These were recrystallized from benzene, yielding 1.2 g. of hard, irregular, white crystals, melting with decomposition at 185–187°. More of these crystals were obtained from the precipitate by leaching the solid with water, leaving 6.5 g. of material, and recrystallizing this residue from benzene to give 0.65 g. of product; yield 20%. Considerable decomposition occurred in the process and other solids were also obtained.

Anal. Calcd. for $(C_6H_5)_4Sn_2Cl_2$: C, 46.74; H, 3.27. Found: C, 45.68; H, 3.58.

Dibromotetrabutylditin.—Dibromodi-*n*-butyltin was coupled with triethylamine in ether in the same way as was used for synthesizing the chloro compounds. Triethylamine was precipitated in 98% yield, and from the filtrate a 61% yield of dibromotetrabutylditin was obtained. The compound first appeared as a pale brown solid, but after four recrystallizations from alcohol fine white crystals were obtained which melted at 103–104°.

Anal. Calcd. for $(C_4H_9)_4Sn_2Br_2$: C, 30.65; H, 5.79. Found: C, 30.82; H, 5.84.

Preparation of Bromochlorodibutyltin.—Bromine (4.79 g., 0.03 mole) in 25 ml. of CCl_4 was added dropwise with stirring to 16.12 g. (0.03 mole) of tetrabutyldichloroditin in 75 ml. of CCl_4 and the solution heated on the steam-bath giving a colorless solution after about 30 minutes. The CCl_4 was distilled off leaving 30 ml. of clear slightly yellow liquid. Distillation at 1 mm. yielded a product boiling at 98–104° which crystallized as white needles, m.p. 32.5–35.5°; yield 60%.

Dichlorotetrabutylditin from Bromochlorodibutyltin.—Bromochlorodibutyltin (8.71 g., 0.025 mole) was partially dissolved in 50 ml. of ether and 2.53 g. (0.025 mole) of triethylamine added. A small amount of curdy white precipitate formed immediately. The addition of 10 ml. of anhydrous ethanol caused sufficient heating to make the ether boil and a very thick white solid formed immediately. After stirring for one hour the mixture was filtered and the residue washed with ether. The residue, 4.12 g., was soluble in water and melted, with darkening, at 235–237°, and was apparently impure triethylamine hydrobromide (m.p. 248°).

Evaporating the filtrate and recrystallizing the resulting solid from acetone gave 6.21 g. (92.4%) of dichlorotetrabutylditin.

Analysis for carbon in organotin compounds gives low results on account of the retention of CO_2 by the SnO_2 residue. Colaitis and Lesbre[3] report that this error may be minimized by using silver vanadate during combustion, and this was done in the analyses reported here.

The experimental evidence suggests that a strong organic base is necessary to make the reaction proceed and it was hoped that a relationship would be found between the strength of the base used and the yield of ditin compound obtained. However, no such relationship was immediately apparent, although the weak bases *o*-nitroaniline and pyridine gave a zero yield of product. A summary of yields with various bases is given in Table I.

TABLE I

EFFECT OF BASE ON YIELD OF DICHLOROTETRABUTYLDITIN

Base	Yield of ditin compd., %
Diethanolamine, $(HOC_2H_4)_2NH$	96.1
Hydrazine, N_2H_4	94.5
Triethylamine, $(C_2H_5)_3N$	93.0
p-Aminodimethylaniline, $H_2NC_5H_4N(CH_3)_2$	82.7
Triethanolamine, $(HOC_2H_4)_3N$	82.4
p-Phenetidine,[a] $C_2H_5OC_6H_4NH_2$	76.3
p-Phenetidine, $C_2H_5OC_6H_4NH_2$	74.4
N,N-Diethylaniline, $C_6H_5N(C_2H_5)_2$	70.5
N-Methyl-N-ethylaniline, $C_6H_5N(CH_3)(C_2H_5)$	65.4
N,N-Diethyl-*o*-toluidine, $CH_3C_6H_4N(C_2H_5)_2$	56.6
N,N-Diethyl-*p*-toluidine, $CH_3C_6H_5N(C_2H_5)_2$	51.4
γ-Picoline, $CH_3C_6H_4N$	46.1
o-Nitroaniline, $NOC_6H_4NH_2$	0
Pyridine, C_5H_5N	0

[a] This result was obtained without the presence of ethanol.

Properties and Reactions of Dichlorotetraalkylditin Compounds.—Dihalotetraalkylditin compounds are white in color and appear as friable, crystalline solids, with a faintly bitter odor. The ethyl and propyl homologs may be recrystallized from methanol or ethanol while the tetrabutyl compound recrystallizes readily from acetone. The bromo compounds are generally more soluble in organic solvents than the chloro compounds. The ethyl-, propyl- and butyldichloroditin compounds are readily soluble in benzene and ether in contrast to dichlorotetraphenylditin which is only slightly soluble in hot benzene.

