* proton, and the two deuterium nuclei further split each component into a quintet of intensity ratio 1:2:3:2:1.[29] Since J_{PH} for the *para* proton in phenylphosphine would be no more than 1 or 2 Hz[30,31] and is within the experimental error of the observed P–H splitting (92.7 ± 1.0 Hz), the orientation factor for the molecular axis can be readily calculated from eq 3, with $\beta = 0°$. Then, the C–P–D bond angle can be calculated from the H–D splitting (27.3 ± 0.5 Hz; $J_{\mathrm{H-D}} = 0$) treating the PD_2 group as rapidly reorientating about the C_2 axis at room temperature. The value obtained is 96.4 ± 1.0°.

The central peak of phenylsilane-d_3 was a septet with a splitting of 23.2 ± 0.2 Hz. The septet was due to the interaction between the *para* proton and the deuterium in the $-SiD_3$ group, and its theoretical intensity ratio is 1:3:6:7:6:3:1.[29] The central peak of benzenethiol-d was a triplet due to the splitting of the deuterium. Its splitting was 29.0 ± 0.2 Hz and the theoretical intensity ratio is 1:1:1; the different widths in the spectrum were caused by the broadening due to other interactions. The orientation factors of the C_2 axes were calculated from eq 3, using the assumed bond angles of 109.5° for phenylsilane-d_3 and 108° for benzenethiol-d.[32] The results are listed in Table I.

Table I. Results of Proton and Deuteron Nmr of Phenylsilane-d_3, Phosphine, Phosphine-d_3, and Benzenethiol-d in Liquid Crystal Solutions

	Solvent,^{a} mol %		Orientation factor of molecular axis	Deuterium quadrupole splitting, kHz
	A	B		
$C_6H_5SiD_3$	60	20	0.171	7.95 ± 0.06
PH_3^{b}	78.4	21.6	0.0137	
$C_6H_5PD_2$	60	20	0.177	14.8 ± 0.1
C_6H_5SD	60	20	0.203	15.9 ± 0.1

^{a} A = butyl *p*-(*p*-ethoxyphenoxycarbonyl)phenyl carbonate; B = *p*-(*p*-ethoxyphenylazo)phenyl heptanoate. ^{b} P = 5.8 atm.

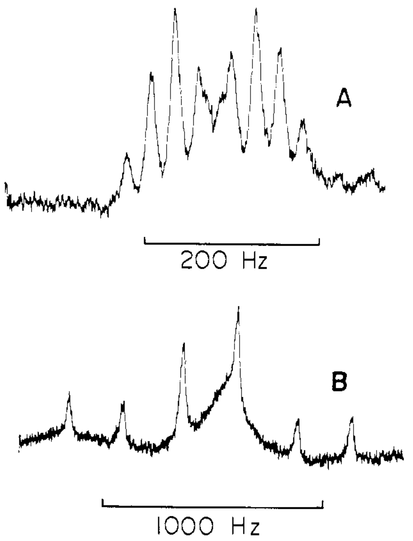

Figure 2. Proton nmr spectrum of (A) the central peaks of phenylphosphine-d_2 and (B) phosphine in liquid crystal solutions at 100 MHz and 25°. For B, the pressure of phosphine was 5.8 atm, and the solvent was a mixture of 21.6 mol % of *p*-(*p*-ethoxyphenylazo)phenyl heptanoate and 78.4 mol % of butyl *p*-(*p*-ethoxyphenoxycarbonyl)phenyl carbonate.

The bond distances used in the above calculations are:[33] C–C, 1.39; C–H, 1.10; C–Si, 1.84; C–P, 1.83;[34] C–S, 1.82; Si–D, 1.48; P–D, 1.42; and S–D, 1.33 Å.

The pmr spectrum of phosphine in a liquid crystal solution was also measured and is shown in Figure 2B. The dipole–dipole interactions between the protons gave rise to a triplet, each component of which was further split by the P–H interactions into two peaks. The splittings were 517 ± 2 Hz and 246 ± 2 Hz, respectively. Saupe, Englert, and Povh[35] have shown that the bond angle of a methyl group can be readily calculated from the pmr spectrum of a C-13 enriched compound in a liquid crystal solution. Using their formulism and the value of $J_{\mathrm{PH}} = 183$ Hz,[36] the H–P–H bond angle was found to be 95.3 ± 1.0°.[37] This is almost the same as the C–P–D angle of phenylphosphine as reported above and indicates a slight expansion of the bond angle of phosphine in liquid crystal compared with the data in the gas phase, 93° 20′.[38]

The deuterium nmr spectra of phenylsilane-d_3, phenylphosphine-d_2, and benzenethiol-d in liquid crystal solutions consisted of a doublet due to the nuclear quadrupole interaction of deuterium. The splittings are listed in Table I. Fine structures due to dipole–dipole interactions were not observed, because they overlapped to give broadened peaks.