An increase in the size of the alkyl group causes a lowering of the melting point. Thus $Et_4Sn_2Cl_2$ melts at 170–176°, $Pr_4Sn_2Cl_2$ at 120.5–121.5°, and $Bu_4Sn_2Cl_2$ at 111–112°. Replacing the chlorine by bromine gives a still lower melting compound, $Bu_4Sn_2Br_2$, melting at 102–103°. No comparisons were made with aryl groups since $(C_6H_5)_4Sn_2Cl_2$, melting with decomposition at 185–187°, was the only compound of this type prepared.

Completely alkylated ditin compounds are rather easily oxidized by air and are readily affected by moisture. In contrast, the replacement of two alkyl groups by chlorine causes pronounced changes in the stability of the molecule. Dichloroditin compounds are not changed by prolonged exposure to air or moisture. Dichlorotetrabutylditin decomposes when distilled at reduced pressure, dichlorodibutyltin being one of the decomposition products.

The analyses and the reactions indicate that the compounds are dihalotetraalkylditins with the formula $R_4Sn_2Cl_2$. In benzene solution cryoscopic determination of the molecular weight did not give the value 536.8 required by this formula for the tetrabutyl compound but gave a series of values ranging from 1040 in 0.0513 molal solution to 365 in 0.0027 molal solution. Similar results were obtained using dioxane as the solvent.

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The Infrared Spectra of Aromatic Compounds. III. The 1045-1185 Cm.$^{-1}$ Vibration in Monosubstituted Benzenes[1]

BY ROBERT D. KROSS AND VELMER A. FASSEL

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One of the frequencies of monosubstituted benzenes in the region 1045–1185 cm.$^{-1}$ is found to be sensitive to the nature of the substituent element. The literature contains conflicting evidence concerning the nature of the mode giving rise to this band. Cole and Thompson,[2] using a simplified potential function and assuming a substituent of infinite mass, calculated that the band in the region of 1065 cm.$^{-1}$ for monosubstituted benzenes is a C–H out-of-plane bending vibration. On the

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(3) D. Colaitis and M. Lesbre, *Bull. soc. chim. France*, 1069 (1952).

(1) Work was performed in the Ames Laboratory of the Atomic Energy Commission.

(2) A. R. H. Cole and H. W. Thompson, *Trans. Faraday Soc.*, **46**, 103 (1950).

other hand, Randle and Whiffen,[3] through both calculation and analogy with C_6H_5D, find bands in this area which correspond to a C–H in-plane bending vibration and a planar ring vibration. The latter is labeled an "X-sensitive vibration," its frequency being sensitive to the nature of the substituent. For chloro-, bromo- and iodobenzene, those authors cite the planar ring vibrational frequencies 1083, 1072 and 1061 cm.$^{-1}$, respectively, which can be seen from Table I to correspond to the band studied in this investigation. However, the frequency which they list for fluorobenzene is 1217 cm.$^{-1}$, while the band chosen in this study falls at 1159 cm.$^{-1}$.

It is not the intent of this note to decide the correct assignment, but rather to present some observations which may be useful in determining the true vibrational mode. These observations were made on a series of compounds of the type (phenyl)$_n$M, where n is the valence of the substituent atom M.

Experimental

The spectra were obtained under the same experimental conditions outlined in paper I[4] of this series.

Results

The frequencies for the investigated vibration for group IVB, VB, VIB and VIIB substituent elements are presented in Table I. Although there is a general tendency toward an inverse frequency–mass relationship, it is apparent that this is not a consistent behavior. Thus, within experimental error, the vibration frequency for each of the pairs of elements phosphorus–germanium, arsenic–tin and selenium–lead is the same. The consistent decrease in frequency with increasing atomic number within each periodic group and the large difference in frequencies between the second and third period elements within each group is significant, since this behavior parallels the electronegativity values for the substituent elements. Or, stated another way, the observed frequencies appear to be related to the partial ionic character of the carbon–substituent element bonds.

Table I

Characteristic Frequencies for Various Substituent Atoms in Monosubstituted Benzene

Compound[a]	Substituent element	Frequency (cm.$^{-1}$)[b]
Fluorobenzene(l)	F	1159
Chlorobenzene(l)	Cl	1082
Bromobenzene(l)	Br	1070
Iodobenzene(l)	I	1066
Diphenyl ether(s)	O	1175
Diphenyl sulfide(l)	S	1080
Diphenyl selenide(l)	Se	1064
Triphenylamine(s)	N	1182
Triphenylphosphine(s)	P	1088
Triphenylarsine(s)	As	1075
Triphenylstibine(s)	Sb	1065
Triphenylbismuthine(s)	Bi	1056
Tetraphenylmethane(m)	C	1188
Tetraphenylsilane(s)	Si	1106
Tetraphenylgermane(s)	Ge	1089
Tetraphenylstannane(s)	Sn	1075
Tetraphenyllead(s)	Pb	1060

[a] l = spectra obtained from liquid sample; m = spectra obtained from Nujol mull; s = spectra obtained from CS_2 solution. [b] A weaker band is also found in the narrow region 1060–1090 cm.$^{-1}$ which does not appear to be sensitive to the nature of the substituent element.

The partial ionic character of a bond is usually expressed in terms of the bond's extra ionic energy, or the difference between the bond's observed energy and its theoretical covalent energy.[5] Unfortunately extra ionic energies are known for only a few types of carbon–M bonds. These data are available for carbon–halogen bonds, and Fig. 1 shows that a linear relationship does exist between the extra ionic energy of the bond and the frequency of the 1045–1185 cm.$^{-1}$ vibration. Pauling[5] has shown that the electronegativities of the elements are proportional to the square roots of the extra ionic energy of the bond formed with other elements. The linear plot of Fig. 1 suggests that a plot of vibration frequency *versus* the square of electronegativity of the substituent element should likewise produce linear curves. This deduction is verified by the curves plotted in Fig. 2. An interesting feature of the plot is its common intercept, which indicates that any number of phenyl groups attached to a central atom of theoretically zero electronegativity will have common vibrations at 984 cm.$^{-1}$.

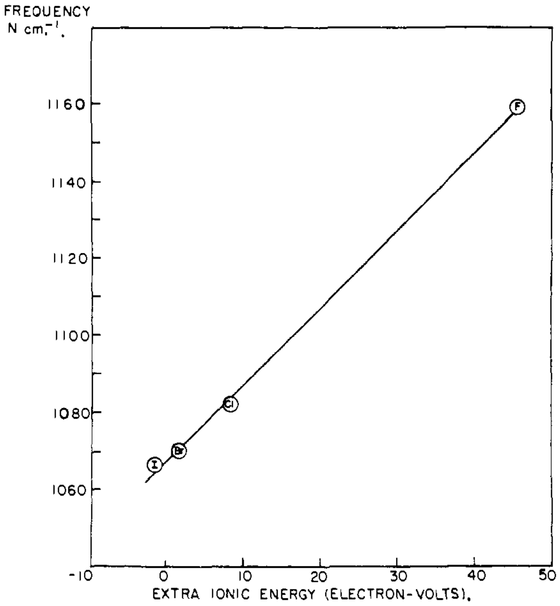

Fig. 1.—Vibration frequency *vs.* extra ionic energy of carbon-halogen bond.

Some comment should be made concerning the deviation of the points for iodine and selenium in the figure. Electronegativity data are available to only the first decimal place (see Table II), hence any error in that figure is squared in obtaining the abscissa values. Iodine shows the largest deviation, but since the iodine point falls on the curve in

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(3) R. R. Randle and D. H. Whiffen, preprint of paper presented at Conference on Molecular Spectroscopy, Institute of Petroleum, October 28–29, 1954.

(4) M. Margoshes and V. A. Fassel, *Spectrochim. Acta*, **7**, 14 (1955).

(5) L. Pauling, "Nature of the Chemical Bond," 2nd Ed., Cornell Univ. Press, Ithaca, N. Y., 1948, p. 59.

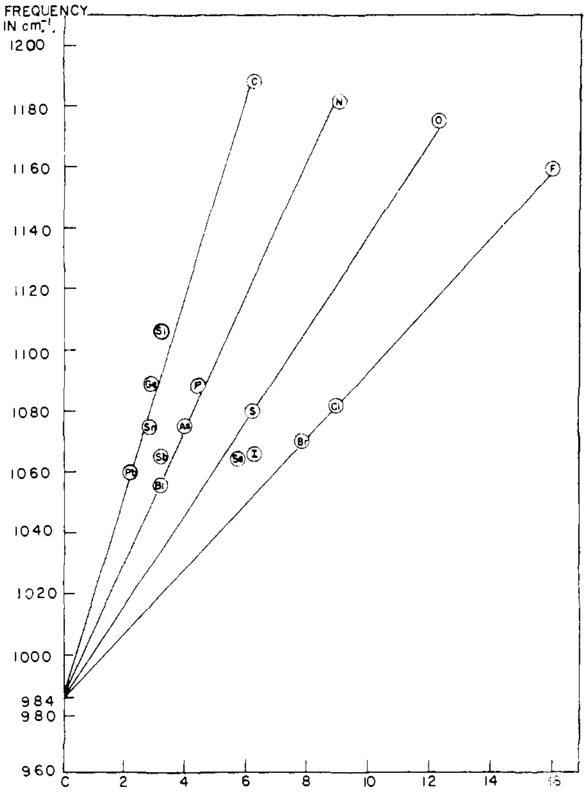

Fig. 2.—Relation between vibration frequency and electronegativity of substituent element.