The deuterium quadrupole coupling constant (e^2qQ/h) were calculated from the quadrupole splittings, using the orientation factors obtained from the proton spectra. The results are listed in Table II. In apply-

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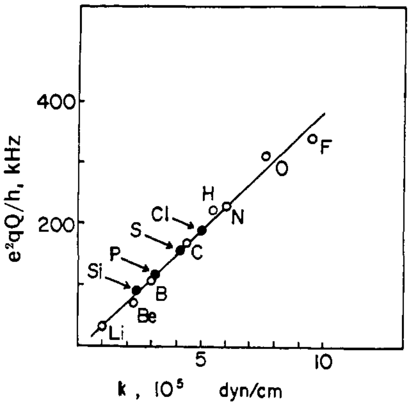

Figure 3. Relation between deuterium quadrupole coupling constants and the corresponding force constants in covalent hydrides. The deuterium quadrupole coupling constants for the third row elements (in full circles) are listed in Table II; those for the other elements (in open circles) are listed in ref 2. The force constants are taken from G. Herzberg, "Spectra of Diatomic Molecules," 2nd ed, D. Van Nostrand Co., Inc., Princeton, N. J., 1950, p 458.

ing eq 2, it was assumed that the field gradient is symmetrical along the X–D bond, *i.e.*, $\eta = 0$. This assumption may cause an error up to about 5%, as pointed out above. For example, the deuterium nmr of benzene-d_6 has been studied in polycrystalline,[15] single crystal,[39] and liquid crystalline[9,15] states. In the temperature range of all those studies benzene is rapidly reorientating about its C_6 axis and $\eta = 0$ was assumed in all the works. Then e^2qQ/h was found to be 193 ± 3,[15] 187 ± 2,[39] and 194 ± 4 kHz,[9] respectively. However, for anthracene-d_{10}, $\eta = 0.064 \pm 0.013$ was observed.[26] If that value is adopted for benzene-d_6 and substituted into (2), the deuterium quadrupole coupling for benzene obtained in the previous works would be reduced to 181, 176, and 182 kHz, respectively. These values then compare more favorably with the value of 181 ± 3 kHz for anthracene-d_{10}.[26] For other covalent compounds without hydrogen bonding, η is likely to remain very small[9] and the assumption of $\eta = 0$ would probably not introduce large errors in calculating deuterium quadrupole coupling constants.

Table II. Deuterium Quadrupole Coupling Constants (e^2qQ/h in kHz) for Deuterides of the Third Row Elements

Al	Si	P	S	Cl
	95[a]		154.7 ± 1.6[b]	190[c]
76[d]	91 ± 2[e]	115 ± 2[f]	146 ± 3[g]	

[a] SiD_4, ref 40. [b] HDS, P. Thaddeus, L. C. Krisher, and P. Cahill, *J. Chem. Phys.*, **40**, 257 (1964). [c] DCl, ref 43. [d] $LiAlD_4$, P. Pyykkö, and B. Pedersen, *Chem. Phys. Lett.*, **2**, 297 (1968). [e] $C_6H_5SiD_3$, this work. [f] $C_6H_5PD_2$, this work. [g] C_6H_5SD, this work.

The data in Table II show that the quadrupole coupling constant for phenylsilane-d_3 is in very good agreement with that of silane-d_4,[40] indicating that the field gradient at the deuterium is not appreciably influenced by the substitution of hydrogen by a phenyl group, which is not unexpected.[7] For phosphorus compounds, we have measured the deuterium nmr of PD_3 in a liquid crystal solution, but the orientation factor (Table I) was too small so that we could not obtain the quadrupole splitting. However, it is believed that the deuterium quadrupole coupling in PD_3 is similar to, and probably slightly higher than, that in $C_6H_5PD_2$, as in the case of the silicon compounds. The only other deuterium nmr study on phosphorus compounds known to the authors is that by Pyykkö,[41] who obtained 91.6 kHz for the deuterium quadrupole coupling in PD_4I. The effect of a formal charge on a hydride may increase or decrease the deuterium quadrupole coupling, as discussed in an earlier paper.[7] The fact that PD_4^+ has a smaller coupling constant than PD_3 implies that the decrease in the electronic part of the field gradient is predominant over the shortening of bond length due to the positive charge. In fact, the P–H distances in PH_3 and PH_4^+ are almost the same.[33] For the difference in the deuterium quadrupole coupling constants in HDS and C_6H_5SD, there may be two causes. The substitution of hydrogen by the phenyl group may decrease the quadrupole coupling, as for the silanes. Slight hydrogen bonding of the thiol with the liquid crystalline solvent would further reduce the coupling constant from its gaseous value.