Fig. 1, this suggests that the published electronegativity value for iodine may be slightly erroneous.

TABLE II

ELECTRONEGATIVITY VALUES

Element	Calcd.	Pauling	Others	Element	Calcd.	Pauling	Others
F	4.00	4.0		As	2.00	2.0	
Cl	3.00	3.0		Sb	1.89	1.8	
Br	2.75	2.8		Bi	1.79	..	1.8[6]
I	2.65	2.5	2.6[6]				1.8[7]
O	3.42	3.5		C	2.51	2.5	
S	2.48	2.5		Si	1.93	1.8	
Se	2.26	2.4		Ge	1.79	1.7	
N	2.96	3.0		Sn	1 66	1.7	
P	2.14	2.1		Pb	1.52	..	1.5[7]

An equation relating the slopes of all of the four lines in Fig. 2 in terms of the valence of the substituent is

$$\text{Slope} = 2^{n/2}[7.70 + (n - 1)0.15] \qquad (1)$$

Incorporating this expression into the general equation for a straight line involving slope and intercept, an equation was obtained which yields electronegativity values directly from knowledge of the corresponding frequency and the valence of the substituent. It is (for the B group elements investigated)

$$E = 2^{-n/4}\left(\frac{\nu - 984}{7.70 + (n - 1)0.15}\right)^{1/2} \qquad (2)$$

Table II shows the good correspondence of electronegativity values obtained from the above equation with those listed by Pauling and others. It should be noted that Haissinsky's value for the electronegativity of iodine is more in agreement with the value obtained in this research, and is probably more nearly correct. The values obtained for germanium and tin also appear more accurate than those of Pauling, since in his table both elements have the same values, which is somewhat unlikely.

An interesting application of equation 2 arises in the case of deuterium. In view of the simple electronic configuration of the hydrogen isotopes, deuterium can be considered as either a group 1 or group 7 element. Since the A and B subdivisions of the groups begin in the fourth period, deuterium can be thought of as the highest member of the halogen series, and thus equation 2 should apply to its phenyl compound, monodeuterobenzene. Comparison of the spectrum of that compound[8] with the spectra of the other monosubstituted benzenes indicates that the monodeuterobenzene band at 1030 cm.$^{-1}$ is the appropriate one to use in equation 2. The calculation leads to an electronegativity of 2.06 for deuterium, which is close to the 2.13 value listed[7] for hydrogen. It should be noted that the 1030 cm.$^{-1}$ band has been assigned fairly conclusively to a C–H planar bending vibration,[8] and since this band varies in position depending on the substituent, the evidence points to the fact that the "X-sensitive vibration" arises from a C–H planar mode.

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(6) M. Haissinsky, *J. phys. radium*, **7**, 7 (1946); *J. Chem. Phys.*, **15**, 152 (1947).

(7) W. Gordy, *ibid.*, **14**, 305 (1946).

(8) C. R. Bailey, R. R. Gordon, J. B. Hale, N. Herzfeld, C. K. Ingold and H. G. Poole, *J. Chem. Soc.*, 299 (1946).

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New Microcatalytic-Chromatographic Technique for Studying Catalytic Reactions

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For several years the analysis of gases and hydrocarbons of low molecular weight by gas chromatographic or thin film chromatographic techniques has been in successful use.[1-7] It has proved especially valuable for the analysis of hydrocarbon in the C_1–C_8 range. The method of operation of such an analytical column is well known and has been described in detail on several occasions.[1-6] It involves adding 1 to 10 mg. of the mixture that is to be analyzed to a stream of some suitable carrying gas such as H_2, He or N_2 and passing it through a chromatographic column (see Fig. 1) packed with a

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(1) C. S. G. Phillips, *Discs. Faraday Soc.*, **7**, 241 (1949).

(2) D. H. James and C. S. G. Phillips, *J. Chem. Soc.*, Part 2, 1600 (1953).

(3) A. T. James and A. J. P. Martin, *Biochem. J.*, **50**, 679 (1952).

(4) N. H. Ray, *J. Appl. Chem.*, **4**, 21 (1954).

(5) N. H. Ray, *ibid.*, **4**, 82 (1954).

(6) F. R. Cropper and A. Heywood, *Nature*, **174**, 1063 (1954).

(7) D. H. Lichtenfels, S. A. Fleck and F. H. Burow, "Gas-Liquid Partition Chromatography" (to be published).