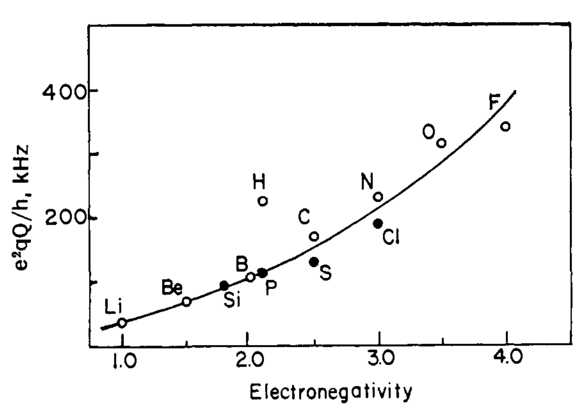

Figure 4. Relation between deuterium quadrupole coupling constants and electronegativities of the elements X in X–D compounds. The values of electronegativity were taken from L. Pauling, "The Nature of the Chemical Bond," 3rd ed, Cornell University Press, Ithaca, N. Y., 1960, p 93.

In Figure 3 we have plotted the deuterium quadrupole coupling constants for the covalent deuterides of the elements in the first three rows of the periodic table *vs.* the force constants of the corresponding hydrides. It is seen that the data for Si, P, S, and Cl fall right on the straight line previously determined.[2] The datum for lithium aluminum deuteride is not included in Figure 3 because in that compound deuterium cannot be considered as covalently bonded to aluminum in a neutral species. The quadrupole coupling constants for deuterium in GeD_4,[42] DBr,[43] and DI[43] are available and would fall on or near the straight line in Figure 3 if they are included. Although different conclusions have been reached from the theoretical discussion[44,45] of the rela-

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tion between the deuterium quadrupole coupling constant and the bond force constant, the *experimental* results shown in Figure 3 indicate that the field gradient at the hydrogen nucleus is almost equal to the force constant (in atomic units)[2] even for rather complicated hydrides.

The deuterium quadrupole coupling constants of the deuterides of the light elements are plotted against their electronegativities in Figure 4. The trend of correlation is very smooth except for hydrogen, which is unique in the periodic table.

In conclusion, we would like to point out that the deuterium quadrupole coupling constant is an important quantity in connection with the electronic structure of molecules. It is directly related to, and sometimes may be used to determine, other properties of a compound. It is only fair to say that the study of deuterium quadrupole coupling deserves more attention.

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Mössbauer Spectra of Tin Complexes of Phthalocyanine and Tetraarylporphines[1]

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Abstract: Mössbauer spectra of a series of phthalocyaninotin(IV) complexes ($PcSnX_2$, where X = F, OH, Cl, Br, I) reveal isomer shifts that vary linearly with the electronegativity of the X ligand. The negative isomer shift for bis(phthalocyanino)tin(IV) confirms the tetravalence of tin, and its magnitude together with a lack of quadrupole splitting indicate eight equivalent Sn–N bonds. Twelve tin porphyrins have been synthesized: the dichloro, dihydroxo, and difluoro derivatives of the tin complexes of tetra(*p*-methoxyphenyl)porphine, tetra(*p*-tolyl)porphine, tetra(*p*-chlorophenyl)porphine, and tetraphenylporphine. Dichlorotetraphenylporphinotin(IV) has been synthesized directly. Isomer shifts vary regularly with the electronegativities of the chloro, hydroxo, and fluoro groups; relative charge densities at the tin nucleus appear to be determined chiefly by σ bonds. The greater quadrupole interactions observed for the phthalocyanine complexes are interpreted in terms of greater tin–nitrogen π bonding in the phthalocyanine than in the tetraarylporphine complexes. The optical spectra of the latter indicate a resonance interaction of the *para* substituents with the porphine ring and possibly with the tin atom.

Linstead's group was the first to study a series of phthalocyaninotin complexes and established the existence of phthalocyaninotin(II), PcSn; dichlorophthalocyaninotin(IV), $PcSnCl_2$; and bis(phthalocyanino)tin(IV), Pc_2Sn (Pc = phthalocyanino ligand, $C_{32}H_{16}N_8$).[4] Pc_2Sn has two phthalocyanine rings bonded to one tetravalent tin atom[5,6] and it has been suggested[7] that this may have eight Sn–N bonds. Recent X-ray analysis by Bennett has established the antiprismatic D_{4d} molecular structure.[8] Kroenke and Kenney have given preparations for the dihalophthalocyaninotin(IV) complexes and the dihydroxo analog[9] and have obtained the infrared spectra of these compounds.[10] They have assigned absorptions at 531, 563, and 299 cm^{-1} to antisymmetric F–Sn–F, O–Sn–O, and Cl–Sn–Cl stretching vibrations.

Whalley[5] reported the visible spectrum of bis(phthalocyanino)tin(IV) and also spectra of the Cu, Ni, Co, Fe, Zn, Pd, and Mg phthalocyanines, which all have an intense narrow band in the 650–675 mμ region. Stöckler, Sano, and Herber[11a] published Mössbauer parameters for PcSn and the $PcSnX_2$ series; a correction of the parameters obtained for $PcSnI_2$ was made,[11b] but no reinterpretation of the data was offered.

The tetraarylporphine ligands used in this study have been previously synthesized[12–15] and three different tin complexes of tetraphenylporphine[16–18] have been

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[3] The Radiation Laboratory is operated by the University of Notre Dame under contract with the Atomic Energy Commission. This is AEC Document No. COO-38-623.

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